

Green Chemistry

Cutting-edge research for a greener sustainable future

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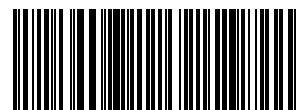


ISSN 1463-9262

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Green chemistry for fuel
synthesis and processing
Themed issue

de Klerk
Environmentally friendly refining
Adebajo
Green chemistry perspectives of
methane conversion



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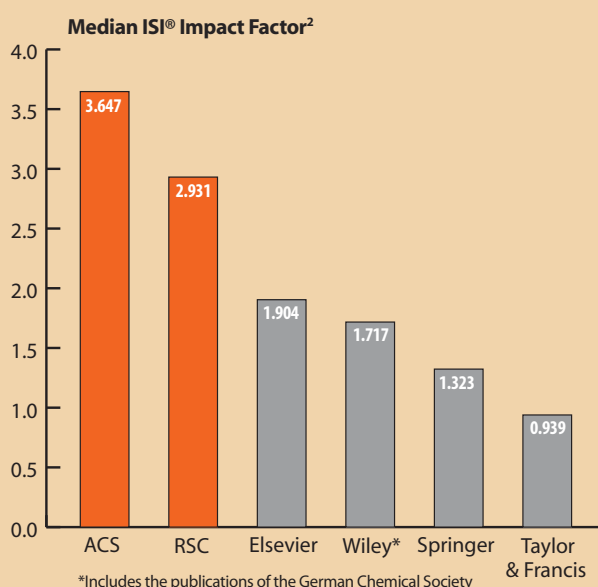
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IN THIS ISSUE

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Cover

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CHEMICAL TECHNOLOGY

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June 2007/Volume 4/Issue 6

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ENERGY AND THE CHEMICAL SCIENCES

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EDITORIAL

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Green chemistry for fuel synthesis and processing

This themed issue contains peer-reviewed papers presented at the Green Chemistry for Fuel Synthesis and Processing Symposium as part of the 232nd National Meeting of American Chemical Society (ACS) held in San Francisco during September 10–14, 2006.



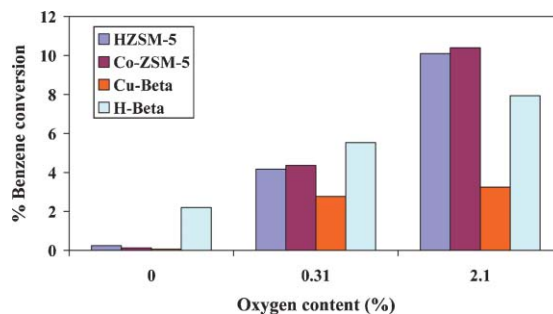
CRITICAL REVIEW

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**Green chemistry perspectives of methane conversion *via* oxidative methylation of aromatics over zeolite catalysts**

Moses O. Adebajo*

Previous studies on the oxidative methylation of aromatics with methane over zeolite catalysts have been critically reviewed and shown, using metrics and the principles and tools of green chemistry, to have positive green chemistry implications.



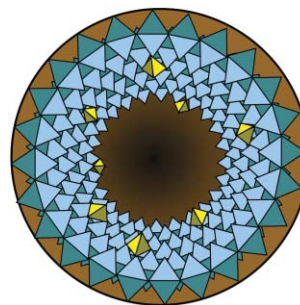
PAPERS

540

Grafting sulfated zirconia on mesoporous silica

Yong Wang,* Kwan-Young Lee, Saemin Choi, Jun Liu, Li-Qiong Wang and Charles H. F. Peden

Sulfated zirconia solid acid catalysts were prepared by grafting zirconium oxide on mesoporous silica with layer-by-layer coverage, followed by depositing sulfate groups on the surface.

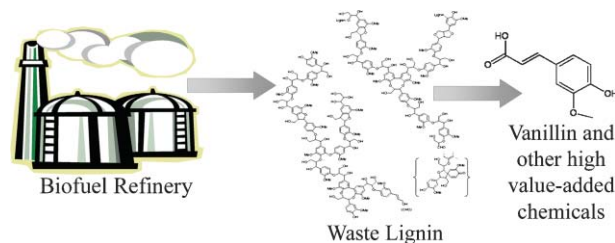


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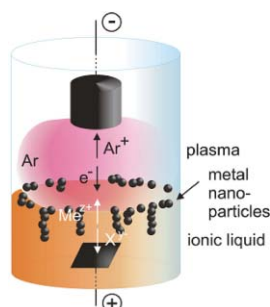
Tunable solvents for fine chemicals from the biorefinery

Charles Eckert,* Charles Liotta, Arthur Ragauskas, Jason Hallett, Christopher Kitchens, Elizabeth Hill and Laura Draucker

The high value chemicals vanillin, syringaldehyde and syringol can be extracted from low value lignin using a novel CO₂-expanded organic solvent.



549



Ionic liquids as green electrolytes for the electrodeposition of nanomaterials

S. Zein El Abedin, M. Pölleth, S. A. Meiss, J. Janek and F. Endres*

In this paper the potential of ionic liquids in the additive free electrodeposition of nanocrystalline metals as well as of plasmas as mechanically contact-free electrodes for the cathodic deposition of nanoscaled metals are described.

554



CO₂ reforming of methane over argon plasma reduced Rh/Al₂O₃ catalyst: a case study of alternative catalyst reduction *via* non-hydrogen plasmas

Zhou-jun Wang, Yu Zhao, Lan Cui, Haiyan Du, Pei Yao and Chang-jun Liu*

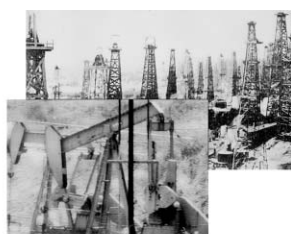
Simple, cheap and effective argon glow discharge plasma was used to reduce a supported Rh catalyst at room temperature, which led to a promising alternative catalyst reduction.

560



Fischer-Tropsch syn crude

?



Crude oil

Environmentally friendly refining: Fischer–Tropsch *versus* crude oil

Arno de Klerk*

Refining of Fischer–Tropsch syncrude is qualitatively compared to crude oil refining, and it is shown that syncrude has better properties for the production of transportation fuel and that syncrude refining is more environmentally friendly.

566



Efficient synthesis of dimethyl carbonate from methanol, propylene oxide and CO₂ catalyzed by recyclable inorganic base/phosphonium halide-functionalized polyethylene glycol

Jie-Sheng Tian, Cheng-Xia Miao, Jin-Quan Wang, Fei Cai, Ya Du, Yuan Zhao and Liang-Nian He*

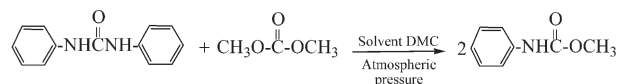
A simple process for DMC synthesis from CO₂, propylene oxide and MeOH, with no need for cyclic carbonate separation.

572

A non-phosgene route for synthesis of methyl *N*-phenyl carbamate derived from CO₂ under mild conditions

Junjie Gao, Huiquan Li,* Yifei Zhang and Yi Zhang

A non-phosgene method for the synthesis of methyl *N*-phenyl carbamate from *N,N'*-diphenyl urea and dimethyl carbonate (DMC), which could be synthesized from CO₂, was investigated under atmospheric pressure when reactant DMC itself was used as solvent.

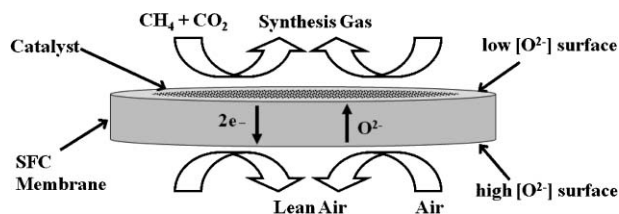


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Mixed-conducting oxygen permeable ceramic membranes for the carbon dioxide reforming of methane

David A. Slade, Andrew M. Duncan, Karen J. Nordheden and Susan M. Stagg-Williams*

This work reports evidence of a synergy between an oxygen-permeable SrFeCo_{0.5}O_x ceramic membrane and a conventional powder Pt/ZrO₂ catalyst for the CO₂ reforming of CH₄.

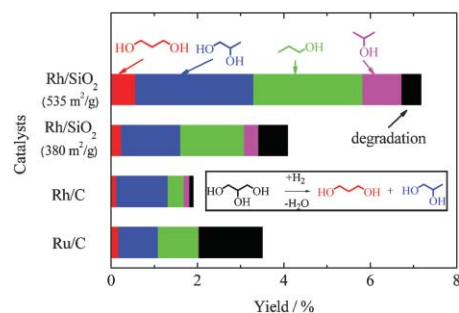


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Catalytic performance of Rh/SiO₂ in glycerol reaction under hydrogen

Ippei Furikado, Tomohisa Miyazawa, Shuichi Koso, Akira Shimao, Kimio Kunimori and Keiichi Tomishige*

Hydrogenolysis of glycerol to propanediols and propanols is catalyzed by Rh/SiO₂ with higher activity and selectivity than Ru/C, one of the conventional catalysts.

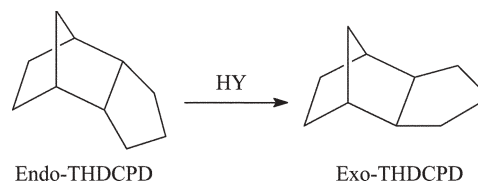


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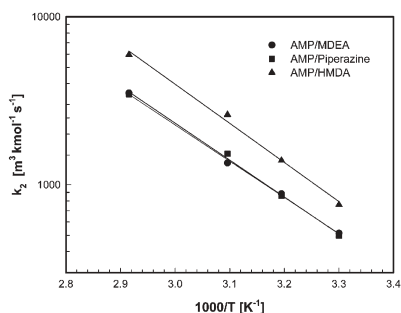
Greener synthesis route for Jet Propellant-10: the utilization of zeolites to replace AlCl₃

Enhui Xing, Xiangwen Zhang,* Li Wang and Zhentao Mi

The isomerization of tetrahydrodicyclopentadiene is investigated: F-modified H-SSY shows equivalent performance as AlCl₃, and the simple mechanism of *endo*-THDCPD isomerization is proposed.



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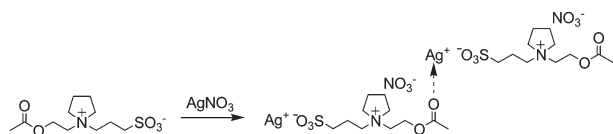


Removal of carbon dioxide by absorption into blended amines: kinetics of absorption into aqueous AMP/HMDA, AMP/MDEA, and AMP/piperazine solutions

Won-Joon Choi, Ki-Chul Cho, Sang-Sup Lee, Jae-Goo Shim, Hye-Ryun Hwang, Sang-Wook Park and Kwang-Joong Oh*

The addition of 1, 3, and 5 wt% HMDA, MDEA or piperazine into 30 wt% AMP increased the absorption rate as compared to AMP alone. The reaction rate constants of HMDA, MDEA and piperazine blended into AMP at 303–343 K were given by $k_H = 3.84 \times 10^{10} \exp(-5361/T)$, $k_M = 6.60 \times 10^9 \exp(-4959/T)$, and $k_P = 9.09 \times 10^9 \exp(-5058/T)$, respectively.

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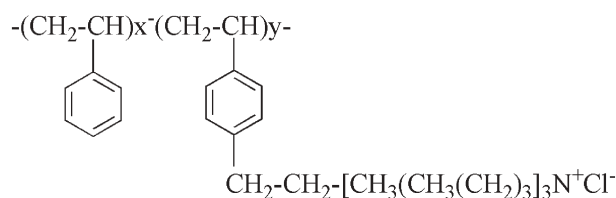


Multi-functional zwitterionic compounds as new membrane materials for separating olefin–paraffin mixtures

Hoon Sik Kim,* Sang Joon Park, Dinh Quan Nguyen, Jin Yong Bae, Hyun Woo Bae, Hyunjoo Lee,* Sang Deuk Lee and Dai Ki Choi

The performance of facilitated olefin transport membranes was greatly improved by the introduction of an ester group on the zwitterionic compound, possibly due to an additional interaction of a silver ion with an ester group.

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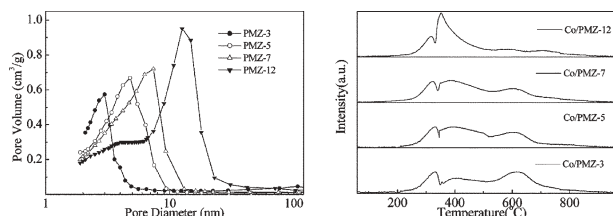


Chemical kinetics of carbon dioxide with glycidyl methacrylate using immobilized tributylamine supported on poly(styrene-co-vinylbenzyl chloride) as a catalyst

Sang-Wook Park,* Byoung-Sik Choi, Dae-Won Park, Kwang-Joong Oh and Jae-Wook Lee

Reaction rate constants of the reaction between GMA and CO₂ with immobilized tributylammonium chloride catalyst were evaluated by the pseudo-first-order reaction method using the absorption data of CO₂.

611



Effect of pore size on the performance of mesoporous zirconia-supported cobalt Fischer–Tropsch catalysts

Yachun Liu, Kegong Fang, Jiangang Chen and Yuhua Sun*

Mesoporous zirconia were used as supports of cobalt catalysts for Fischer–Tropsch synthesis. It was found that the catalytic activity and C₅⁺ selectivity were enhanced, whereas C₁ selectivity decreased with increasing the pore sizes of mesoporous zirconia. This result was attributed to the enhancement of the cobalt reducibility and improvement of chain growth capability derived from the larger pore size of the mesoporous support.

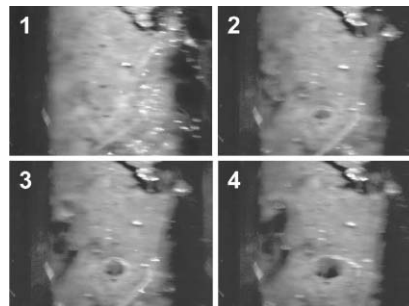
PAPERS

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Synthetic natural gas from biomass by catalytic conversion in supercritical water

Frédéric Vogel,* Maurice H. Waldner, Ashaki A. Rouff and Stefan Rabe

Visualization of the onset of gas evolution above a grain of nickel catalyst, inside a sealed quartz capillary during the hydrothermal gasification of a wood sawdust slurry.

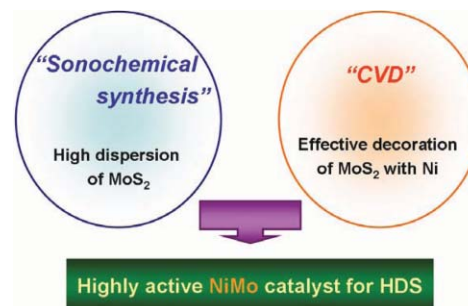


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Performance of NiMoS/Al₂O₃ prepared by sonochemical and chemical vapor deposition methods in the hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene

Ara Cho, Jung Joon Lee, Jae Hyun Koh, Anjie Wang and Sang Heup Moon*

NiMoS/Al₂O₃ catalysts prepared by a combination of sonochemical synthesis and chemical vapor deposition methods showed higher HDS activities than those prepared by impregnation.

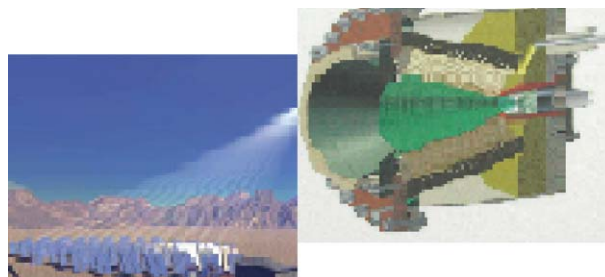


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Steam reforming of methane on a Ru/Al₂O₃ catalyst promoted with Mn oxides for solar hydrogen production

Alexander Berman,* Rakesh Kumar Karn and Michael Epstein*

Catalytic elements for use in a solar volumetric reformer have been developed and tested. A Ru/Al₂O₃ catalyst promoted with Mn oxides was found to be stable even after operation at 1100 °C for 500 hours.

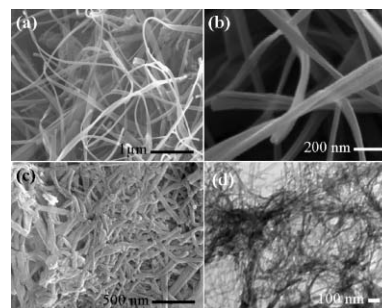


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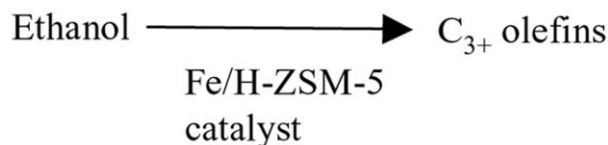
Green approach to bulk and template-free synthesis of thermally stable reduced polyaniline nanofibers for capacitor applications

Mallikarjuna N. Nadagouda and Rajender S. Varma*

A bulk and template-free synthesis of narrow diameter reduced polyaniline nanofibers with excellent thermal and dielectric properties using acetic acid at room temperature is reported.



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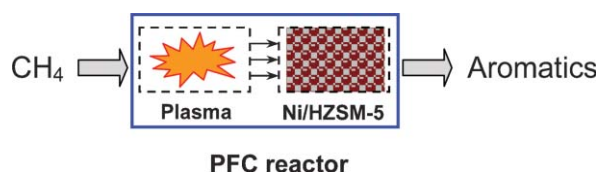


Production of olefins from ethanol by Fe-supported zeolite catalysts

Megumu Inaba,* Kazuhisa Murata, Masahiro Saito and Isao Takahara

C_{3+} olefins can be obtained from EtOH with Fe/H-ZSM-5 catalysts in high selectivity. The selectivity is decreased with time-on-stream: however, iron(III) sulfate and iron(III) chloride, used as Fe sources, can inhibit the decrease.

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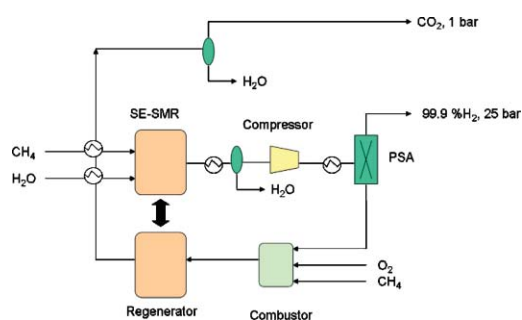


A process for a high yield of aromatics from the oxygen-free conversion of methane: combining plasma with Ni/HZSM-5 catalysts

Xiao-Song Li, Chuan Shi, Yong Xu, Kang-Jun Wang and Ai-Min Zhu*

A process for a high yield of aromatics and co-produced hydrogen from the oxygen-free conversion of methane using a two-stage plasma-followed-by-catalyst (PFC) reactor at atmospheric pressure and low temperature is reported.

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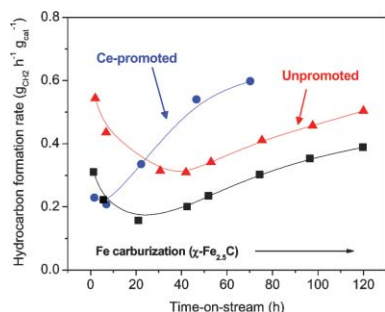


Process design simulation of H_2 production by sorption enhanced steam methane reforming: evaluation of potential CO_2 acceptors

Esther Ochoa-Fernández, Geir Haugen, Tiejun Zhao, Magnus Rønning, Ingrid Aartun, Børre Børresen, Erling Rytter, Morten Rønnekleiv and De Chen*

Sorption enhanced steam reforming is a promising route for H_2 production with CO_2 management. In this study, an effort has been made to optimise the system configuration and screen different CO_2 acceptors.

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Evolution of the bulk structure and surface species on Fe–Ce catalysts during the Fischer–Tropsch synthesis

F. J. Pérez-Alonso, T. Herranz, S. Rojas, M. Ojeda, M. López Granados, P. Terreros, J. L. G. Fierro,* M. Gracia and J. R. Gancedo

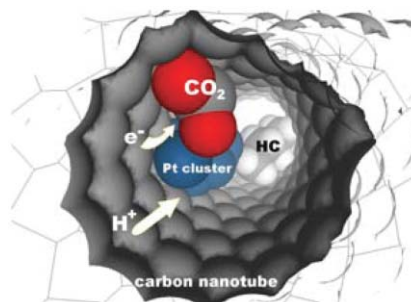
Two Ce-loaded iron oxide catalysts and a bulk $\alpha\text{-Fe}_2\text{O}_3$ catalyst were tested in the synthesis of hydrocarbons from $\text{CO} + \text{H}_2$ gas mixtures (Fischer–Tropsch synthesis).

671

Electrocatalytic conversion of CO₂ to long carbon-chain hydrocarbons

Gabriele Centi,* Siglinda Perathoner,* Gauthier Winé and Miriam Gangeri

Pt nanoparticles confined in carbon-based electrodes can convert CO₂ to long carbon-chain hydrocarbons (>C₅) at room temperature and atmospheric pressure in a continuous flow cell having the working electrode directly in contact with the CO₂ in the gas phase.

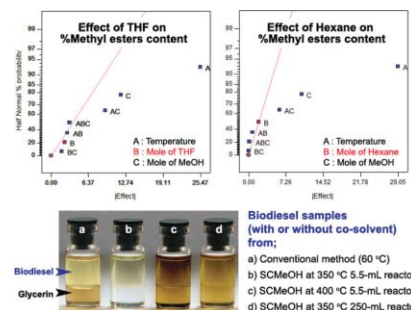


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Effect of co-solvents on production of biodiesel via transesterification in supercritical methanol

Ruengwit Sawangkeaw, Kunchana Bunyakiat and Somkiat Ngamprasertsith*

The effect of co-solvents on biodiesel production was investigated by factorial design. The strength of co-solvents had no significant effect on methyl esters content, but temperature, concentration of methanol and their interaction did.

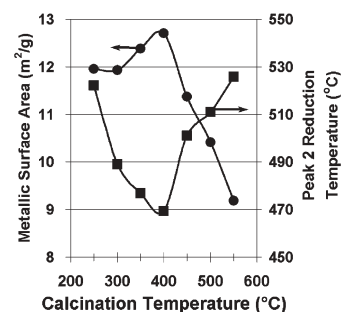


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Effect of synthesis parameters on the catalytic activity of Co–ZrO₂ for bio-ethanol steam reforming

Hua Song, Lingzhi Zhang and Umit S. Ozkan*

The synthesis parameters such as calcination temperature and reduction temperature were found to affect the metallic surface area, reducibility and, in turn, ethanol chemisorption and ethanol reforming activity of Co–ZrO₂ catalysts.

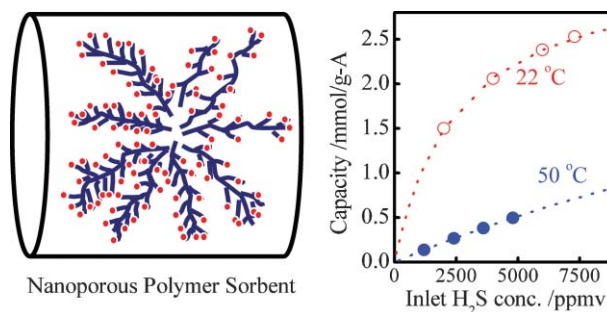


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A nanoporous polymeric sorbent for deep removal of H₂S from gas mixtures for hydrogen purification

Xiaoxing Wang, Xiaoliang Ma, Lu Sun and Chunshan Song*

A nanoporous polymeric sorbent, PEI/SBA-15, has been synthesized and used for deep removal of H₂S from gas mixtures for H₂ purification, and exhibited very good H₂S sorption performance.



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Chemical Technology

Washing with eutectic solvents cleans up biodiesel and produces glycerol

Mild green ionic liquids

Biodiesel production could become more environmentally friendly thanks to researchers in the UK who are using non-toxic ionic liquids to remove unwanted by-products.

The main by-product in the production of biodiesel from vegetable oils is glycerol. This syrupy sugar alcohol must be removed from the fuel as it can damage engines. Andrew Abbott and colleagues from the University of Leicester have developed a simple new approach to this sticky problem: they use green ionic liquids called deep eutectic solvents to just wash the glycerol out of the biodiesel.

Deep eutectic solvents are two or more substances mixed in a ratio that has a melting point much lower than any of the constituents. These are generally made from an organic halide salt that is complexed with something that will form a hydrogen bond. Abbott's team used quaternary ammonium salts complexed with glycerol as the washing liquid. This green washing



liquid has many advantages including its low cost and toxicity; in fact, one salt used is choline chloride – vitamin B4.

This procedure not only has potential as a greener method of cleaning up biodiesel, but also as a method of producing pure glycerol. Alexei Lapkin of the University of Bath commented that the work 'is a very interesting development for downstream glycerol treatment and utilisation'.

Making a green process even greener

Abbott hopes that 'further research will reveal a better method for recycling the salt and recovering the glycerol'. He added that the team want 'to collaborate with a biodiesel producer to test this technology on a practical scale'.

Wendy Crocker

Reference

A P Abbott et al, *Green Chem.*, 2007 (DOI: 10.1039/b702833d)

In this issue

Hot-wiring enzymes for fuel cells

Linking laccase to electrodes delivers electrons straight to the active site

The clean art of conservation

Supercritical carbon dioxide used to restore ancient cloth

Interview: Health and natural hazards

José A Centeno talks to Kathryn Lees about how Mother Nature affects our health

Instant insight: Back in black

Hydrothermal carbonisation of biomass: an efficient process to treat the CO₂ problem?



The latest applications and technological aspects of research across the chemical sciences

Application highlights

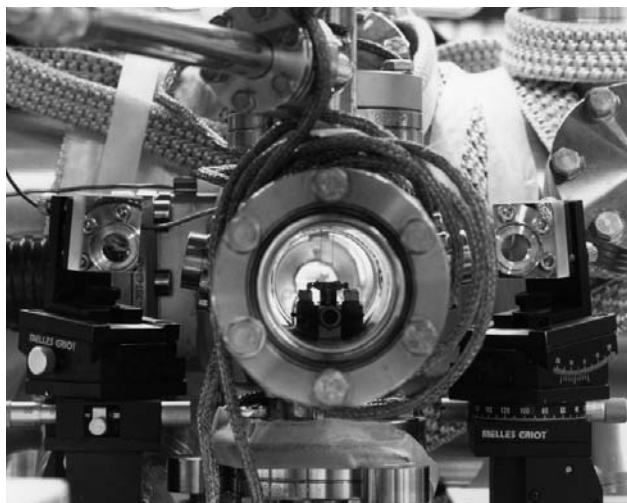
Polycrystal catalysts studied by IR at realistic pressures

Bridging the industry–laboratory gap

The challenge of relating results from laboratory tests of single crystal catalysts to their more complex industrial applications is being met head on by researchers at Shell Global Solutions.

Forming long chain hydrocarbons from carbon monoxide and hydrogen by the Fischer–Tropsch process is of huge interest. Unfortunately most studies into new catalysts do not use catalysts or conditions that reflect their use in industry. However, Heiko Oosterbeek at Shell Global Solutions in the Netherlands has studied the surface science of Fischer–Tropsch catalysts under more realistic conditions to try and bridge the gap between lab and industrial conditions.

Traditionally, catalyst characterisation is done under conditions very different to those found in industry, for example, ultra high vacuum (UHV) characterisation of catalysts to be



Lab tests are often under unrealistic conditions

Reference

H Oosterbeek, *Phys. Chem. Chem. Phys.*, 2007, DOI: 10.1039/b703003g

used at high pressures. Oosterbeek prepared both single and polycrystals of cobalt that resembled real Co/SiO₂ catalysts. He then used infra-red techniques to characterise them, and tested the catalysts at both UHV and high pressure.

‘The work aims to show the synergy between robust industrial experience and subtle theoretical insight into the structural aspects of heterogeneous catalysis,’ said Oosterbeek.

These methods could lead to valuable new discoveries. Carlos Otero Arean from Universidad de las Islas, Spain, said ‘Oosterbeek’s work precisely addresses the gap between model studies and working catalysts, as applied to Fischer–Tropsch synthesis. He successfully shows how a combination of carefully designed experimental work and state-of-the-art techniques holds the potential to yield highly relevant new insights.’

Oosterbeek said the next challenge is to apply the techniques at pressures above atmospheric pressure and further close the material, pressure and instrument gap between the lab and industry. *Edward Morgan*

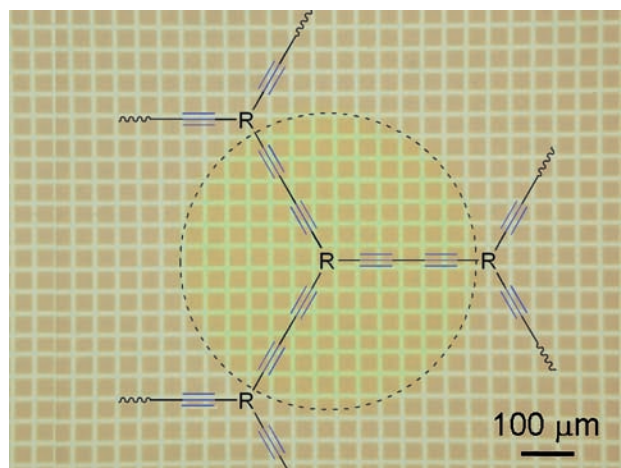
Organometallic cluster enhances polymer’s optical properties

Tunable photonics with high refractive index

Scientists in Hong Kong have created a polymer with a refractive index that can be tuned as high as 1.81.

The refractive index (RI) is a measure of how much the speed of light is reduced in a medium. Conventional organic glasses such as PMMA have a particularly low RI and also within a narrow range. Therefore although they are cheap to produce, flexible and easy to coat onto large surfaces, their optical properties are limited.

Ben Zhong Tang’s group from the Hong Kong University of Science and Technology have attached organometallic nanoclusters to the triple bond network of a hyperbranched polydiyne. This had the effect of increasing the refractive index to 1.81, vastly improving its optical performance.



In addition, they discovered that under UV irradiation the organometallic moiety broke away from the polymer complex. This caused the RI to drop by as much as 0.05 in the 1500–1600 nm region,

The polymer is a hyperbranched polydiyne

producing a visible photochromic response.

‘Such an unusually high RI change makes our polymer an interesting material for waveguide, memory and holographic storage applications,’ said Tang.

In the future, the group hope to induce the change in the RI of this polymer in a reversible manner. They believe that this could lead to write and read as well as erase and rewrite optical memories. ‘Such photonic materials could dramatically enhance the data processing speed and give optical holographic data storage applications with much higher accessible capacity,’ said Tang. *Jenna Wilson*

Reference

M Häußler et al, *Chem. Commun.*, 2007, DOI: 10.1039/b702915b

Supercritical carbon dioxide used to restore ancient cloth

The clean art of conservation

Scientists have developed the first environmentally friendly approach to cleaning fragile historic textiles that have seen better days.

Ana Aguiar-Ricardo from the New University of Lisbon, Portugal, and colleagues, used liquid and supercritical carbon dioxide (CO_2) as dry cleaning solvents to restore the garments of the Virgin and Child, an eighteenth century sculpture from Necessidades Palace in Lisbon.

The cleaning of antique textiles is often an unavoidable step in their conservation, but many traditional mechanical or wet methods are considered too harsh to use on much deteriorated textiles. In this situation the conservator may decide the risk is too great or use dry cleaning with perchloroethylene and other toxic organic solvents that remove the dirt and stabilise the textile.

There is an urgent need to preserve our history and cultural heritage. However, to do this art and science must work together so that technological developments do not harm the environment or our quality of life, said Aguiar-Ricardo.



Time has not been kind to the clothes on the Virgin and Child

Using CO_2 is perfect as it is considered non-flammable, relatively non-toxic and relatively inert: 'It allows the conservation and restoration of the textile without being harmful to the operator and the environment,' said Aguiar-Ricardo. Above a critical temperature and pressure CO_2 will become supercritical and have gas-like viscosities and liquid-like densities. Small changes in temperature or pressure cause dramatic changes in its density, viscosity and dielectric properties making it an unusually tunable, versatile and selective solvent.

'What a beautiful application of supercritical carbon dioxide,' said Martyn Poliakoff, an expert on clean technology at the University of Nottingham, UK. 'Scaling this up to work on real objects will provide wonderful opportunities for interdisciplinary research between chemists, engineers and conservators,' he said.

Sarah Corcoran

Reference

M Sousa et al, *Green Chem.*, 2007, DOI: 10.1039/b617543k

Linking laccase to electrodes delivers electrons straight to the active site

Hot-wiring enzymes for fuel cells

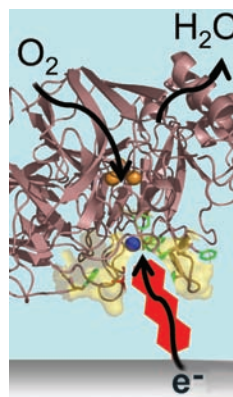
Stable enzyme-modified graphite electrodes could be used in fuel cells, according to researchers in the UK.

Laccases are copper-containing enzymes that use electrons to reduce oxygen to water efficiently, making them of interest as electrocatalysts at the cathodes of hydrogen-oxygen fuel cells. In this type of fuel cell, hydrogen is oxidised to hydrogen ions and electrons, which flow to the cathode (supplying power) where they reduce oxygen.

Fraser Armstrong and colleagues at the University of Oxford chemically attached anthracene to graphite electrodes to form a

stable attachment between the electrode and laccase. Armstrong described anthracene as 'a long hydrophobic molecule, similar to laccase's own substrate molecules, which can penetrate the active site pocket and approach closely to one of the copper atoms' where the oxygen reduction takes place. The anthracene not only binds the laccase to the electrode, but, as it can conduct electrons, it also delivers them deep into the enzyme close to the site for oxygen reduction.

The anthracene 'plug' modification of the electrode is essential to provide the high and long-term oxygen-reduction activity. Without it, the electrons



Reference

C F Blanford, R S Heath and F A Armstrong, *Chem. Commun.*, 2007, 1710

are not delivered efficiently into the enzyme and the binding of the laccase to the electrode is not stable, both of which leads to reduced activity. The ability to use graphite is also an advantage; it is relatively cheap compared to precious metals, such as gold, which have been previously used as electrodes for laccases.

To complete the fuel cell, Armstrong said that in future research they would like to 'identify rational attachment strategies for other enzymes, particularly hydrogenases, which can be incorporated with laccases to produce small fuel cells'.

Nicola Convine

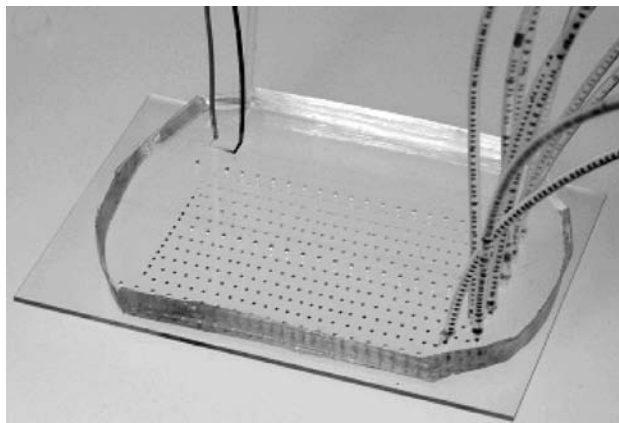
A range of conditions can be quantitatively assessed in a few hours

On-chip solubility screening

Scientists in France have devised a new way to rapidly and cheaply screen how soluble compounds are.

Chemical and biological systems often rely on a large number of parameters. Complete investigations of these parameters need time and significant amounts of product. Currently these investigations use robotic fluidic workstations, but these are expensive, and require labour and large product volumes. Alternatively, high throughput microfluidic techniques are used as they allow rapid screening, but fabrication and multiplexing are difficult.

Philippe Laval and colleagues working for a joint Rhodia–CNRS research centre have produced a chip for screening phase and solubility conditions. A series of droplets with differing compositions is produced by



mixing silicone oil and aqueous phases at different rates. Ten channels containing different droplet compositions can be created in less than 20 minutes.

After the device is full it is rapidly cooled to induce crystallisation. Once the solutions have

A heat gradient is applied to a 2D array of concentrations

Reference
P Laval et al, *Lab Chip*, 2007, DOI: 10.1039/b700799j

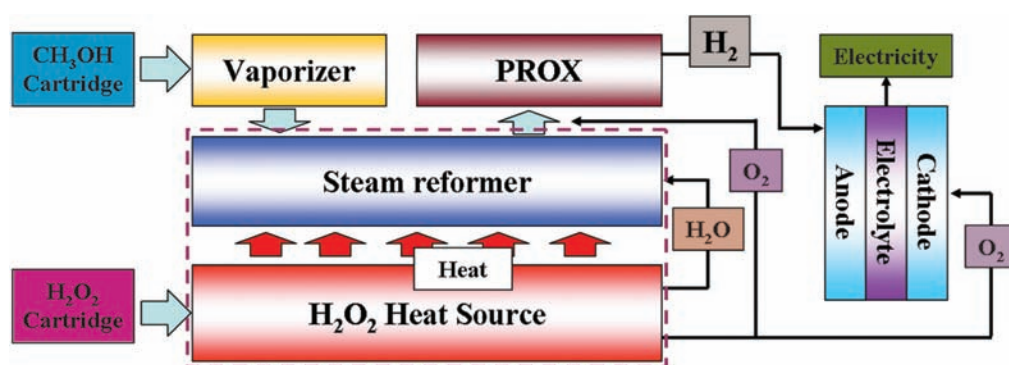
crystallised, a temperature gradient is applied to produce a two-dimensional array of droplets of different concentrations at different temperatures. In droplets where the temperature is higher than the solubility temperature, the crystals dissolve. In other droplets the crystals are partly solubilised, but still exist in equilibrium, producing a direct and quantitative solubility assessment.

‘The microfluidic device has been developed to improve research productivity’, said Laval, adding ‘This low cost system, compared to robotic platforms, enables us to carry out high throughput screening of concentration vs. temperature diagrams with very little amount of products’. He continued that an additional advantage is that ‘tens of experimental conditions can be tested in just a few hours’.

Vikki Chapman

Hydrogen peroxide is decomposed to provide heat for fuel cells

The drive to reform methanol



Researchers in Korea have increased the efficiency of polymer electrolyte membrane (PEM) fuel cells by about 10%.

Sejin Kwon and colleagues at the Korea Advanced Institute of Science and Technology, Daejeon, used the decomposition of hydrogen peroxide to provide the heat needed to drive the production of hydrogen

from methanol.

PEM fuel cells produce electrical energy from hydrogen and oxygen. But since hydrogen has such a low energy density when stored as a gas, it is often stored indirectly as a liquid fuel, such as methanol. Hydrogen is produced from the methanol as required in a process called ‘steam reforming’, but as

Crucially, the water and oxygen also produced is recycled

this process is endothermic a heat source is also needed.

Kwon made a compact methanol reformer that uses the decomposition of hydrogen peroxide as the heat source. One of the key features of the reformer is that the products of the reaction, water vapour and oxygen, are then recycled. The water vapour is used for the steam reforming and the oxygen to oxidise any carbon monoxide produced during methanol reforming and also to supplement the oxygen from the air in the fuel cell itself. Furthermore, this oxygen enrichment boosts the efficiency of the fuel cell.

The researchers envisage the use of such a system as substitutes for batteries in mobile applications.

Madelaine Chapman

Reference
S Kwon, J S Hwang and T Kim, *Lab Chip*, 2007, DOI: 10.1039/b700040e

Instant insight

Back in black

Markus Antonietti, Arne Thomas and Maria Titirici discuss the hydrothermal carbonization of biomass – is it a solution to the CO₂ problem?

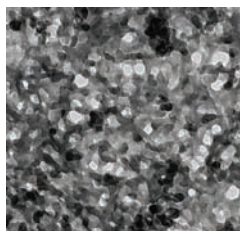
The global atmospheric concentration of carbon dioxide (CO₂) has increased markedly as a result of human activities since the industrial revolution. The inevitable impact on the world climate, recently announced by the IPCC (Intergovernmental Panel on Climate Change),¹ has prompted intensive discussions from politics, industry and the scientific community about how to treat the CO₂ problem.

Energy storage and saving and a more responsible usage of the remaining energy resources is unavoidable. Replacing parts of the energy production system by biomass schemes (bioethanol, -diesel or -gas) or the artificial sequestration of CO₂ (in the ocean or into underground geological formations) are also under discussion. All these methods can lower future CO₂ emission, but cannot compensate for past and current emissions of CO₂ from fossil fuels. However, the IPCC report claims that anthropogenic warming and sea level rise will continue for centuries due to the timescales associated with climate processes and feedback, even if greenhouse gas concentrations were to be stabilized immediately. It would therefore be highly desirable to not only slow down further CO₂ emissions, but also to invert the current development by sequestering the atmospheric CO₂ released by many years of industrialization.

The biggest carbon converter, with the highest efficiency to bind CO₂ from the atmosphere, is biomass. Interestingly, the removal of just 8.5% of freshly produced biomass from active ecosystems would compensate for all the CO₂ liberated from oil. Coal formation from biomass is one of the natural sinks that has been active in the past on the longest scale. Natural coalification of biomass takes place on a timescale of some hundred



Biomass can be converted to a form of carbon much like coal



A variety of nanostructures and porous architectures can be made

(peat) to hundred million (black coal) years. Due to its slowness, it is usually not considered in renewable energy exploitation schemes or as an active sink in CO₂ cycles. Nevertheless, it is obvious that carbon fixation into coal is a lasting effort, as brown or black coal are practically not biodegradable. Thus, turning coal formation into an active element of carbon sequestration schemes would be very meaningful, but requires the acceleration of the underlying coalification processes.

Hydrothermal carbonization (HTC) can be such a process:² HTC describes heating carbohydrate sources in water, e.g. biomass dispersions, in a closed reaction vessel for 4–24 h to temperatures around 200°C. Upon dehydration of the carbohydrates, carbon with a chemical composition similar to brown coal is observed. Thus, HTC is an extremely simple, cheap and easily scalable process. Furthermore, it was shown that HTC of carbohydrates can yield interesting carbon micro- and nanostructures, such as carbon microspheres. Using suitable additives, carbon nanocables and fibres, porous carbon architectures and metal–carbon composite materials can be generated.

In CO₂ conversion schemes, HTC

has a number of other practical advantages: once activated, HTC is a spontaneous, exothermic process, it liberates up to a third of the combustion energy stored in the carbohydrate throughout dehydration. Furthermore, HTC inherently requires wet starting products or biomass, as effective dehydration only occurs in the presence of water, plus the final carbon can be filtered easily from the reaction solution. This way, complicated drying schemes and costly isolation procedures can be avoided. In addition, most of the original carbon stays bound to the final structure. Carbon structures produced by this route—either for deposit or materials use—are therefore the most CO₂-efficient.

Thus, the carbonization of biomass from fast growing plants can be an efficient process for removing atmospheric CO₂. For a negative atmospheric CO₂ balance, the generated carbonaceous materials have to be deposited on a large scale, and potential carbon landfills may lay the foundations for chemical starting materials of the next century. Another quite attractive application with immediate impact is the use of such carbons as water- and ion-binding components to improve soil quality. This is a chemical process that is also found in nature, and 'carbonaceous soil' is the largest active carbon sink on earth. Instead of clearing the rainforest for questionable palm oil production, such a 'carbon-reinforced rainforest' would produce at least 10 times the energy, but stored in carbon, while also being CO₂-benign for the climate and supporting biodiversity at the same time.

In that sense, HTC can be seen as much more than just a technique for making carbon-rich substances.

Read the full Opinion article in issue 6 of New Journal of Chemistry.

References

- 1 <http://www.ipcc.ch/>
- 2 M-M Titirici, A Thomas and M Antonietti, *New J. Chem.*, 2007, DOI: 10.1039/b616045j

Training for Industry 2007

Each year the RSC organises a programme of events dedicated to the advancement of the chemical sciences. With over 30 conferences, one-day symposia and training courses, we offer a range of development and networking opportunities at the cutting edge of science for members and non-members across academia and industry. The remaining training courses organised for 2007 are listed below.

Essential Skills Management Courses

Date and Location

Fundamentals of Project Management	11–12 September	London
Networking	26 September	London
Presentation Skills	2 October	London
Thinking Strategically	11–12 October	London
Team Working and Co-operation	1–2 November	London
Change Management	19–20 November	London
Time Management and Personal Effectiveness	29 November	London

4 Chemists Courses

Chemical Biology 4 Chemists	18–20 June	Leeds
Chemistry 4 Chemical Engineers	4–6 September	Leeds
Concepts of Chemical Engineering 4 Chemists	10–12 September	London
Molecular Modelling 4 Chemists	17–19 September	Cardiff
Formulation 4 Chemists	27 September	Bristol

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Interview

Health and natural hazards

José A Centeno talks to Kathryn Lees about how Mother Nature affects our health



José A Centeno

José A Centeno is a physical chemist and senior research scientist at the US Armed Forces Institute of Pathology in Washington, D.C., and a member of the editorial board for the *Journal of Environmental Monitoring*. His research in the area of medical geology brings together toxicology, geosciences, environmental medicine and human health.

What is medical geology?

Medical geology is the scientific relationship between natural geological factors and their impact on the development of health problems in humans and animals. The natural environment could be the geochemical composition of rocks or contaminants in water or soil. Medical geology aims to understand how natural geological events, such as dust storms, earthquakes and volcanic eruptions, affect disease and other population health issues.

But medical geology is not a new area: it's been with us for centuries. What is new are the worldwide efforts to improve interactions and research opportunities between environmental scientists, toxicologists, epidemiologists, biologists, earth scientists, public health authorities, pathologists and clinicians to better understand how the natural environment impacts our health.

Recently, the International Medical Geology Association (www.medicalgeology.org) has been launched. This association is a unique opportunity for medical scientists, geoscientists, epidemiologists and toxicologists to share the latest goings-on in medical geology.

What problem poses the greatest challenge for medical geologists?

Earth scientists and medical professionals have long been interested in studies such as water quality, arsenic, mercury and radon. Today, an important research area involves understanding more about how we can map geochemical information and correlate this with environmental epidemiology and disease registry data. If you can overlap local, regional or global geochemical data with disease registry data you could potentially identify what the likelihood is of a particular population developing particular kinds of diseases.

We have disease registry data going back to the 1900s from which we have been able to study, retrospectively, diseases such as the flu pandemic – if you can overlap this health information with geochemical data, it could be a fascinating area.

Is there an undiscovered problem that medical geology could be used to solve in the future?

One of the most challenging problems will be understanding and characterising the environmental and natural factors that contribute to emerging and re-emerging infectious diseases. Infectious diseases are a major cause of human suffering and mortality. Soil-borne and dust-borne human pathogens are potential contributors to the rapid transportation of many infectious agents.

Many regional and local measurements have been taken but, in my opinion, the problem is global. An important step in elucidating the role of natural dust as a contributor of disease is to facilitate cooperation among medical professionals, geologists, climatologists and microbiologists, which will assist in characterising the properties of geogenic dusts, their dispersal and the toxicological pathways of infectious agents they may transport.

So, how much of a threat do dust storms pose?

Research shows that there are ecological and health problems associated with geogenic dust. For example, in the south west of the US, the dust has a peculiar fungus in it which is characteristic of the soil in the region. Geochemical disturbances which cause soil disruption, like earthquakes and human activities such as deforestation and construction, release the fungus. In humans and animals, it can cause respiratory problems, which if undetected, can spread to other parts of the body and cause organ damage.

Recent research by leading organisations has shown that cadmium, mercury, arsenic, lead and chromium could be mobilised in dust. As medical geologists, we need to understand the chemistry and the health implications of these elements.

Can science make a difference to these problems or do solutions depend on government cooperation?

It is evident that governments have to be involved in both the short and long term. They have to be involved in every aspect of medical geology and environmental medicine, and develop programmes to improve integration of these areas.

As a way to initiate integration between earth sciences and public health, the United Nations and the International Union of Geological Sciences have recently launched a global activity – International Year of Planet Earth (IYPE). This aims to demonstrate the societal benefits of geosciences and the need for developing international collaborations. IYPE have selected medical geology as one of the ten topics to focus on in geosciences and public health. As a result, there will be emphasis on outreach programmes and on achieving high quality research.

What message do you have for young scientists?

To look for what is not only academically interesting but for what benefits society as well. Scientists should try and work in areas which benefit the public. That's what makes me passionate about what I do.

Pioneering RSC work on RSS feeds

First came enhanced HTML in electronic journal articles in the first phase of Project Prospect – now further developments means RSC Publishing has become the first ever publisher to enhance RSS feeds with structured subject and compound information.

Journal RSS feeds from RSC Publishing were the first from a scientific publisher to include the graphical abstract. This latest innovation means that RSS feeds from RSC journals will also display ontology terms and compound details, including the 2D image. Users will be able to see at a glance whether the paper is relevant to their research. In addition, hidden coding within the RSS feed allows the metadata to be read by machine – another step towards the ‘semantic web’.

This is the latest development

in Project Prospect, a unique service developed by RSC Publishing with academic partners. Phase one, launched in February 2007, provided



hyperlinked compound information within the HTML, links to terms from the IUPAC Gold Book, plus links from ontology terms to definitions and related papers. Enthusiastically

received by authors and readers, feedback since launch has also resulted in improvements to the Toolbox from which these enhancements are available.

Compound structures are now shown with a single click, navigation within the Toolbox has been enhanced – and the Toolbox itself can be made transparent, avoiding any interference in visibility when viewing the article.

To see for yourself, look out for the Project Prospect icon in RSC journal contents lists that identifies enhanced articles. So far, 500 articles have been published that feature these enhancements.

Find out more at: www.projectprospect.org

Books on chemistry in industry

The RSC is continually aiming to provide both scientists in the lab and those working in industry with reliable and high-quality reference material. Three recently published titles focus on industry-related topics and make excellent reading:

Concepts of Chemical Engineering 4 Chemists (S Simons) – An essential handbook and resource guide for scientists who find themselves working in a chemical engineering-type environment.

Metal-Catalysis in Industrial Organic Processes (G P Chiusoli, P Maitlis) – Covers the major areas of the field, discussing the logic of using catalysis in industrial processes as well as the mechanisms involved.

Article breaks new ground

Research from across four institutions, in two countries, and involving eight researchers published in *Molecular BioSystems* has become the first RSC Open Science paper. Authors from the UK and US collaborated on the work, which involved screening chemical compounds and monitoring changes in tissue during early skeletal development in zebrafish.

The study is an excellent example of research carried out at the chemistry–biology

interface, which is a prime focus of the *Molecular BioSystems* journal.

Zebrafish embryos can be monitored relatively easily outside of the uterus and are transparent, so changes can be clearly observed. They serve as models in the study of Menkes disease in humans, a developmental disease associated with copper metabolism.

In the study, mercaptopyridine-*N*-oxide (MCP) was found to affect the development

of the notochord, an important tissue involved in early skeletal development. Results suggested that MCP targets the copper-dependent enzyme lysine oxidase.

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Energy & the Chemical Sciences

Sugar catalysts can turn waste vegetable oil into biodiesel

A sweet future for biodiesel

As fossil fuel reserves start to run dry, alternative fuel sources such as biodiesel, which is made from renewable biological material, are needed. Now, Min-Hua Zong at the South China University of Technology, Guangzhou, and colleagues have used a sugar catalyst to prepare biodiesel from waste vegetable oil. Sugar catalysts, made by the sulfonation of partially carbonized D-glucose, have previously been used for making biodiesel from new vegetable oils, but had never been successfully used in making biodiesel from waste oil.

According to Zong, one factor holding back the widespread use of biodiesel is the cost of the vegetable oil starting materials. And the presence of free fatty acid impurities in waste vegetable oil makes it difficult to convert this cheap and readily available potential fuel source into biodiesel. A number of solid acid catalysts, such as zeolites, have found limited success in converting waste oil to biodiesel,



but they can't operate effectively under the required harsh conditions. Sulfated zirconia has shown to be a very effective

Sugar catalysts aren't put off by the impurities in waste vegetable oil

catalyst for the reaction, but the cost of the rare zirconium metal is prohibitive. Zong's sugar catalysts have a higher activity than zeolites, and are cheaper to prepare than the zirconia catalysts.

Zong is committed to further research in this area. 'Environmentally-friendly production of cheap renewable fuels is very important,' she said. 'I am sure that biodiesel research is a growth area and that sugar catalysts will be an important part of it.'

Mark Keane, a chemical engineer at Herriot-Watt University, Edinburgh, UK, agreed that this work could be significant. 'The use of sugars as catalytic agents to convert waste oils is certainly intriguing and could potentially serve as a progressive approach to a burgeoning waste treatment issue,' he said.

Rebecca Gillan

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Min-Hua Zong et al., *Green Chem.*, 2007, 9, 434
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Energy themed issues in RSC journals

Green Chemistry presents research on Fuel Synthesis and Processing

PCCP explores Alternative Fuel Technologies in a series of issues

New Energy Materials are highlighted in the *Journal of Materials Chemistry*

Dalton Transactions is hosting a web theme issue on CO₂ at Metal Centres

Journal of Environmental Monitoring takes a look at Organic Contaminants: Sources, Fate, Behaviour & Effects



To find out more about energy at the RSC visit: www.rsc.org/energy

Research Highlights

Rhenium builds model bridges with uranium

Safer storage of nuclear waste

Nuclear waste repositories could be safer places, thanks to UK chemists, who have revealed the likely structure of a contaminant in reprocessed nuclear fuel.

Nuclear fuel is generally reprocessed by extracting out the actinide metals uranium and plutonium. However, this extracted material is often contaminated with another radioactive metal, technetium, which can catalyse unwanted side reactions and complicate waste storage. Now, Iain May, David Collison and colleagues at the University of Manchester have discovered how technetium, in the form of pertechnetate [TcO_4^-], is extracted during reprocessing.

'Pertechnetate would traditionally be classed as a weakly coordinating anion,' said May, 'and we were very interested in why pertechnetate so effectively co-extracted.' Pertechnetate contaminates the extracted material by forming a



Reprocessed nuclear fuel often contains radioactive technetium as a contaminant

complex with uranium, said May. Studying perrhenate, [ReO_4^-], a non-radioactive analogue of pertechnetate, the team showed that perrhenate can act as a bridge between two uranium ions, as well as a simple, singly bonding ligand.

'The demonstration of perrhenate as an inner-sphere ligand in these

uranyl complexes serves as a good model for how pertechnetate may coordinate actinyl compounds in general,' said Thomas Albrecht-Schmitt, an expert in actinide complexes at Auburn University, Alabama, US.

'A better molecular understanding of the behaviour of pertechnetate in this waste could ultimately aid safe and cost-effective treatment and disposal,' said May. 'Nuclear power is now being seriously considered by many countries as a key component of a secure "carbon neutral" energy policy. Future fuel processing technology will require a sound fundamental understanding of actinide and fission product coordination chemistry.'

James Mitchell Crow

Reference

Gordon H. John *et al.*, *Dalton Trans.*, 2007, 1603 DOI: 10.1039/b614481k

Enzymes bound to electrode take away the need for mediator molecule

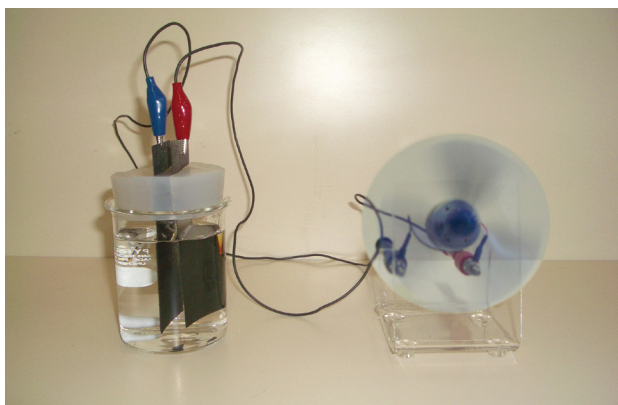
Simply biofuels

A simple enzyme-based biofuel cell has been made by a team of Japanese scientists.

The cell, made by Kenji Kano, Seiya Tsujimura and colleagues at Kyoto University, Japan, uses enzymes to catalyse oxidation of D-fructose and reduction of dioxygen to generate electricity.

The fuel is oxidised by one enzyme at the anode, and the electrons reduce dioxygen via another enzyme at the cathode.

Most previous biofuel cells have needed a mediator molecule, which is stable in two oxidation states, to speed up electron transfer from the enzyme to the electrode. By engineering carbon electrodes with carbon nanoparticles, the team bound a fructose oxidising enzyme, D-fructose dehydrogenase, onto



The cell in action

Reference

Y Kamitaka *et al.*, *Phys. Chem. Chem. Phys.*, 2007, DOI: 10.1039/b617650j

the electrode surface, increasing the speed of electron transfer to the anode without needing a mediator. Another enzyme, laccase from *Trametes sp.*, was used to reduce dioxygen at the anode, completing

the circuit.

Eliminating the need for mediators may simplify the construction of biofuel cells, and as the device can operate under mild conditions, Kano hopes that 'one compartment biofuel cells may be developed as power sources of implantable devices within humans, such as pacemakers, insulin pumps, sensors and prosthetic units.'

Frederic Barriere of the University of Rennes, France, said the work is a significant development, and that he 'awaits impatiently future developments such as refining such electrodes towards a layer by layer approach to increase the maximum current density.'

Victoria Chapman

To find out more about energy at the RSC visit: www.rsc.org/energy

Interview

Investing in a greener future

Richard Pike gives his thoughts on the energy debate



Richard Pike

Richard Pike is the Chief Executive of the Royal Society of Chemistry. Dr Pike has worked in a wide spectrum of scientific, engineering and management roles in the UK and internationally, with a long track record in the chemical sector notably in the oil, gas and petrochemicals industries.

What do you think are the important issues in the energy sector at the moment?

Undoubtedly climate change and security of energy supply, but also clarity in what we teach our children about energy, its use and consequences.

What motivated you to work in the energy industry?

It was probably a classic example of parental influence! My father worked as a chartered engineer, in the shipping sector of the oil industry. As a child, I was surrounded by books on science and engineering, and experienced - even as a ten-year old - having a tour of the engine room of one of the world's largest oil tankers, and being shown around an oil refinery. At school I was interested in mathematics and the physical sciences, and at Cambridge University studied engineering with a BP scholarship. Energy has been in my blood since!

What attracted you to the job of CEO of the RSC?

I had had a fascinating 30 years in the oil and gas industry, working all over the world, with a 5-year interlude as Director General of the Institution of Mechanical Engineers. It meant I appreciated the significance of chemistry in underpinning many of the issues facing the world - and their solutions - and had the experience of running a learned society. But I was not entirely familiar with all the topics now covered by the chemical sciences, nor indeed the precise workings of the chemistry profession, and therefore the job would be an interesting challenge. And that is what it has turned out to be!

How do you think the RSC can contribute to the energy debate?

We lobby key decision makers on matters relating to energy policy, research, funding and the availability of highly skilled people. And, the RSC educates people at all levels about the key scientific and technical issues associated with energy.

In the next 20-50 years what do you think the key challenges are for the chemical sciences in terms of energy?

There is a need to decarbonise transport by developing highly efficient biofuels, lightweight construction materials, hybrid and electric vehicles, battery technology and hydrogen as a fuel. Additionally, there is a need to maximise the efficiency of conventional vehicles and fuels. We must harness renewable energy more efficiently,

particularly to improve the efficiency in the next generation of photovoltaic cells. It is important to develop carbon capture and storage technology so that the vast coal reserves and the remaining oil and gas resources that will be exploited are done so with minimal green house gas (GHG) emissions. Finally, and perhaps most importantly we must invest in skilled people and high quality research and development such that sustainable energy technologies can be developed for the future.

How can the chemical sciences help with the energy problem?

The chemical sciences underpin almost all aspects of energy and are critical in developing new energy options. Perhaps the most exciting issues are the development of photovoltaics, new biofuels and solving the problem of energy storage. For photovoltaic devices the key issues are improving efficiency and reducing cost - work on artificial photosynthesis is particularly exciting. For biofuels, which are currently made from food crops, there is competition for land between food and fuel. This could be eliminated if next generation biofuels are made from lignocellulosic biomass, such as straw or wood. This may result in yield improvements and carbon emission reduction compared with current biofuels. Finally, energy storage is a critical issue as there are limited options for both large and small scale storage. Hybrid and electric vehicles and intermittent renewable energy sources (e.g. wind power) are limited by current storage technologies. New developments here, such as those in the areas of lithium based batteries and "lab on a chip" devices could be vital in developing new energy technologies.

Are there any scientists you most admire and why?

I admire those who have challenged the status quo, and have provided order to what seemed uncoordinated or inconsistent observations at the time. I always have time to read about Darwin, Mendeleyev, Einstein and Bohr. More latterly, the popular work of Crick and Watson, and others, in understanding the genetic code has been fascinating.

The next generation of scientists will play a key role - if you had one piece of advice to pass onto them, what would it be?

Be enthusiastic, look at the big picture, and make a difference.....but get your facts straight!

To read the full interview visit: www.rsc.org/energy

News & Policy

The RSC responds to the energy challenge

Filling the energy gap

The next half-century will almost certainly be a period of significant change in Europe and globally when it comes to the provision of energy. Concerns over energy security and improved predictions on the consequences and costs of climate change will be key drivers toward an energy policy that promotes diversity over reliance on one or two main energy sources.

In July 2006 the government published a report 'The Energy Challenge' which described its energy policy and the long term challenges facing the UK. In particular that the UK will become increasingly reliant on imported oil and gas as North Sea reserves diminish, and that several nuclear and coal fired power stations are closed. Indeed, it is expected that the UK will be importing as much as 90% of its gas requirements by 2020, and in the medium term the UK will have a shortfall in electricity of approximately 25GW by 2025. To put this in perspective the current peak electricity demand is 60GW.

To counteract the growing



The UK will be importing as much as 90% of its gas requirements by 2020

reliance on imported energy the report proposed a number of measures. These included extending the EU Emissions Trading Scheme and Climate Change Levy to encourage companies to invest in cleaner energy-producing technology both in the UK and abroad; encouraging individuals and companies to save energy through education and new products; encouraging the use of cleaner-combined heat and power plants; developing a diverse energy system based on several fuel types, routes and storage facilities and finally investing in new power stations.

The RSC responded to the report with the following key points. The UK energy policy must promote a diverse energy mix avoiding over reliance on a single energy source; a clear coordinated energy policy is essential and should be long-term, unbiased toward specific technologies and independent (there must be cross party consensus); that technology alone will not be enough in closing the gap, reducing demand must also

be addressed; and finally that the chemical sciences will play a crucial role in developing clean energy technologies in the medium and long term. The RSC also believe that a UK geological repository for nuclear waste is also necessary as part of the long term solution.

It is clear that the chemical sciences will make important contributions in the development and implementation of new energy strategies. The transition from an economy based on fossil fuels to a more sustainable energy mix will require considerable ingenuity from chemists and the other science and engineering disciplines. Scientists will have to develop both sustainable energy systems and also find more efficient ways of producing, refining and using fossil fuels during the transition.

To read the full report 'The Energy Challenge' visit www.dti.gov.uk/energy/review/ and to find out more about the RSC energy policy please contact Dr Jeff Hardy (tel: +44 (0)20 7440 3395; email: hardyj@rsc.org)

Focusing on the future

The rapid growth of interest in energy and environmental issues has created the need for authoritative reviews on such matters. This need has been addressed by many RSC authors and much of this work is presented in the renowned book series Issues in Environmental Science and Technology, titles include *Transport and the Environment* and *Chemicals in the Environment: Assessing and Managing Risk*. Other popular titles include *Clean Energy* (Dell, Rand), *Sustainability and Environmental Impact of Renewable Energy Sources* (Harrison, Hester) and *Management of Aging Graphite Reactor Cores* (Neighbour).

Expanding on this, is the world class Specialist Periodical Report



Key energy related books from the RSC

on Catalysis, Volume 19.

Catalysis is essential in the processes used to find cost efficient and environmentally sound methods of converting natural resources into fuels and energy. This book, fully referenced to the primary literature, brings together the most recent work of recognised international experts and includes chapters on The Catalysis of Biodiesel Synthesis, and Catalytic Reforming of Liquid Hydrocarbon Fuels for Fuel Cell Applications, Promotion Effects in Co-based Fischer-Tropsch Catalysis.

To find out more visit the RSC eBook Collection www.rsc.org/ebooks
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RSC Publishing

Green chemistry for fuel synthesis and processing

DOI: 10.1039/b706803b

This themed issue contains peer-reviewed papers presented at the Symposium on Green Chemistry for Fuel Synthesis and Processing as a part of the 232nd National Meeting of the American Chemical Society (ACS) held in San Francisco during September 10–14, 2006. The guest editors are grateful to the Division of Fuel Chemistry of ACS for the sponsorship.

Syntheses, processing and consumption of fuels represent many local and global environmental and safety challenges. The major issues in green chemistry for fuel synthesis and processing include eliminating waste from the production and consumption of fuels, utilizing alternative feedstocks to the depleting petroleum-based feedstocks (in the short term) or other fossil-based feedstocks (in the long term), developing novel catalysts and processes, using clean fuels, improving energy efficiency, and identifying renewable energy resources for future applications. Green chemistry for fuel synthesis and processing will remain a great

challenge and also a tremendous opportunity to chemists and engineers worldwide.

This themed issue is the first one on fuel in the *Green Chemistry* journal. The papers in this issue present the very recent progresses in this very important field. They cover most of the important topics as responses to the above-mentioned challenges. The contents include alternative feedstocks (mostly methane-based feedstocks and biomass), Fischer–Tropsch synthesis, novel catalysts, new environmentally benign technologies, new energy materials, as well as CO₂ separation and utilization, which are immediately needed for the current demanding energy and environmental situations. Several new concepts presented in this issue, such as the development of an economically viable bio-refinery for the production of fine chemicals, sorption-enhanced steam reforming of methane for hydrogen production with CO₂ capture, *etc.*, will become important technologies for future fuel syntheses and processing.

Another upcoming symposium in this series will be held in 2008 during the 235th National Meeting of the American Chemical Society in New Orleans, USA. The focus will be on “Green Chemistry for Sustainable Energy Supply and Conversion”. We are convinced that we will see more significant progress in this important field of research and application.

We acknowledge all authors for their contributions to the success of the symposium and this themed issue. Thanks are also due to all of the referees. It is their careful review of the creative work that makes this issue possible. We also owe special appreciation to the managing editor of *Green Chemistry*, Sarah Ruthven, for her interest and support for this topic.

Chang-jun Liu, Tianjin University, China, (ughg_cjl@yahoo.com), **Ben W.-L. Jang**, Texas A&M University-Commerce, USA, (Ben_Jang@tamuc-commerce.edu) and **Roger Glaeser**, University of Stuttgart, Germany, (roger.glaeser@itc.uni-stuttgart.de).

Green chemistry perspectives of methane conversion *via* oxidative methylation of aromatics over zeolite catalysts†

Moses O. Adebajo*

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DOI: 10.1039/b614281h

Methane gas is known to be the most destructive greenhouse gas. The current world reserves of natural gas, which contains mainly methane, are also still underutilized due to high transportation costs. Thus, considerable interest is presently shown in conversion of methane to transportable liquid fuels and chemicals of importance to the petrochemical industry. The catalytic methylation of aromatics is one possible new route for converting methane to more valuable higher hydrocarbons. This paper provides a general overview of the recent work that we and other researchers have done on the utilisation of methane for catalytic methylation of aromatic compounds and for direct coal liquefaction for the production of liquid hydrocarbons. In particular, the paper presents a detailed description of more recent substantial experimental evidence that we have provided for the requirement of oxygen as a stoichiometry reactant for benzene methylation with methane over moderately acidic zeolite catalysts. The reaction, which has been termed “oxidative methylation”, was thus postulated to involve a two-step mechanism involving intermediate methanol formation by methane partial oxidation, followed by benzene methylation with methanol in the second step. However, strongly acidic zeolites can cause cracking of benzene to yield methylated products in the absence of oxygen. The participation of methane and oxygen, and the effective use of zeolite catalysts in this methylation reaction definitely have some positive green chemistry implications. Thus, the results of these previous studies are also discussed in this review in light of the principles and tools of green chemistry. Various metrics were used to evaluate the greenness, cost-effectiveness, and material and energy efficiency of the oxidative methylation reaction.

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† Electronic supplementary information (ESI) available: Supplementary data and information – oxidative methylation of aromatics over zeolite catalysts. See DOI: 10.1039/b614281h



Moses O. Adebajo

Dr Moses Olorunfunmi Adebajo was born in Nigeria and studied Chemistry at the University of Ife (now Obafemi Awolowo University), Ile-Ife, Nigeria where he received his B.Sc. (Hons) and M.Sc. degrees. He also holds the M.Sc. Chemistry degree from The University of Manitoba, Winnipeg, Canada. He obtained his PhD in Chemistry at The University of New South Wales, Sydney, Australia. He is currently a Research Fellow at The

University of Queensland, Brisbane, Australia. His research interests include nanoporous and nanostructured materials and their environmental and catalytic/photocatalytic applications (e.g. methane conversion, hydrogen production and photo-degradation of air and water pollutants).

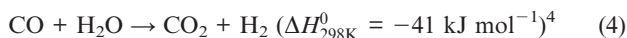
1 Introduction

Methane gas has been identified to be the most destructive greenhouse gas.¹ The gas is also the major constituent of natural gas, the current world reserves of which are still underutilised due to high costs of transportation, especially from the remote areas of Asia, Siberia, Western Canada and offshore reservoirs of Australia where they are located. Hence, considerable interest is presently shown in the conversion of methane to transportable liquid fuels and chemicals of importance to petrochemical industry in addition to its previous sole use for heating purposes by combustion. One problem with methane conversion is the stability of the methane molecule, with a C–H bond energy of 439 kJ mol^{−1}, which makes it resistant to many reactants.² Hence, considerable efforts have been made by researchers on the development of catalytic processes for activation of methane. The conventional catalytic technology for the conversion of methane to liquid fuels and feedstocks involves a two-step process in which methane is first converted to synthesis gas by steam reforming (eqn (1)), CO₂ reforming (eqn (2)), or partial oxidation (eqn (3)),³ followed by either Fischer–Tropsch synthesis of hydrocarbons or methanol synthesis and conversion to hydrocarbons.



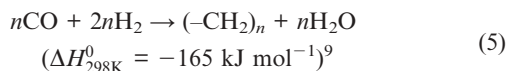


The catalytic steam reforming process is conducted over a supported nickel catalyst and is an established technology.⁷ The water–gas shift reaction (eqn (4)) which is used to adjust the H_2/CO ratio to suit the subsequent use to which the synthesis gas is to be put is also an established technology:



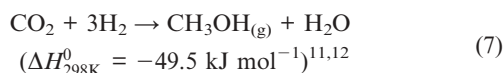
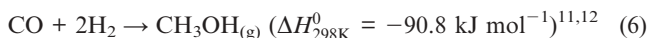
The overall reforming reaction is highly endothermic and consumes a considerable amount of energy. The process is generally regarded as being inefficient and very costly, constituting about 70% of the investments in a methanol plant.⁸

The Fischer–Tropsch synthesis represented by eqn (5) is essentially an oligomerisation/polymerisation process involving the conversion of the synthesis gas to higher hydrocarbons covering a fairly wide range of molecular weights. Since the hydrocarbons produced are mainly aliphatic in nature and usually without extensive chain branching, further processing is required if a high-octane gasoline is the desired end product.



The classical Fischer–Tropsch process is conducted over an iron catalyst and is a developed technology.¹⁰

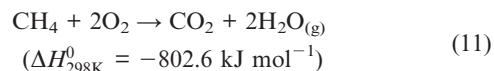
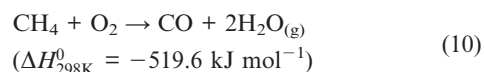
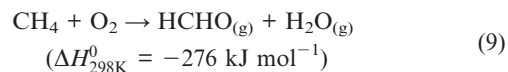
The conversion of synthesis gas to methanol for subsequent conversion of the methanol to hydrocarbons *via* the methanol-to-gasoline (MTG) Mobil Technology process is also an established process represented by the following reactions:



The modern low-pressure methanol synthesis technology developed by ICI involves the passage of a gas mixture containing H_2 , CO and CO_2 over a catalyst containing Cu , ZnO and Al_2O_3 at temperature of about 250–300 °C and 50–100 atm pressure.¹³ The MTG process is conducted over HZSM-5 catalyst, and it is generally agreed that the reaction is Brønsted acid catalysed, and proceeds first to the formation of C_2 and C_3 olefins which undergo chain length by step-wise chain growth and by oligomerisation followed by cyclisation and aromatisation to give aromatics in the C_6 – C_{10} range.¹³

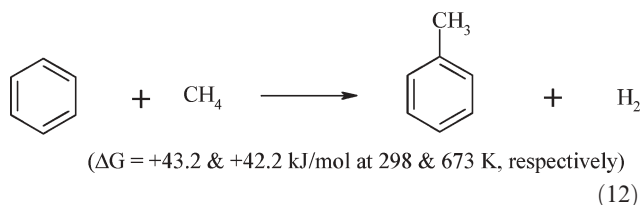
Other approaches of catalytic methane conversion that have been extensively investigated but not yet implemented on an industrial scale include catalytic partial oxidation of methane to methanol (eqn (8)) and oxidative coupling to C_2 hydrocarbons. The direct partial oxidation of methane to methanol would be a highly desirable alternative to the synthesis gas route since it is exothermic, and because, in

principle, a single step process would be technically simpler, particularly in relation to the efficiency of heat recovery upon which the synthesis gas route depends for its economic viability. Unfortunately, the complete or ‘deep’ oxidation to CO and CO_2 (eqn (10) and (11)) is thermodynamically even more favourable so that it is necessary to preserve the valuable primary oxygenated product which can be done by either product removal or suppression of secondary reactions.^{11,12}



Several reviews^{3–6,12–20} on these processes and other methane catalytic conversion processes have been published.

One possible new route for the utilisation of methane derived from natural gas or other sources for conversion to more valuable higher hydrocarbons is the methylation of aromatic hydrocarbons. This route has been the subject of some recent investigations.^{21–32} For example, the direct methylation of naphthalene, toluene and phenol with methane over aluminophosphate molecular sieves in a high pressure batch reactor has been demonstrated.^{21,22} More recent batch reaction investigations^{25,26} have also revealed the incorporation of methane in the presence of Cu-beta, H-beta and CuZSM-5 into a variety of organic substrates (*eg.* benzene, toluene, phenol) which model petroleum, coal and liquefaction residue structures. The utilisation of methane in this way is one of the possible uses of natural gas in the petrochemical industry for the production of chemicals of industrial importance. Methane can also be used in such methylation reactions as a hydrogen-rich reagent, in place of the more expensive hydrogen that is currently used, for the production of liquid hydrocarbons by direct coal liquefaction at pyrolysis temperatures. For example, Long *et al.*³³ have demonstrated the reactivity of methane with a range of coals in the temperature range of 350–400 °C and pressure range of 6.0–8.3 MPa over aluminophosphate or zeolite catalysts. However, in contrast to these previous findings, other workers have also reported that methane did not take part in forming methylated aromatic products,²⁴ an issue that the results of our investigations have now resolved. The direct methylation of aromatics with methane (represented by eqn (12) for benzene) is not thermodynamically feasible under normal conditions, but significant yields of methylated products are feasible if the reaction is carried out in the presence of a large excess of methane. Thus, the reactions have often been carried out under high methane pressures (up to 6.9 MPa or 1000 psi), although some investigators have reported high yields of methylated products at only 1 atm and at temperatures as low as 100 °C using superacid catalysts.³⁴



We had previously carried out a series of studies to address the challenges of thermodynamic barrier and inconsistency in previous results with respect to methane participation. These studies were also conducted to investigate the possible role of oxygen in the reaction and to develop better catalysts for methane activation. This paper provides a general overview of such investigations and those of other researchers on the use of methane for catalytic methylation of model aromatic compounds and for direct liquefaction of coal for the production of liquid hydrocarbons. In particular, we present here a detailed discussion of recent substantial experimental evidence that we have provided for the requirement of oxygen as a stoichiometric reactant for benzene methylation with methane over moderately acidic zeolite catalysts. Such an oxidative methylation reaction was postulated to involve a 2-step mechanism involving intermediate methanol formation by methane partial oxidation followed by benzene methylation with methanol in the second step. However, strongly acidic zeolites were found to cause cracking of benzene to yield methylated products in the absence of oxygen. These results have now resolved the lack of agreement in previous studies. Furthermore, our findings that both methane and oxygen participated in the reaction and zeolites were effectively used as catalysts in the methylation reaction definitely have some green chemistry implications. Thus, we also present in this paper a discussion of these previous studies of the aromatics oxidative methylation reaction in light of the principles and tools of green chemistry.

2 Utilisation of methane in catalytic methylation of aromatics

2.1 Direct catalytic methylation of aromatics with methane

As already mentioned, the activation of methane for direct methylation of hydrocarbons is one possible way of utilising methane derived from natural gas or other sources for conversion into more valuable higher hydrocarbons. In this regard, Long and co-workers^{21,22} have previously demonstrated that substituted aluminophosphate molecular sieves catalysed the methylation of naphthalene, toluene and phenol in a batch reactor at 400 °C and 6.9 MPa methane pressure. These workers then subsequently confirmed using a ¹³CH₄ isotropic tracer experiment that the methyl groups in the substituted naphthalene products were derived mainly from methane, thereby indicating direct methylation of naphthalene.²³ Thus, for example, the GC-mass spectrometric analysis of the products of the reaction using ¹³CH₄ showed that the methyl-naphthalene formed from naphthalene contained principally one ¹³C atom and the dimethylnaphthalene contained two ¹³C atoms per molecule. A further confirmation was also obtained from ¹H NMR spectra of the products,

which indicated an estimate of 73% ¹³C in the methyl groups of the products of the ¹³CH₄ experiment. Long *et al.*²⁵ have also demonstrated in a later ¹³CH₄ isotopic tracer study that the reaction of benzene with methane over H-beta and Cu-beta at 400 °C and 5.5 MPa methane-¹³C pressure yielded toluene and xylene products containing substantially methyl-¹³C substituents. This then confirmed that direct methylation of benzene with methane was possible under their reaction conditions in a batch reactor. However, these workers also proposed a second mechanism in which the methylated products are formed by fragmentation and rearrangement of benzene rather than from the reactions of methane itself. It was then suggested that this other mechanism would be favoured by a more acidic zeolite catalyst, since acidity generally promotes cracking and coking of hydrocarbons. In a later investigation by Long *et al.*,²⁶ two mechanisms were also identified for the conversion of methane by a reaction with a wide range of organic substrates (*e.g.* benzene, toluene, phenol *etc.*) over Cu-beta, H-beta and CuZSM-5 catalysts at 350–450 °C and 3.5–9 MPa pressures. According to these workers, one mechanism involved direct methylation by addition of methyl groups while the other involved a disproportionation process probably resulting in carbon deposition.

In contrast to these findings, earlier ¹³CH₄ studies^{35,36} of the methylation of benzene and some other hydrocarbons with methane over nickel on silica and alumina catalysts showed that the methyl group was largely derived from sources other than methane gas. Carbonaceous species were thought to supply part of the carbon for methylation. A more recent ¹³CH₄ isotopic tracer investigation by Lunsford and co-workers²⁴ also failed to reveal the presence of any detectable ¹³C in the methylated products of the methylation of benzene over H-beta catalyst in a flow reactor at 400 °C and 4.8 MPa pressure. They then concluded that benzene served as the sole source of carbon in all of the observed products under their reaction conditions.²⁴ Thus, it appears that there was lack of agreement in previous reported studies with regard to the participation of methane for the supply of methyl groups in the methylation reactions.

2.2 Oxidative methylation of benzene with methane over zeolite catalysts

The question of whether or not methane can be activated over zeolite catalysts to methylate aromatics is an important one to answer in the context of new routes for the utilisation of methane derived from natural gas. Adebajo *et al.* have therefore carried out a series of investigations^{27–29,32,37} on the methylation of benzene with methane over zeolite catalysts that have now resolved the lack of consistency in the previous reported studies as to the actual source of methyl groups in the methylation reactions. A factor not considered in previous work that was looked at in these investigations is the possible role of oxygen in the autoclave during the loading of reactants. These workers have now been able to demonstrate that the presence of oxygen is actually required for the production of methylated products in the methylation of benzene with methane at 400 °C over zeolite catalysts in a high-pressure batch reactor. This is illustrated in Fig. 1 for experiments with

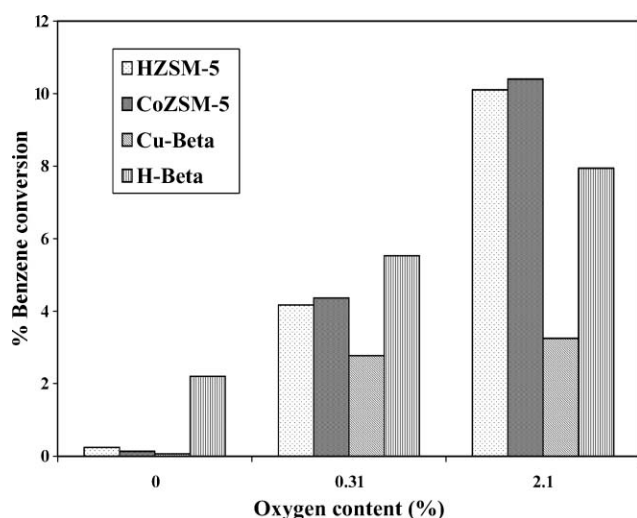


Fig. 1 Variation of benzene conversion with oxygen content for the methylation of benzene with methane in a batch reactor at 400 °C and 6.9 MPa pressure for 4 h.^{27,28}

four different catalysts. It is shown clearly in Fig. 1 that only in the case of zeolite H-beta is there a significant benzene conversion in the absence of oxygen. Fig. 1 also shows that there is an increase in conversion with an increase in the residual oxygen content for all the catalysts.

Experiments with $^{13}\text{CH}_4$ also confirmed the earlier reports that methyl groups in the toluene and xylene products originate at least in part from methane. This is illustrated in Table 1 and Fig. 2 and 3. The results of GC/MS analysis of reaction products of one $^{13}\text{CH}_4$ experiment shown in Table 1 indicate that the toluene product increased in molecular weight by one mass unit on substitution of $^{13}\text{CH}_4$ for $^{12}\text{CH}_4$, while *p*-, *m*-, and *o*-xylenes each increased in molecular weight by two mass units. These results, therefore, confirm that additional C atom(s) in the reaction products originated from methane itself. Fig. 2 shows the ^{13}C solution NMR spectrum of the reaction products of the $^{13}\text{CH}_4$ experiment. This

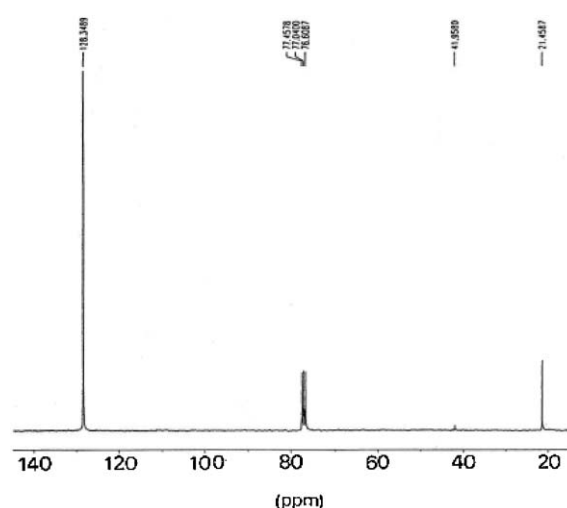


Fig. 2 ^{13}C solution NMR spectrum of CDCl_3 solution of products of reaction of $^{13}\text{CH}_4$ with benzene over CoZSM-5 at 400 °C and 7.1 MPa pressure for 4 h.

spectrum shows a strong signal at 128.3 ppm which is primarily due to benzene. The signal normally observed at 125.3 ppm due to the aromatic toluene carbons alone is not visible in Fig. 2 due to the relatively small amount of toluene produced in the $^{13}\text{CH}_4$ experiment. Nevertheless, the signal at about 21.5 ppm assigned to methyl groups of toluene is very strong implying that the isotopic abundance in the methyl group is at least an order of magnitude above that of the aromatic nucleus. Thus, Fig. 2 indicates that ^{13}C from the $^{13}\text{CH}_4$ was incorporated into the methylated reaction products. Fig. 3 shows the methyl region of the ^1H NMR spectrum of the reaction products of the $^{13}\text{CH}_4$ experiment. The $^{13}\text{C}/^{12}\text{C}$ ratio in the methyl groups in the sample can be estimated by comparison of the J-coupled methyl resonance of $^1\text{H}-^{13}\text{C}$ (satellite peaks on the left and right) and the unsplit methyl resonance of $^1\text{H}-^{12}\text{C}$ (centre signal). From the intensities of these peaks, it was estimated that 92% of the methyl carbon originated from the methane- ^{13}C gas when Co-ZSM-5 was used as catalyst. It is therefore concluded that

Table 1 Relative peak intensities in GC/MS analysis of products of reaction of $^{13}\text{CH}_4$ with benzene over Co-ZSM-5 at 400 °C and 7.1 MPa for 4 h

Product	Methane- ^{12}C reaction	Methane- ^{13}C reaction
Toluene		
$m/z = 90$	—	12.9
$m/z = 91$	105.8	26.9
$m/z = 92$	100.0	108.4
$m/z = 93$	13.6	100.0
$m/z = 94$	—	8.4
<i>p</i> / <i>m</i> -xylene		
$m/z = 105$	17.5	135.7
$m/z = 106$	100.0	57.1
$m/z = 107$	7.5	78.6
$m/z = 108$	—	100.0
$m/z = 109$	—	—
<i>o</i> -xylene		
$m/z = 105$	43.3	52.9
$m/z = 106$	100.0	29.4
$m/z = 107$	7.5	50.0
$m/z = 108$	—	100.0
$m/z = 109$	—	—

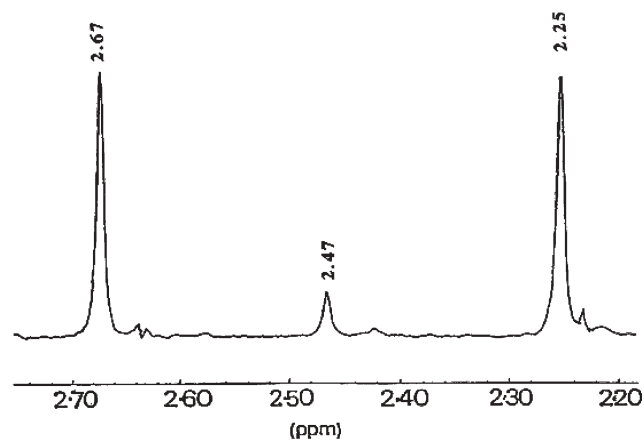


Fig. 3 ^1H solution NMR spectrum of CDCl_3 solution of products of reaction of $^{13}\text{CH}_4$ with benzene over CoZSM-5 at 400 °C and 7.1 MPa pressure for 4 h.

Table 2 Conversion of benzene and selectivity to products for the reaction of benzene with (1) methane + air, (2) under nitrogen and (3) under hydrogen³²

1. Methane + air ^a				
Catalyst	Conversion (%)	Selectivity to products (%)		
		Toluene	Ethylbenzene	Xylenes
None	0.77	33.3	10.0	28.9
HZSM-5	9.32	65.7	17.4	15.5
CoZSM-5	8.14	48.1	31.5	18.5
MnZSM-5	8.46	40.6	40.6	16.4
CuZSM-5	8.02	41.4	37.7	18.5
NaZSM-5	7.93	51.4	28.8	18.2

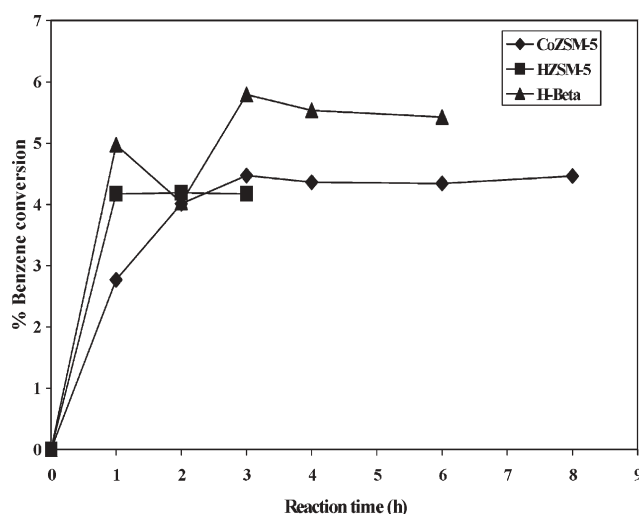
2. Nitrogen ^b				
Catalyst	Conversion (%)	Selectivity to products (%)		
		Toluene	Ethylbenzene	Xylenes
HZSM-5	0.08	65.4	34.6	—
CoZSM-5	0.28	63.0	28.1	8.88
MnZSM-5	0.14	61.1	38.9	—
CuZSM-5	0.07	66.0	34.0	—
NaZSM-5	0.18	54.2	33.2	12.6

3. Hydrogen ^c				
Catalyst	Conversion (%)	Selectivity to products (%)		
		Toluene	Ethylbenzene	Xylenes
HZSM-5	1.25	65.1	22.6	12.3
CoZSM-5	1.06	50.8	37.1	9.62
MnZSM-5	0.76	46.8	36.5	16.6
CuZSM-5	0.30	36.9	50.5	5.61
NaZSM-5	0.29	60.2	39.8	—

^a 400 °C, 6.9 MPa CP grade methane, 4 h reaction time, no removal of residual air. ^b 400 °C, 6.9 MPa nitrogen, 4 h reaction time, no removal of residual air (*i.e.* same reaction conditions as for methane, except that methane is replaced with nitrogen). ^c Same reaction conditions as for methane except that residual air is removed and methane is replaced with hydrogen.

the methane unequivocally provided the methyl groups incorporated into the substituted aromatic products. As shown in Table 2, blank experiments with catalysts but in which methane was replaced with 6.9 MPa nitrogen have further demonstrated the participation of methane in the reaction to produce methylated products.³² Table 2 also demonstrates the importance of the presence of zeolite catalysts for converting benzene to methylated products, since blank runs without a catalyst yielded only 0.8% benzene conversion compared with 8–9% conversions obtained when catalysts were included.

The participation of methane in the reaction was also shown to be limited by the amount of oxygen present in the reaction system.³² Adebajo *et al.* also observed in their investigations that when catalyst was excluded and the batch reactor was flushed with oxygen prior to adding methane, methanol was the major product obtained (about 86% selectivity).²⁸ Furthermore, the methanol was not detected in the presence of zeolite catalysts when oxygen was introduced into the reactor. This suggests that all of the methanol reactant, being more reactive than the initial methane reactant, was consumed to form methylated products over the catalysts. Reactions in the presence of catalyst but at the exclusion of benzene yielded significant amounts of aromatic hydrocarbons (mainly

**Fig. 4** Variation of benzene conversion with reaction time for the methylation of benzene with methane without removal of residual air in batch reactor at 400 °C and 6.9 MPa pressure.²⁸

benzene, toluene and xylenes) that are expected for methanol conversion over acid catalysts. These workers have shown that such methanol-to-aromatics conversion contributes significantly to the benzene methylation reaction.³¹

Adebajo *et al.* further indicated that the addition of methanol to the batch reactor containing benzene, methane and catalyst which had been totally purged of oxygen gave conversions and product selectivities similar to those found in the presence of oxygen.^{27,28} For example, addition of 1.2 mol% methanol gave 0.75% conversion of benzene to toluene and 10.4 mol% methanol gave 5.6% conversion of benzene. It has been demonstrated too that there is no significant effect on benzene conversion and product selectivity on increasing the reaction time beyond 2 h.^{27,28} This is illustrated in Fig. 4 for benzene conversion. This cannot be due to catalyst poisoning (*e.g.* by coke deposition), since it has been shown that catalysts recovered from the reactor could be reused without loss of performance (Table 3).³⁸ The XRD patterns of the zeolites catalysts were also observed to remain unchanged after reaction, as illustrated in Fig. 5 for H-beta. The observation can rather be attributed to the reaction being limited by the amount of oxygen in the reactor, which has already been shown to be the case.³²

Thus, on the basis of these observations reported by Adebajo *et al.*, the reaction was postulated to go *via* a two-step

Table 3 Comparison of fresh with used ZSM-5 catalysts for methane reaction with benzene in the presence of residual air at 400 °C and 6.9 MPa pressure³⁸

Reaction time/catalyst	Benzene conversion (%)	Selectivity to products (%)		
		Toluene	Ethylbenzene	Xylenes
2 Hours				
Fresh HZSM-5	4.19	92.9	4.25	2.86
Used HZSM-5	4.01	91.7	4.34	3.98
4 Hours				
Fresh CoZSM-5	4.36	91.4	3.85	4.75
Used CoZSM-5	3.39	94.1	2.65	3.30

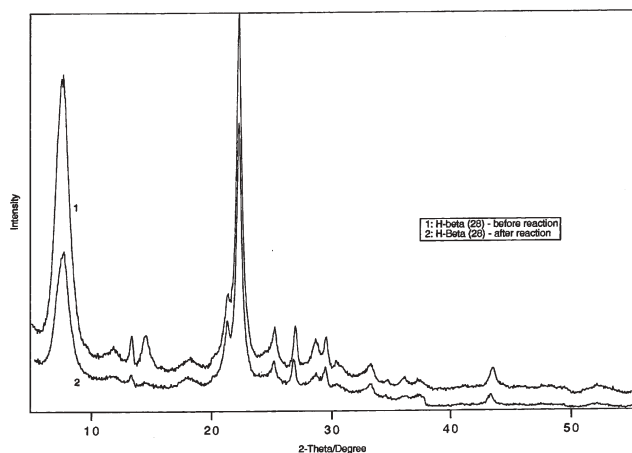


Fig. 5 XRD patterns of H-beta before and after reaction.³⁸

mechanism involving the intermediate formation of methanol by partial oxidation of methane followed by the methylation of benzene with methanol in the second step. The two steps of the reaction are therefore represented by eqn (13) and (14) as follows:



It then follows that the overall reaction is given by eqn (15):



In support of this mechanism, the performance of the catalysts for both benzene methylation with methanol (low pressure flow reaction) and with methane in the presence of oxygen (high pressure batch reaction) have subsequently been demonstrated to show excellent correlation.³⁷ However, in the case of H-beta that exhibits strong acidity, it was shown that methyl aromatics could be formed in the absence of oxygen. This is consistent with an earlier report by Lunsford *et al.*²⁴ that these products are formed from the cracking of benzene over the acidic zeolite. The zeolites provide the small number acid sites of moderate strength that are necessary for the reaction.^{27,28}

Adebajo *et al.*²⁹ have also previously shown that the purity of methane used in the methylation of benzene over zeolite catalysts is critical in determining conversion and product selectivities. Trace amounts of ethylene impurities in the methane used was found to enhance benzene conversions and selectivities to ethylbenzene. However, methane containing ethane impurities yielded negligible benzene conversion in the absence of oxygen over CoZSM-5 catalyst while a much higher conversion was obtained over H-beta due mainly to cracking of benzene.²⁴ These observations are illustrated in Tables 4 and 5.

It therefore appears from the findings reported by Adebajo and co-workers that the zeolites that were used in their series of investigations are not capable of directly activating methane under the relatively mild conditions that they employed. The function of the zeolite catalysts in the high pressure batch reactor was also reported to be the provision of acid sites of

Table 4 Effect of the purity of methane on methylation of benzene²⁹ under standard conditions^a

	Type of methane used ^b	HZSM-5	CoZSM-5
Benzene conversion (%)	CP grade	9.32	8.14
	UHP grade	4.17	4.36
Selectivity to toluene (%)	CP grade	65.7	48.1
	UHP grade	93.0	91.4
Selectivity to ethylbenzene (%)	CP grade	17.4	31.5
	UHP grade	4.05	3.85
Toluene/ethylbenzene ratio	CP grade	3.78	1.53
	UHP grade	23.0	23.7

^a Reaction conditions: 400 °C, 6.9 MPa methane, 4 h reaction time, no removal of residual air. ^b CP methane is chemically pure grade (>99.0% pure) and UHP methane is ultrahigh purity grade (>99.97% pure).

Table 5 Effect of adding ethane and ethylene to the methane used in the methylation of benzene over CoZSM-5 catalyst²⁹ under standard conditions^a

	UHP methane + 2.1% ethane ^b (nil O ₂)		UHP methane + 2.1% ethylene ^b (nil O ₂)	
	CoZSM-5	H-beta	CoZSM-5	H-beta
Benzene conversion (%)	0.60	2.76	28.9	35.5
Selectivity to toluene (%)	66.3	87.7	20.9	23.8
Selectivity to ethylbenzene (%)	33.7	12.3	59.7	62.7
Toluene/ethylbenzene ratio	1.97	7.13	0.35	0.38

^a Reaction conditions: 400 °C, 6.9 MPa methane, 4 h reaction time, removal of residual air. ^b Ethane/benzene and ethylene/benzene molar ratio in the feed 0.64.

moderate strength to catalyse the methylation of benzene (or other aromatics) by methanol.^{27,28} Strong acidity, such as that exhibited by zeolite H-beta, causes cracking of the aromatics and should therefore be avoided.^{24,27,28}

However, Adebajo *et al.* have been able to convincingly demonstrate that *in situ* methylation using methane can be achieved by combining methanol synthesis by partial oxidation of the methane with methylation of aromatics with the methanol intermediate. This concept is very similar to the earlier demonstration by Gesser and co-workers³⁹ that methane partial oxidation could be combined with methanol conversion to gasoline in a two-stage continuous flow reactor.

2.3 Thermodynamics of oxidative methylation of benzene with methane

Fig. 6 shows the plots of the free energies and heats of reaction (ΔG and ΔH), and $\ln K$ against temperature for the oxidative benzene methylation reaction (eqn 15). The regression equations for the ΔG and ΔH plots are as follows:

$$\Delta G = 0.045T - 198.557 \quad r = 1.000 \quad (16)$$

$$\Delta H = -2.714 \times 10^{-6}T^2 + 7.228 \times 10^{-3}T - 202.225 \quad r = 0.9995 \quad (17)$$

Unlike the direct methylation reaction (eqn (12)), Fig. 6 indicates clearly that the overall oxidative methylation reaction

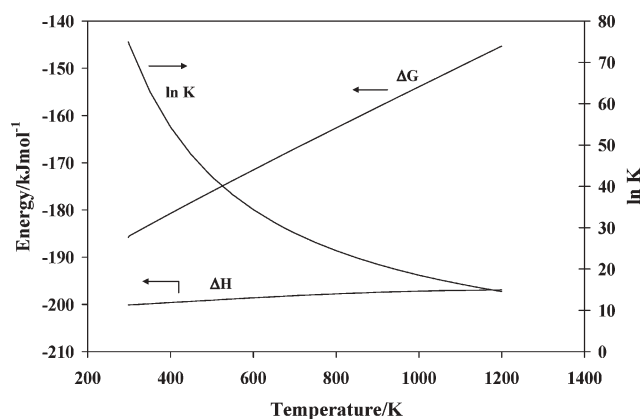
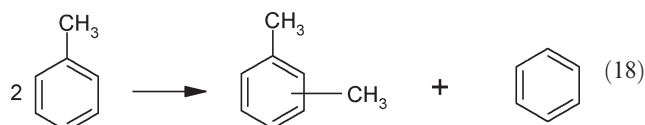
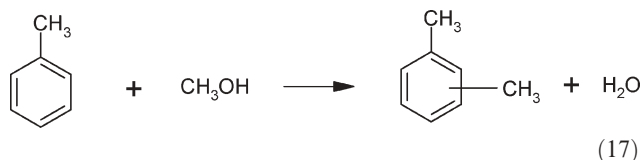


Fig. 6 Plots of ΔG , ΔH and $\ln K$ against temperature for the oxidative benzene methylation eqn (15).

is thermodynamically feasible with highly negative ΔG and ΔH over the temperature range from ambient to 1200 K. Both ΔG and ΔH are shown in Fig. 6 to increase with increase in temperature. Fig. 6 also shows that the equilibrium constants of the reaction over the whole temperature range are very large due to the highly negative free energies of reaction. 100% benzene conversion is therefore predicted for the whole temperature range. The equilibrium constant is also shown to decrease with an increase in temperature, which is consistent with the exothermic nature of the reaction. Thus, it is clear from the thermodynamic data that the oxidative benzene methylation reaction is much more feasible, and therefore more likely to occur, than the direct non-oxidative methylation eqn (12). It is therefore possible to conduct the oxidative reaction using air or O_2 at atmospheric pressure and much lower temperatures. This is an area for further investigation.

2.4 Oxidative methylation of toluene with methane

In view of the two-step mechanism *via* intermediate formation of methanol proposed by Adebajo *et al.*^{27–29,32,37} for the oxidative methylation of benzene with methane over acidic zeolites in a high-pressure batch reactor, a preliminary investigation was carried out by these workers³⁰ on the reaction of toluene with methane over acidic ZSM-5 catalysts in a batch reactor containing residual air to determine the actual contribution of direct methylation (*via* intermediate methanol formation) to the observed reaction products. The reactions were carried out at 400 °C and 6.9 MPa pressure. The major reaction products obtained by these workers were benzene and xylenes. Smaller amounts of ethylbenzene, trimethylbenzene and other higher aromatics were also produced. Over acidic catalysts, the conversion of toluene can, in principle, occur through two different reaction pathways: methylation by methane *via* methanol (as in the case of benzene methylation) and disproportionation, as shown in eqn (17) and (18):



The formation of the methanol by partial oxidation of methane is shown in eqn (13). Both pathways produce xylene products, but only disproportionation produces benzene. Further methylation of xylenes will produce C_9 and higher aromatics, but such molecules may also be formed by disproportionation of xylenes. The selectivity data in Table 6 show that the disproportionation of toluene is a significant pathway over all the zeolite catalysts when the reaction was carried out in the presence of methane–air mixtures since benzene is a major product of the reaction. In an attempt to separate the methylation and disproportionation pathways, Adebajo *et al.* carried out the reaction of toluene over the same catalysts in the presence of nitrogen alone. Under these conditions, disproportionation is the only possible pathway. Their results shown in Fig. 7 and Table 6 indicate that disproportionation is the major pathway followed over the zeolites containing a greater number of acid sites [*i.e.* HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 35$), CoZSM-5 and MnZSM-5]. This is because toluene conversion and product selectivities are similar in both methane–air and nitrogen mixtures over these catalysts, although over the CoZSM-5 and MnZSM-5, the yields of C_9

Table 6^{28,30} Conversion of toluene and selectivity to products for the reaction of toluene (a) with methane + air, (b) under nitrogen and (c) under hydrogen

(a) Methane + air ^a					
Catalyst	Conversion (%)	Selectivity (%)			
		Benzene	Ethylbenzene	Xylenes	C_9+ aromatics
CuZSM-5	8.42	33.8	3.69	17.5	44.9
MnZSM-5	14.9	52.1	2.95	33.5	11.4
Co-ZSM-5	14.8	40.9	3.64	42.1	13.3
NaZSM-5	15.0	46.2	3.59	34.9	15.4
HZSM-5 ^b	7.41	37.5	3.44	23.0	36.0
HZSM-5	33.0	54.3	2.27	39.5	3.95
(b) Nitrogen ^c					
Catalyst	Conversion (%)	Selectivity (%)			
		Benzene	Ethylbenzene	Xylenes	C_9+ aromatics
CuZSM-5	4.48	85.9	1.19	12.1	0.78
MnZSM-5	16.0	60.2	1.09	35.7	2.97
Co-ZSM-5	17.6	63.8	0.88	33.6	1.70
NaZSM-5	3.11	72.7	2.00	22.7	2.62
HZSM-5 ^b	4.66	76.2	1.87	19.5	2.46
HZSM-5	36.0	58.9	0.86	38.1	2.13
(c) Hydrogen ^d					
Catalyst	Conversion (%)	Selectivity (%)			
		Benzene	Ethylbenzene	Xylenes	C_9+ aromatics
CuZSM-5	7.00	52.8	0.38	45.5	1.29
NaZSM-5	10.3	57.8	0.51	40.4	4.15

^a 400 °C, 6.9 MPa methane, 4 h reaction time, no removal of residual air. ^b $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for this catalyst is 140. ^c Same reaction conditions as for methane, except that methane is replaced with nitrogen. ^d Same reaction conditions as for methane, except that methane is replaced with hydrogen.

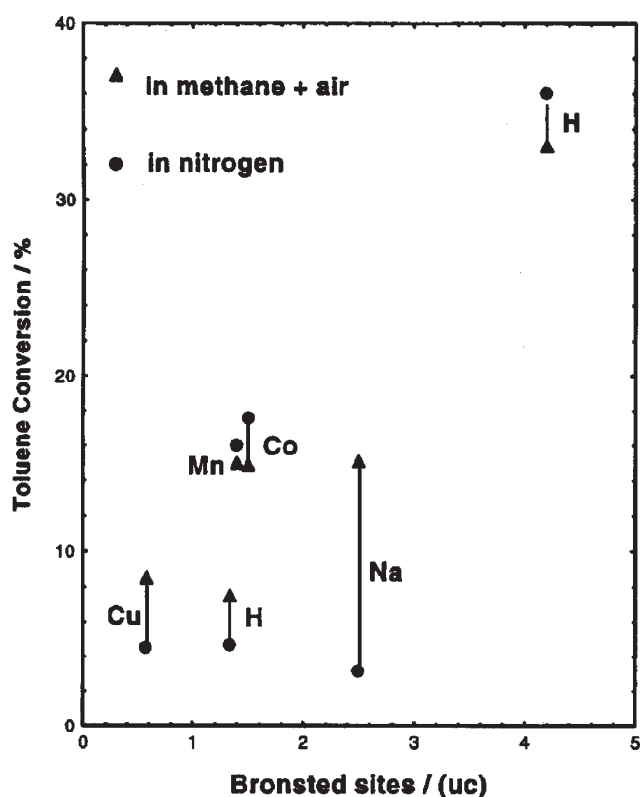


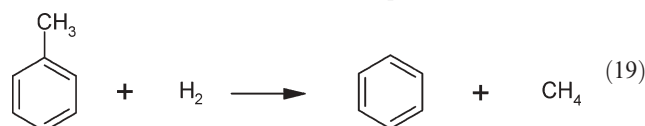
Fig. 7 Plots of toluene conversion against Brønsted acid concentration for reactions carried out in methane–air and in nitrogen.³⁰

and higher aromatics are slightly enhanced in methane–air mixtures. The contribution from disproportionation is reduced and the methylation reaction is enhanced over NaZSM-5 that contains an alkali metal cation and over CuZSM-5 and HZSM-5 that have fewer acid sites. Thus, there are significant differences in the conversions and product selectivities in nitrogen and methane–air mixtures over these catalysts, as shown in Fig. 7 and Table 6.

Adebajo *et al.*³⁰ therefore concluded that in the reaction of toluene with methane in the presence of air, the relative contributions of the methylation and disproportionation reactions depend on the concentrations and strengths of acid sites in the zeolite catalysts used. Disproportionation appears to be reduced and methylation significantly enhanced over catalysts containing fewer acid sites and alkali metal cations. Since the metal-substituted aluminophosphate catalysts employed in the study of toluene methylation reported in earlier investigation²² do not contain strong acid sites, it is likely that the xylenes observed in that work result from the methylation reaction rather than disproportionation. However, it was then suggested by these workers³⁰ that disproportionation must always be considered as a possible reaction pathway in reactions of all aromatic compounds with methane under these conditions in the presence of catalysts containing acid sites.

Adebajo and co-workers²⁸ have also observed considerable toluene conversions over CuZSM-5 and NaZSM-5 when methane was replaced with hydrogen as shown in Table 6. This suggests that the conversion of toluene also involved

hydrodealkylation and hydrocracking reactions in addition to the disproportionation reaction. The hydrodealkylation reaction involves reaction of the toluene with hydrogen to produce benzene and methane as shown in eqn (19):



Huang and Howe⁴⁰ had also previously reported that the toluene reaction over Mo-exchanged ZSM-5 when hydrogen was used as the carrier gas consisted mainly of disproportionation, hydrodealkylation and hydrocracking reactions. However, the toluene conversions obtained from the hydrogen runs over CuZSM-5 and particularly over NaZSM-5 are lower to some extent than the values obtained from the methane runs (Table 6). Therefore, a certain degree of methylation by some reaction with methane might have also occurred in addition to the hydrodealkylation reaction. It was therefore concluded by Adebajo and co-workers that the methylation of toluene with methane in the presence of oxygen over zeolite catalysts is complicated by extensive disproportionation, hydrodealkylation and hydrocracking reactions. Nevertheless, it appears that these undesired reactions can be minimised to enhance the methylation reaction, by using zeolites with reduced Brønsted acidity or containing alkali metal cations.

3 Utilisation of methane in coal liquefaction (or hydrogenation)

3.1 Coal and the mechanism of coal hydrogenation process

Coal is combustible rock consisting mainly of an organic material mixed with some inorganic compounds. It is a hydrogen deficient energy source and its chemical structure can generally not be defined as it is a heterogeneous combination of variable components. The mechanism of the coal hydrogenation process is therefore complex and depends on the type of coal and the severity of reaction conditions such as temperature and hydrogen pressure. Hence, reactions are only understood in general terms. Coals are classified into different ranks according to the degree of coalification, *i.e.* the degree of the chemical change that has taken place due to the decay of the original organic matter from which the coal was formed. Lignite, sub-bituminous, bituminous and anthracite are different ranks of coal. Anthracite, which has the lowest H/C ratio, is the highest ranked coal, while lignite, having highest H/C ratio, is the least coalified.

The development of coal as a source of chemical feedstocks or liquid fuel has experienced a long history. It has been responsible for powering the industrial revolution in Europe and America for more than a century. However, since World War II, coal as a primary energy source has been somewhat controlled by access to crude oil, which is cleaner and more convenient to handle and process. However, coal may once again become a major source of liquid fuels and organic chemicals if coal gasification and direct liquefaction *via* hydrogenation become economically feasible. Low ranked coals, such as lignite and bituminous coals, may be used as a source

of a liquid fuel (synthetic crude) by raising their H/C ratio to a level comparable to that of some crude oils. This could be done by a non-catalytic or a catalytic hydrogenation process.

Coal liquefaction is normally carried out in the pressure range of 200–250 bar and temperature range of 400–450 °C. Lower pressures and short contact times produce heavier liquids while higher temperatures and long contact times reduce liquid yield and increase the amount of gases produced.⁴¹ Iron oxide, iron oxide mixed with alumina, molybdenum and cobalt oxides supported on a highly porous alumina, and oxides of other metals such as nickel and tungsten or their mixtures are used as catalysts for the liquefaction of coal.⁴¹ These catalysts are similar to those used in the hydrodesulfurisation reaction which, together with hydro-denitrogenation reaction, takes place during the hydro-liquefaction of coals.⁴¹

It is generally believed that coal liquefaction occurs *via* a free radical mechanism, and one of the earlier mechanistic details was provided by Curran *et al.*^{42,43} The mechanism involves a free radical process in which coal is thermally decomposed into free radicals, which are capped with or stabilised by abstraction of a hydrogen atom from a donor molecule, such as tetralin. Molecules smaller than the original coal are then formed from this process, thereby resulting in liquefaction. The donor molecule is then hydrogenated by molecular hydrogen such that the liquefaction process continues in a cyclic manner. This mechanism has been expanded by other workers.^{44,45} Most of the hydrogen consumed in the liquefaction reaction comes from molecular hydrogen. It has also been shown that, under hydrogen pressures, the stabilisation of coal-generated free radicals by direct proton abstraction from molecular hydrogen competes favourably with the donor solvent route.⁴⁶

3.2 Liquefaction of coal by catalytic reaction with methane

Current processes for direct coal liquefaction utilise expensive hydrogen (H₂) gas at high pressures. The total hydrogen consumption is usually about 3–5% by weight of the coal feed and most of this hydrogen comes from molecular H₂, while the donor solvent acts mainly as shuttle medium for the H₂ supply⁴⁷ to enhance the hydrogen transfer. Previous cost analyses have shown that a substantial part of the overall operating cost of direct coal liquefaction (about 40–50%) would go into hydrogen generation.^{48,49} Thus, if coal could be liquefied by using an alternative, less expensive gas, up to 50% savings would be achieved. A good substitute for hydrogen which is currently being given some consideration is natural gas, which contains mainly methane. Since methane is rich in hydrogen and has the same bond dissociation energy ($\Delta H^\circ_{300\text{K}} = 439 \text{ kJ mol}^{-1}$) as hydrogen, the direct use of methane derived from natural gas would eliminate the expensive intermediate step of H₂ production. Homolytic scission of hydrogen is unfavourable at coal liquefaction temperatures of 400–450 °C. Hydrogen gas is activated by organic free radicals from coal and a similar activation of methane could also occur to produce methyl and methylene free radicals.

The presence of a catalyst such as Fe₂O₃ during coal liquefaction with methane would fulfil the following functions.

The catalyst would first enhance the dissociation of methane into hydrogen radicals and methyl/methylene radicals. The free radicals produced would then be chemisorbed on the catalyst surface where they would be available for further reactions such as polymerisation into higher molecular weight hydrocarbons. Transition metal catalysts such as iron are known to be capable of dissociative chemisorption of C₁ molecules and hydrogen gas.^{50,51} Long and co-workers have previously demonstrated that microporous aluminophosphate catalysts could activate elemental hydrogen.^{52,53} The catalytic activity was enhanced by the incorporation of common metals such as lead and bismuth and these catalysts were observed to methylate toluene with methanol and to convert methanol to dimethylether. These workers have also subsequently shown that the aluminophosphate catalysts could activate methane during the methylation of naphthalene, toluene and phenol and that H-beta and Cu-beta were also capable of methylating benzene with methane.^{21–23,25} A more recent investigation by Long *et al.*²⁶ have also demonstrated the incorporation of methane in the presence of Cu-beta, H-beta and CuZSM-5 into a variety of organic substrates which model petroleum, coal and liquefaction residue structures. The reaction was carried out at 350–400 °C and 3.5–9 MPa pressure. According to these workers, one mechanism involved direct methylation by addition of methyl groups while the other involved a disproportionation process resulting in carbon deposition.

Initially, methane was reported by Cypres and Furfari⁵⁴ to be chemically inert in their investigation of low-temperature pyrolysis of coal under pressures of H₂–CH₄ mixtures. Later, methane was reported to be very reactive in coal pyrolysis on the basis of greatly increased C₂ and liquid yields.^{55,56} Since then, there now seems to be increasing evidence that methane can react directly with coal at coal liquefaction temperatures^{48,49,57,58} Sundaram *et al.*⁵⁷ in a US patent have shown that in the temperature range of 350–450 °C at 6.9–17.2 MPa, more coal is converted to volatile products under methane than under argon. A hydrogen donor solvent was used in these experiments, typically with a coal-to-solvent ratio of 3 : 1. Smith *et al.*⁵⁸ have also previously reported that methane in combination with small amounts of oxygen or nitric oxide reacts with coals to produce significantly higher yields of hydrocarbons than can be obtained with either helium or methane alone. Egiebor and Gray⁴⁸ have also been able to show in 1 : 1 coal-to-tetralin ratio experiments at 450 °C and 19–24 MPa that conversions to gaseous and liquid products were higher under methane than under hydrogen. These workers further reported that during pyrolysis without tetralin, coal conversions under methane gas pressures were higher than those observed in the runs under argon atmospheres, but lower than under hydrogen. It was shown that methane was consumed in methane atmosphere experiments and that liquefaction with methane produced more than seven times as much C₂–C₅ gases as with hydrogen and eleven times the amount produced with argon. Furthermore, the hydrogen/carbon ratios of the toluene-soluble products from the methane experiments were higher than those from the argon experiments. On examining the solvent, the amounts of methyl-naphthalenes formed were found to be greater under methane than under hydrogen or argon. This appears to be

definitive proof for the reaction of methane during coal liquefaction even in the absence of catalyst. Ozawa and co-workers have provided further support for the reactivity of methane during asphalt degradation over molten tin at 400 °C.⁵⁹

Long *et al.*⁴⁹ further demonstrated the reactivity of methane with a range of coals in the temperature range of 350–400 °C and pressure range 6.0–8.3 MPa over aluminophosphate or zeolite catalysts (CuZSM-5, zeolite beta and Cu-beta). Yields of dichloromethane extractable material were increased by using methane rather than nitrogen atmosphere and different catalysts were observed to assist dissolution to various extents. These workers observed that surface exchanged catalysts were effective but incorporation of metals during aluminophosphate lattice formation was detrimental. Aluminophosphate catalysts were also found to be unstable to water produced during coal conversion but were still able to increase extraction yields. Furthermore, these workers reported that there was a synergistic effect of methane–hydrogen atmosphere for coal liquefaction using their catalyst system, since the conversion under methane–hydrogen was close to that obtained under hydrogen alone, rather than that predicted if an inert gas had been substituted for hydrogen. It was then concluded that involvement of the methane–hydrogen mixtures rather than hydrogen alone might be beneficial in coal conversion processes. Methane incorporation may be oxidative in the presence of coal oxygen and small amounts of ketones have been observed⁴⁹ when oxygen has not been adequately removed in model compound studies. Small amounts of oxygen were also found to affect yields in model compound investigations.⁴⁹

There may be other beneficial flow-on effects once methane is incorporated. Vassallo *et al.*^{60,61} have previously demonstrated that methyl groups on coal macromolecules play a crucial role in capping radicals generated by pyrolysis and are therefore key entities in forming liquid products. Thus, methyl groups in coal or from other reagents assist in promoting oil yields from coal. Highly reactive methyl radicals actively promote liquefaction. Tetramethyl or tetraethyl lead⁶² was found to be a superb additive for increasing oil yields at low hydrogen pressures.

4 Green chemistry perspectives

4.1 Advantages of the oxidative methylation reaction in light of green chemistry principles

According to the book written by Anastas and Warner,⁶³ green chemistry is defined as “the utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products”. In green chemistry, efficiency (or the concept of atom economy that focuses on optimising the incorporation of all materials used in a synthetic process into the final product) is now becoming extremely important in the design or synthesis of a chemical product. Thus, environmental, health, safety and economic considerations are now taken into account by synthetic chemists. If the tools and principles of green chemistry listed and discussed by Anastas and Warner⁶³ in their book are considered, the participation of

methane and oxygen, and the effective use of zeolite catalysts in the aromatics methylation, as well as the thermodynamic feasibility of the reaction all contribute positively to these important considerations and focus of green chemistry. In the light of these tools and principles of green chemistry, the advantages of the oxidative methylation reaction and areas for further development are clearly identified and discussed as follows:

The use of methane in the methylation reaction to produce the value-added higher aromatics is definitely advantageous as it is a very destructive greenhouse gas. Methane conversion is also important because the gas is a hydrogen-rich reagent; thus, this methylation route could be applied in production of liquid hydrocarbons by direct coal liquefaction with methane rather than with the more expensive and hazardous hydrogen that is commonly used in current processes.

The effective catalytic conversion of methane is beneficial, as the use of catalytic reagents is generally superior to stoichiometric reagents. In particular, the fact that zeolite catalysts are active for the oxidative methylation reaction has positive green chemistry implications as they are relatively non-hazardous. Of course, better catalysts can still be developed and the knowledge gained from previous studies by Adebajo and co-workers^{27,28,38} that moderate acidity is all that is needed for the activity of the catalysts can be taken into consideration in the development of more active and selective catalysts.

Although, an intermediate oxidation step requiring stoichiometric use of oxygen is involved in the reaction, air or at worst safe amounts of oxygen below the explosive limit of oxygen/methane mixtures can be used as the auxiliary substance for the oxidation step.

The high thermodynamic feasibility and exothermic nature of this oxidative methylation reaction are crucial as it is thus possible to conduct the reaction, using air or oxygen, more safely at much lower pressures (or even atmospheric pressure) and temperatures. It is no longer necessary to carry out the reaction under high methane pressures to drive the reaction forward towards the production of methylated products. Consequently, the reaction has higher energy efficiency, especially as the route is also catalytic. The conduction of the reaction at atmospheric or close to atmospheric pressures and lower temperatures than previously investigated, especially using a flow reaction system, is an area that is identified for further study.

Finally, it is worthwhile to note that only water is produced during the oxidative reaction in addition to the industrially important higher aromatics; no CO, CO₂, or H₂ were detected in gas products of the reaction as reported by Adebajo *et al.*³² Thus, there appears to be no significant complete or incomplete combustion of methane during the reaction.

4.2 Evaluation of the “greenness” and efficiency of the oxidative methylation reaction using green chemistry metrics

The quantitative determination of the greenness of the oxidative methylation reaction described in this article is important for the identification of any hazardous or inefficient procedures with unfavourable environmental impact as well as for minimization of cost. Such quantitative evaluation would

Table 7 Reaction metrics for oxidative benzene methylation with methane (eqn (15)) and the more traditional benzene methylation with methanol (eqn (14))

	Oxidative benzene methylation with methane using HZSM-5 catalyst (eqn (15))		Benzene methylation with methanol reaction (eqn (14))		
	Experiment 1 using 0.31% O ₂	Experiment 2 using 2.1% O ₂	HZSM-5 catalyst	CoZSM-5 catalyst	CuZSM-5 catalyst
Benzene conversion (%)	4.17	10.1	44.3	46.4	46.5
Methanol conversion (%)	—	—	74.6	76.0	75.9
Toluene selectivity (%)	93.0	84.6	52.2	52.0	53.5
Toluene yield (%)	3.88	8.54	23.1	24.1	24.9
Atom economy (%)	83.6	83.6	83.6	83.6	83.6
Carbon efficiency (%)	93.0	84.6	107.3	102.7	105.5
Reaction mass efficiency (%)	77.8	70.8	82.2	79.1	81.3
Effective mass yield (%)	91.1	82.8	82.2	79.1	81.3
Mass intensity/kg kg ⁻¹	4.23	2.75	3.18	3.24	3.15
Mass productivity (%)	23.6	36.4	31.4	30.9	31.8
Raw material cost/\$ kg ⁻¹	2934.34	1331.80	136.33	130.66	126.72
Raw material cost at 100% yield/\$ kg ⁻¹	113.80	113.80	31.53	31.53	31.53

therefore enable one to identify areas for improvement, thus optimizing the process accordingly. Various green chemistry metrics that allow for measured, objective analysis for comparison of competing reactions and processes have been developed and recently reviewed.⁶⁴ It is always necessary to consider the purposes of evaluation prior to the choice of metrics. For example, in the evaluation of an industrial process, metrics that emphasize the measurement of efficiency and cost, in addition to evaluation of chemical hazards would prove to be most useful. It is generally agreed that good and useful metrics must be clearly defined, simple, measurable, objective, and must ultimately drive the desired behaviour.⁶⁵ According to the review by Constable *et al.*,⁶⁴ some of the metrics that have been developed include Trost's atom economy⁶⁶ (AE), effective mass yield⁶⁷ (EMY), E-factor^{68,69} (EF), mass intensity^{64,70} (MI), mass productivity⁶⁴ (MP), carbon efficiency⁷⁰ (CE) and reaction mass efficiency⁷⁰ (RME). Andraos⁷¹ has also recently assessed another metric known as the raw material cost (RMC) for evaluating the costs of raw materials that are used in the particular chemical reaction or process. Energy intensity (EI) metrics has also been used to quantitatively evaluate energy usage.^{65,72,73}

As shown in Tables 7 and 8, all these metrics, except the E-factor, have been used to quantitatively determine the greenness of the oxidative benzene methylation with methane. The more traditional or commercial alkylating agents for the alkylation of aromatics are alkyl halides, alcohols and ethers, alkenes, alkynes and dienes.^{74–77} Incidentally, the second step

of the oxidative benzene methylation with methane is the more traditional benzene methylation with methanol. As mentioned earlier in section 2.1, the results of the investigation of benzene methylation with methanol over zeolite catalysts have demonstrated excellent correlation of the performance of catalysts for both this traditional methylation reaction and the new oxidative methylation with methane.³⁷ The metrics for the oxidative methylation reaction are therefore also compared with the values for the more traditional methylation of benzene with methanol (Tables 7 and 8). EF is a measure of the amount of waste produced per unit mass of desired product, and it takes into account the mass of the materials used in the process including water that is a benign waste. The generation of significant amounts of such a benign waste like water can make the environmental impact appear to be much worse than it actually is. Thus, instead of EF, the effective mass yield, EMY is used in this study. This is because EMY, which is expressed as the percentage of the mass of desired product relative to the mass of all non-benign materials used in the reaction or process, excludes any benign materials such as water, dilute ethanol or acetic acid or low concentration of benign inorganic salts. EMY is actually approximately the reciprocal of EF expressed as a percentage.

The values of percentage of benzene and methanol conversion, toluene selectivity and toluene yield for both types of methylation reaction are included in Table 7. Data and sample calculations used to calculate all the metrics in Tables 7 and 8 are presented in the ESI†. Table 7 shows that the yield of

Table 8 Energy Intensity metrics at 298 and 673 K for the same reactions (eqn (15) and (14) as in Table 7

	Oxidative benzene methylation with methane (eqn (15))	Benzene methylation with methanol reaction (eqn (14))
ΔG at 298 K/kJ mol ⁻¹	-185.8	-74.0
K_{eq} at 298 K	3.7×10^{32} (L mol ⁻¹) ^{1/2}	7.76×10^{12}
ΔG Energy intensity at 298 K/MJ kg ⁻¹	-2.02	-0.80
ΔH at 298 K/kJ mol ⁻¹	-200.1	-73.7
ΔH Energy intensity at 298 K/MJ kg ⁻¹	-2.17	-0.80
ΔG at 673 K/kJ mol ⁻¹	-168.2	-75.5
K_{eq} at 673 K	7.76×10^{12} (L mol ⁻¹) ^{1/2}	7.18×10^5
ΔG Energy intensity at 673 K/MJ kg ⁻¹	-1.83	-0.82
ΔH at 673 K/kJ mol ⁻¹	-198.3	-71.0
ΔH Energy intensity at 673 K/MJ kg ⁻¹	-2.15	-0.77

toluene in the oxidative methylation reaction is much lower than that of the methylation with methanol reaction. However, the selectivity to toluene is actually much higher in the oxidative methylation reaction and it has been demonstrated that the oxidative methylation reaction is limited by the amount of oxygen in the reactor.³² Thus, both benzene conversion and toluene yield increased with increase in amount of oxygen in the reactor. So, it is possible to raise the yield of toluene in the oxidative methylation reaction to compare favourably with that of benzene methylation with methanol by increasing further the amount of oxygen in the reactor. However, one should ensure that the amount of oxygen does not exceed the explosive limit of the oxygen–methane mixture.

Atom economy is a measure of how much of the reactants remain in the final product. Reaction yield and molar excesses of reactants are ignored in the calculation of this metric. Solvents and reagents are also not taken into consideration in the calculation of AE. It has been suggested that AE alone would not be enough to indicate whether a process for synthesizing a material is 'greener' or 'cleaner'.⁷⁰ Nevertheless, Table 7 shows that AE is same value of 83.6% for both types of methylation reactions which is quite good. It is less than 100% due to formation of water as a by-product. The product yield and stoichiometry of reactants and products are accounted for in the calculation of carbon efficiency. CE is the percentage of carbons in the reactants that remain in the final product. The CE values listed in Table 7 for the oxidative methylation reaction account for the less than 100% yield of toluene produced. On the other hand, the CE of more than 100% obtained for methylation with methanol reactions reflects the much higher methanol conversion than benzene conversion. This high methanol conversion has been demonstrated to be due to methanol conversion over the acidic zeolites into aromatic products and secondary alkylation reaction of methanol with benzene that involves consumption of additional methanol molecules.³¹

Reaction mass efficiency is the percentage of the mass of the reactants that remain in the desired product. Atom economy, yield and the stoichiometry of reactants are included in the calculation of RME. This metric is regarded to be probably the most helpful metric for chemists to focus attention on how far from 'green' current processes are being operated.⁶⁴ According to Constable *et al.*,⁶⁴ RME is more likely to drive chemical and technology innovations that will lead to more sustainable business practices. It is therefore very encouraging that RME values obtained for the oxidative methylation reaction are again quite good and compare favourably with those obtained for methylation with methanol reactions, as shown in Table 7.

The concept of effective mass yield was proposed by Hudlicky *et al.*⁶⁷ and is calculated as the percentage of the mass of desired product relative to the mass of all non-benign materials used in its synthesis. This metric therefore gives a good indication of greenness of reactions and processes. In the oxidative methylation reaction considered in this paper, non-benign reagents were taken to be those that are classified as hazardous in the MSDS according to the criteria of National Occupational Health and Safety Commission (NOHSC) of Australia, namely benzene and oxygen. For the methylation with methanol reaction, methanol is as well taken to be

non-benign as it is also classified as a hazardous substance by NOHSC. The values of EMY listed in Table 7 indicate that the oxidative methylation reaction utilizing lower oxygen concentration is greener than the other, more traditional, methylation with methanol reaction. It is also shown that the greenness of the former reaction at the higher oxygen concentration is even still comparable to that of the later, more traditional, reaction.

The mass intensity metric was discussed extensively by Constable *et al.*^{64,70} MI is defined as the total kilogram mass used in a process or process step divide by the kilogram mass of the desired product. MI takes into account the yield, stoichiometry, solvent, and the reagent used in the reaction mixture, and it is expressed on a weight/weight basis rather than as a percentage. An ideal value of MI would be close to 1. Total mass includes the masses of every substance that is used in a process or process step except the environmentally benign water, that is, reactants, solvents, reagents, catalysts, *etc.* It is clear from Table 7 that the MI values obtained for the oxidative methylation reaction are not too bad when compared to the values obtained for the more traditional methylation reaction, and that it can even be slightly better for the former reaction when higher, but safe, amounts of oxygen are used. However, future efforts need to be directed to lowering the MI values closer to 1. As suggested by Constable *et al.*,⁶⁴ the mass intensity may be more usefully expressed as mass productivity in terms of broader understanding by business managers, since the latter metric highlights utilization of resources. MP is simply the reciprocal of MI expressed as a percentage. In other words, MP is the percentage of the desired product in the total mass used in a process or process step. The MP data in Table 7 indicates that only a slightly higher amount of the total mass used in producing the desired toluene product is wasted in the oxidative methylation reaction (76.4%) than in the methylation with methanol reaction (68–69%). The MP value of 36.4% in the oxidative methylation reaction utilizing a higher, but safe, amount of oxygen also indicates that it is possible to achieve wasting even smaller amounts of the total mass used in the toluene production by increasing the amount of oxygen.

The concept of raw material cost was recently discussed by Andraos.⁷¹ In calculating RMC, the costs per unit mass of the reagents, the stoichiometry and the product yield are accounted for. The RMC at 100% yield, denoted by RMC₁₀₀ can be obtained by multiplying RMC by the product yield. RMC data in Table 7 were obtained by using the costs of the largest quantities in the catalogues of Sigma–Aldrich and BOC for high purity grades of the liquid and gaseous reactants, respectively. The costs of the catalysts are, however, not included in the calculations. The data for calculating the RMC values in Table 7 and sample calculations are included in the ESI.† The RMC data in Table 7 shows that the oxidative methylation reaction is much more expensive than the benzene methylation with methanol reaction. However, the data also shows that the cost of the former reaction can be brought closer to the later reaction again by using a higher (but safe) amount of oxygen, thus increasing the yield of the toluene product and wasting much less of the total mass used in toluene production, as discussed earlier. The lowering of the cost by increasing the product yield is reflected in the RMC₁₀₀ value for the oxidative reaction, which is now even much closer

to that obtained for the methylation with methanol reaction. Both RMC and RMC₁₀₀ can also be lowered by using less expensive air instead of oxygen as the auxiliary substance for the oxidation step. Another factor that must have contributed to the much higher RMC values for the oxidative methylation reaction is the use of the very expensive BOC methane gas used in the oxidative methylation reaction. As pointed out by one of the referees, improved utilization of methane could lead to significant future industrial importance, especially as methane produced by animal and vegetable metabolic processes is a renewable resource that is not well recognized. The use of methane, and even benzene, obtained from such renewable biological feedstock could also significantly lower the cost of the oxidative methylation reaction.

Lastly, the values of the thermodynamic parameters, ΔG and ΔH were used to estimate the energy intensity values at 25 and 400 °C for both types of methylation reaction and the data obtained are presented in Table 8. The EI values are expressed as MJ kg⁻¹ toluene product. The equilibrium constants for both reactions at the two temperatures are also included in Table 8 for comparison. The data in Table 8 clearly indicates that the oxidative methylation reaction is more energy efficient and more feasible than the traditional use of methanol as methylating agent. In particular, it is also shown in Table 8 that the oxidative methylation reaction appears to be more spontaneous and slightly more energy efficient at the lower temperature. The conduction of the oxidative methylation at lower temperatures and pressures than previously investigated using a flow reaction system has earlier been identified as an area for further investigation. The conduction of the reaction at such milder reaction conditions can also ultimately lower the cost of the reaction.

It is therefore clear from the foregoing discussion that the greenness of the oxidative methylation reaction is quite good and compares favourably with the more traditional methylation with methanol reaction. Interestingly, the methylation with methanol is also actually the second step of the oxidative methylation route. In other words, the production of methanol (*via* the partial oxidation of methane) for methylating the aromatic hydrocarbon is incorporated into the oxidative methylation route, and therefore constitutes a big advantage.

5 Conclusions

This paper provides a general overview of the recent work that has been done on the use of methane for catalytic methylation of aromatic compounds and for direct liquefaction of coal for the production of liquid hydrocarbons. Such methylation reactions constitute a new route for the utilisation of methane derived from natural gas or other sources for conversion to more valuable hydrocarbons. In conclusion, it is shown clearly from the review that the activation of methane for subsequent reaction with aromatics and coal is made easier in the presence of oxygen to yield methylated products. The oxidative methylation mechanism therefore appears to be a common feature of methylation reactions with methane. Zeolites which have been commonly used as catalysts provide the required acid sites of moderate strength. Strong acidity, such as that exhibited by H-beta, causes cracking of aromatics and should

be avoided. Traces of ethylene impurities in the methane used have significant effect on benzene conversion and product selectivity. These results have now resolved the lack of agreement in previous reported studies with respect to methane incorporation into the methylated products. Positive green chemistry implications of these findings include the following:

(1) Catalytic conversion of greenhouse methane *via* this route to value-added chemicals which are important to petrochemical industry.

(2) As methane is a hydrogen-rich reagent, this oxidative methylation route could be applied in production of liquid hydrocarbons by direct coal liquefaction with methane rather than with the more expensive and hazardous hydrogen that is commonly used in current processes

(3) Only water is produced during the oxidative reaction in addition to these industrially important higher aromatics. No CO, CO₂ or H₂ was detected in gas products.

(4) Relatively non-hazardous zeolite catalysts are active for the reaction.

(5) Air, or at worst safe amounts of O₂ below the explosive limit of oxygen–methane mixtures, can be used as the auxiliary substance for the oxidation step.

(6) Due to the high thermodynamic feasibility and exothermic nature of the oxidative reaction, it is possible to conduct the reaction, using air or O₂, more safely at atmospheric pressure and much lower temperatures with higher energy efficiency than previously investigated. This is an area that is identified for further study.

(7) The greenness, cost-effectiveness, material and energy-efficiency are quantitatively substantiated using a variety of reaction metrics and are demonstrated to compare favourably with the more traditional or commercial use of methanol as the methylating agent.

(8) An advantage of the oxidative methylation route is the incorporation of the methanol production by the partial oxidation of methane for subsequent use in methylating the aromatic hydrocarbon as it is done in the more traditional methylation method.

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Grafting sulfated zirconia on mesoporous silica†

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Recently, sulfated zirconia has received considerable attention as a potential solid acid catalyst to replace problematic homogeneous acid catalysts. In this paper, the preparation and properties of acid catalysts obtained by grafting zirconia with atomic precision on MCM-41 mesoporous silica were studied. TEM and potential titration characterizations revealed that $\text{ZrO}_2/\text{MCM-41}$ with monolayer coverage can be obtained using this grafting technique. Sulfated $\text{ZrO}_2/\text{MCM-41}$ exhibits improved thermal stability than that of bulk sulfated zirconia, as evidenced by temperature programmed characterizations and XRD analysis. Temperature programmed reaction of isopropanol was used to evaluate the acidity of sulfated $\text{ZrO}_2/\text{MCM-41}$. It was found that the acid strength of sulfated $\text{ZrO}_2/\text{MCM-41}$ with monolayer coverage is weaker than bulk sulfated zirconia but stronger than $\text{SiO}_2\text{--Al}_2\text{O}_3$, a common strong acid catalyst.

Introduction

Solid acid catalysts have attracted considerable attention as a potential replacement of homogeneous catalysts to solve the environmental and operational problems in corrosion, separation, recovery, and reutilization.¹ Sulfated zirconia is one of the most promising catalysts since it possesses the strongest acidity among the solid acid catalysts that have been reported.^{2–6} Conventional synthetic methods to prepare sulfated zirconia include zirconium hydroxide impregnation with ammonia sulfate or sulfuric acid treatment with further calcination in air, calcination of zirconium sulfates, and sol–gel coprecipitation. However, materials prepared using these conventional methods generally have relatively small surface area and microporosity. One approach to overcome these two problems is to develop mesoporous materials.

Mesoporous materials based on self-assembly principles, first reported by Mobil Oil in 1992,^{7,8} are novel materials with high surface area ($>1000 \text{ m}^2 \text{ g}^{-1}$), large pore volume, uniform pore size, tailored and ordered structures. Direct synthesis of mesostructured zirconia using a template route typically results in an unstable structure in thermal treatment at temperatures above 500°C or at the step of template removal by thermal decomposition.^{9,10} Alternatively, an increase in the surface area and porosity can be achieved by supporting the sulfated zirconia on previously synthesized mesostructured oxides such as silica. Silica based mesoporous materials are thermally stable (up to 900°C), and have nominally inert and homogeneous surfaces. The unique characteristics and the advanced properties exhibited by mesoporous silica make

them ideal supports for the development of a new class of sulfated zirconia catalysts. Impregnation,^{11–13} physical mixing,^{14,15} and condensation between coordination metal complexes and the surface hydroxyl groups of the support¹⁶ have been previously used to graft transition metal oxides such as zirconia onto silica. However, it is difficult to achieve grafting of zirconia with atomic precision with these methods. We have recently developed a novel grafting method which is capable of achieving up to monolayer coverage of various metal oxides such as zirconia, tungsten oxide, vanadia, and titania on mesoporous silica.^{17–21} Iteration of this technique can lead to multi-layer coverage with the same or different metal oxide layers. This method was the extension of a surface sol–gel process which was originally developed by Ichinose *et al.*^{22,23} to grow metal oxide thin films on a 2D planar surface. Ichinose's method is composed of four steps: chemisorption of alkoxide, rinsing with solvent to remove non-chemisorbed alkoxide precursors, hydrolysis of the chemisorbed alkoxide, and drying. In this paper, we report the studies of preparation and properties of sulfated zirconia on mesoporous silica obtained using this novel approach. The sample preparation process and resulting structural and chemical characteristics of the synthesized catalysts were evaluated using various bulk and surface techniques such as ^{29}Si NMR, TGA/DTA, TEM, XRD, and potentiometric titration. Catalytic activity of the solid acid catalyst was evaluated using dehydration of isopropanol as a model reaction.

Experimental

Sample preparation

MCM-41 silica with a BET surface area of $780 \text{ m}^2 \text{ g}^{-1}$ and monodimensional pores of $50 \text{ \AA}$ was synthesized using a protocol reported elsewhere.^{7,8} Mesoporous silica was first calcined at 540°C to ensure there is no noticeable silanol present on the silica surface as confirmed by the sole presence of Q^4 species in the ^{29}Si NMR spectra (Fig.1(a)) and by a separate TGA study. Thermally treated mesoporous silica was

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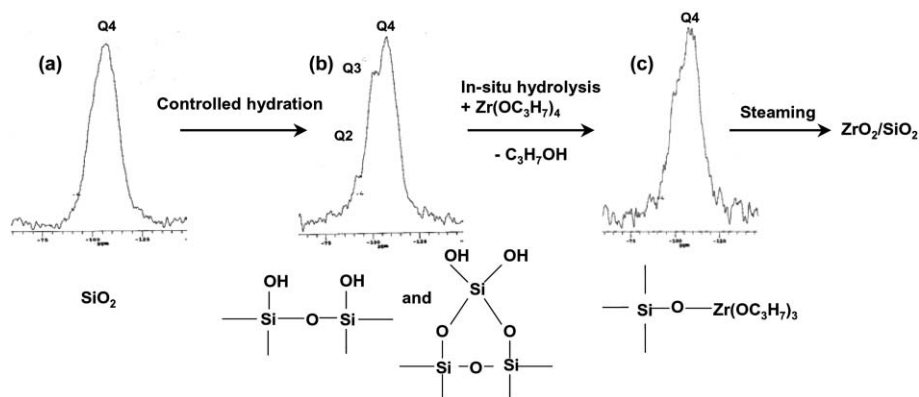


Fig. 1 Synthesis schemes of ZrO_2 on MCM-41 mesoporous silica as supported by ^{29}Si NMR: (a) ^{29}Si NMR spectra of a fully dehydrated and dehydroxylated silica; (b) ^{29}Si NMR spectra of silica after controlled hydration; and (c) ^{29}Si NMR spectra of silica with controlled condensation of surface hydroxyls and zirconium isopropoxide.

suspended in toluene ($8 \text{ ml toluene g}^{-1} \text{ SiO}_2$) and stirred at room temperature for 4 h and then taken to reflux, followed by addition of controlled amounts of de-ionized water under reflux. The amount of water added dictates the coverage of ZrO_2 on silica and can be up to that required to fully cover the surface silicon molecules with silanol groups. The stoichiometry was based on the measured surface area of silica and the assumption of 5×10^{18} silicon molecules m^{-2} .²⁴ Zirconium isopropoxide was added to the mixture and reflux was continued for 8 h. The amount of zirconium isopropoxide added was based on the assumption that each silanol on the mesoporous silica can hydrolyze one molecule of zirconium isopropoxide. After washing the reaction mixture with toluene several times until no zirconium isopropoxide could be detected from the washing solvent, the sample was dried in a vacuum oven at 100°C overnight and treated in a steam environment at 110°C for 4 h. The sample prepared using this procedure is denoted as 1z/ms with a BET surface area of $656 \text{ m}^2 \text{ g}^{-1}$, an average pore size of $39 \text{ \AA}$, and 18.6 wt% zirconia measured by ICP analysis. This process was iterated to prepare a sample denoted as 3z/ms with a BET surface area of $554 \text{ m}^2 \text{ g}^{-1}$, an average pore size of $36 \text{ \AA}$, and 32.2 wt% zirconia measured by ICP analysis. Bulk zirconia, denoted as “bulk z”, was prepared by simply hydrolyzing zirconium isopropoxide followed by drying and calcining. 1z/ms and 3z/ms samples were impregnated with an aqueous $(\text{NH}_4)_2\text{SO}_4$ solution using an incipient wetness method ($0.35 \text{ g } (\text{NH}_4)_2\text{SO}_4$ per gram of 1z/ms or 3z/ms), followed by drying at 100°C and calcining at 550°C . The sulfated 1z/ms and 3z/ms samples are denoted as 1sz/ms and 3sz/ms, respectively. Bulk sulfated zirconia, denoted as “bulk sz”, was obtained from MEI and calcined at 550°C with a BET surface area of $170 \text{ m}^2 \text{ g}^{-1}$. A solid acid catalyst $\text{SiO}_2\text{--Al}_2\text{O}_3$ ($\text{Si/Al} = 28$) with a BET surface area of about $380 \text{ m}^2 \text{ g}^{-1}$ was obtained from Aldrich.

Characterization

Solid state ^{29}Si MAS (magic angle spinning) NMR experiments were carried out with a Chemagnetics spectrometer (magnetic field 7.05 T, resonance frequency 59.3 MHz) using a variable temperature double-resonance probe. Samples were loaded into 7 mm Zirconia PENCILTM rotors and spun at

3–4 kHz. Single pulse (SP) spectra were collected with a $4.5 \mu\text{s}$ (90°) ^{29}Si pulse, and a repetition delay of 10–60 s. The number of transients was 1000–3000. SP ^{29}Si MAS NMR spectra with ^1H decoupling were obtained for all samples spun at 3–4 kHz. The ^{29}Si NMR chemical shift was referenced to tetramethylsilane at 0 ppm. Transmission electron microscopy (TEM) was performed on a JEOL 1200 microscope at 120 kV. The TEM samples were prepared by grounding the powder and dispersing it on a TEM copper grid with suspended carbon films. The composition was also analyzed using the energy dispersive spectroscopy technique (EDS). Catalyst samples were dispersed in an aqueous solution and zeta potentials with pH were measured on a Matec-Applied-Sciences AcoustoSizerTM at 25°C . X-ray diffraction (XRD) patterns were collected on a Philips X'Pert MPD (Model PW3040/00) diffractometer using $\text{Cu K}\alpha$ radiation. The TGA/DTA experiments were performed using a Netzsch STA 409C. BET surface area and pore size distributions were determined from BJH and multi-point BET methods, respectively, using a Quantachrome Autosorb 6-B gas sorption system.

Acidity and activity were evaluated using temperature programmed reaction (dehydration) of isopropanol in RXM-100 (ASDI, Inc). 50 mg of catalyst with less than 100 mesh was loaded in the sample holder and was calcined *in situ* at 350°C in He prior to the test. The temperature programmed reaction was conducted by ramping from 50°C to 200°C at 1°C min^{-1} in a flowing mixture of isopropanol and He with a total flow rate of 20 ml min^{-1} . Catalyst particle size and total gas flowrate were chosen to eliminate both internal and external mass transfer limitations. Isopropanol was introduced through a saturator kept at 0°C using He as a carrier gas.

Results and discussion

^{29}Si NMR was used to understand the synthesis process of grafting zirconia on mesoporous silica and to ensure the hydrolysis of zirconium isopropoxide mainly occurs on the silica surface. Fig. 1(a) shows that there is no noticeable silanol present on the silica surface after mesoporous silica was thermally treated, as confirmed by the sole presence of Q⁴ species in the ^{29}Si NMR spectra. The controlled formation of

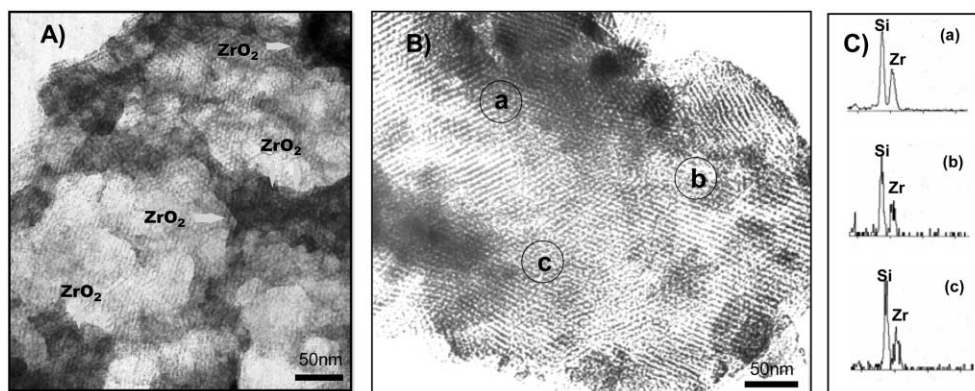


Fig. 2 (A) TEM micrograph of 18.6 wt% $\text{ZrO}_2/\text{MCM-41}$ prepared using a conventional solution impregnation method. (B) TEM micrograph of 1z/ms prepared using a grafting method. (C) EDS spectra obtained in three random probed areas in (B).

surface hydroxyls was achieved by adding controlled amounts of de-ionized water under reflux in toluene, as evidenced by the appearance of Q^2 and Q^3 species in the ^{29}Si NMR spectra as shown in Fig. 1(b). The hydrolysis of zirconium isopropoxide resulted in complete consumption of hydroxyls due to the condensation between hydroxyls and zirconium isopropoxide, as confirmed by the nearly complete disappearance of the Q^2 and Q^3 species in the ^{29}Si NMR spectra as shown in Fig. 1(c). Apparently, there are several key features with this novel grafting method: first, toluene is chosen as a solvent such that the interaction between water and silica is dominant; second, zirconia are precisely formed on the support surface solely due to the reaction between the organo-metallic compounds and the functional groups of the support; and third, the segregated zirconia phases are minimized or eliminated due to absence of free water. This novel synthesis strategy based on “surface organo-metallic chemistry” can be used to achieve high dispersion and can be repeated to form more than one monolayer of zirconia coverage on the mesoporous silica.

To confirm that ZrO_2 is uniformly grafted on mesoporous silica with this grafting technique, TEM characterizations were conducted. For comparison, a 18.6 wt% $\text{ZrO}_2/\text{MCM-41}$ sample was prepared by impregnating a MCM-41 support with zirconium isopropoxide solution using a conventional incipient wetness method. Fig. 2(A) and (B) show TEM micrographs for the sample prepared using the conventional incipient wetness method and the 1z/ms sample prepared using this novel grafting technique, respectively. Fig. 2(A) clearly indicates the presence of large zirconia particles in the conventionally prepared sample. On the other hand, Fig. 2(B) shows that zirconia is highly dispersed on silica in the 1z/ms sample prepared by this grafting method. The uniform dispersion of zirconia in the 1z/ms sample is further confirmed by relatively constant Si/Zr ratio in three EDS spectra (Fig. 2(C)) obtained at three random probed areas (a, b, and c) in Fig. 2(B).

The highly dispersed feature and the zirconia coverage on mesoporous silica are further confirmed by potentiometric titration. Potentiometric titration measures the surface charge of metal oxides as a function of pH, characteristic of both external and internal surfaces of porous metal oxides.²⁵ If the sample is completely covered with ZrO_2 , it should exhibit the surface properties of bulk ZrO_2 . For comparison, potential

titrations of the parent mesoporous silica support (ms) and a bulk zirconia “bulk z” prepared by hydrolysis of zirconium isopropoxide were measured and compared with that of 1z/ms. As shown in Fig. 3, both bulk ZrO_2 and 1z/ms show nearly identical isoelectric points (IEPs), while that of parent mesoporous silica is clearly different. The potential titration results indicate that the SiO_2 surface was fully covered by ZrO_2 . Since zirconia were grafted on the silica surface in the 1z/ms sample mainly due to the hydrolysis of zirconium isopropoxide by surface hydroxyls as confirmed by ^{29}Si NMR discussed above, it is likely that a monolayer zirconia is grafted on mesoporous silica in the 1z/ms sample.

In addition to morphologic and surface charge characterization, the thermal stability of mesoporous silica supported sulfated-zirconia prepared using the novel grafting method was studied using TGA/DTA and XRD. Fig. 4(A) shows the TGA/DTA results of the 1sz/ms, bulk sz, and 1z/ms samples. The 1z/ms sample exhibits a thermal effect at around 400 °C due to the crystallization of zirconia as confirmed by a separate XRD analysis (XRD pattern of 1z/ms, 550 °C in Fig. 5). Bulk sulfated zirconia and 1sz/ms show major weight losses at around 650 and 750 °C, respectively, due to the loss of sulfate as confirmed by separate TPD spectra in Fig. 4(B) and 4(C). Apparently, the thermal stability of 1sz/ms was enhanced by

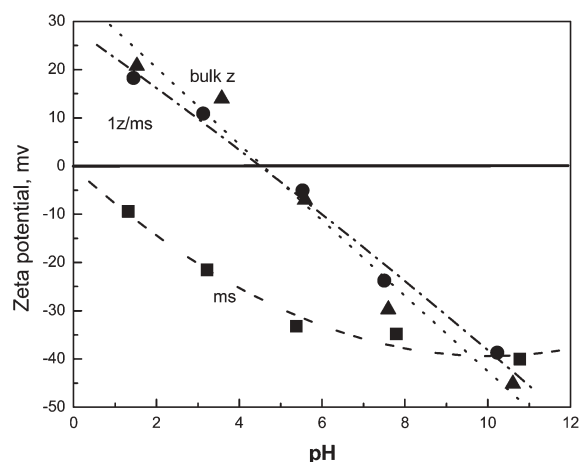


Fig. 3 Surface charge of ms, bulk ZrO_2 , and 1z/ms as a function of pH.

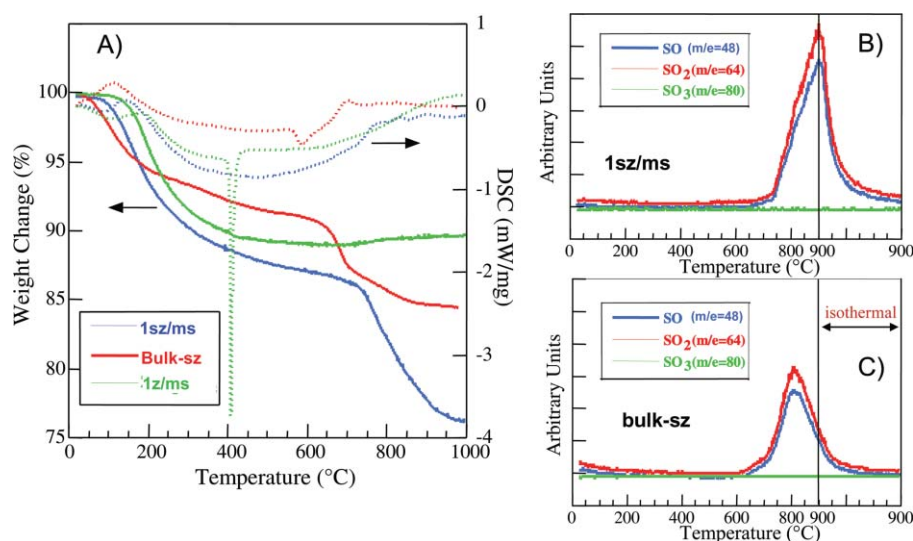


Fig. 4 (A) TGA/DTA characterization of 1sz/ms, bulk sz, and 1z/ms. (B) TPD spectra of 1sz/ms. (C) TPD spectra of bulk sz.

about 100 °C when compared with bulk sulfated zirconia. This may be due to the interactions between sulfated zirconia and silica support resulting from this unique grafting method. The enhanced thermal stability by Si was also recently reported by Ivanov *et al.* by doping Si in sulfated zirconia.²⁶ One of the major issues with sulfated zirconia catalysts is rapid deactivation due to coke formation. Thermal regeneration of coked catalyst may lead to the loss of sulfate since the thermal stability of sulfated zirconia is relatively poor as the case with bulk sulfated zirconia. However, the stability enhancement of the 1sz/ms sample implies a potential of regenerating coked catalysts without losing sulfate. The high dispersion and

improved thermal stability of sulfated zirconia in 1sz/ms were further confirmed by XRD analysis. Fig. 5 shows that the crystallization of bulk sulfated zirconia to form the tetragonal phase occurred even when calcined at 550 °C while the 1sz/ms sample remains amorphous at up to 700 °C.

Temperature programmed dehydration of isopropanol was previously used to measure the acidity of sulfated zirconia,^{27–29} and was used in this research to study the catalytic activity and acid strength of mesoporous silica supported sulfated zirconia. The dehydration reactivity of the adsorption complexes of alcohol can be used as a measure of the acidity.^{30,31} It has been reported that the propene formation from the dehydration of

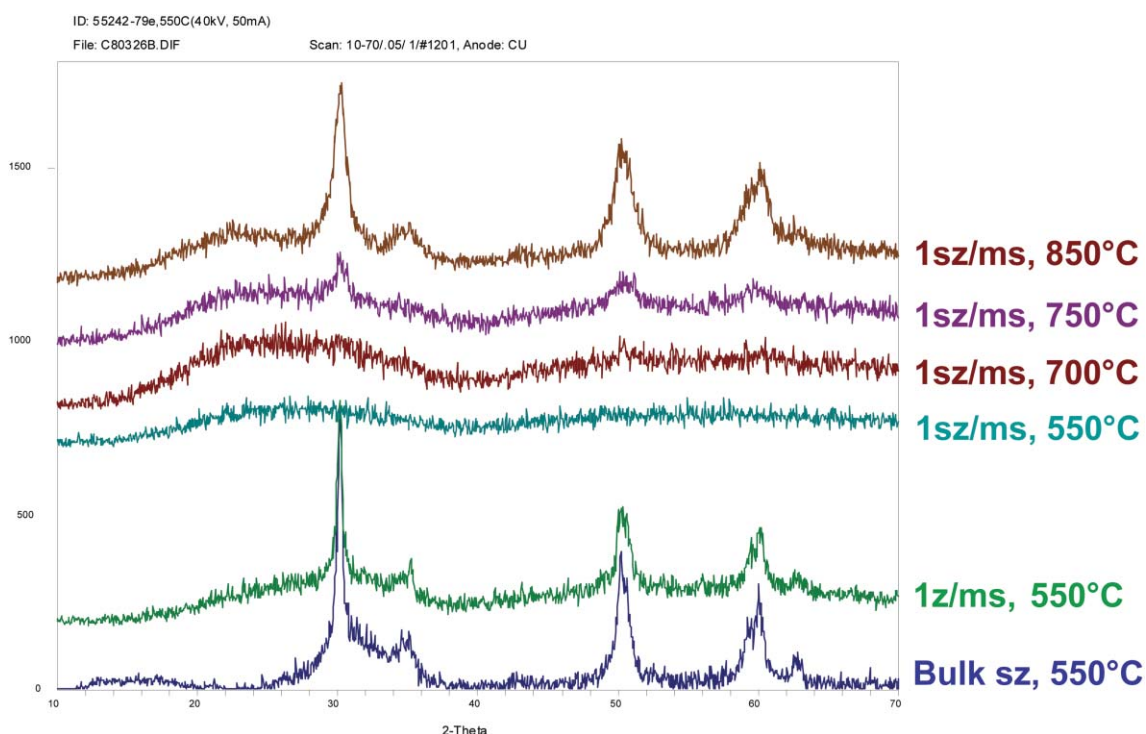


Fig. 5 XRD spectra of bulk sz calcined at 550 °C, 1z/ms calcined at 550 °C, and 1sz/ms calcined at various temperatures.

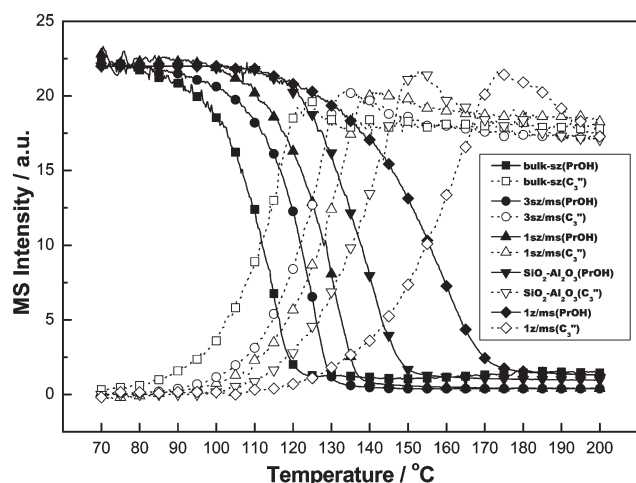


Fig. 6 Programmed reaction of isopropanol.

isopropanol depends mainly on the Brønsted acidity.³² Fig. 6 shows the changes of the reactant (isopropanol) and product (propene) during TPR (temperature programmed reaction) of isopropanol. For comparison, a 3sz/ms sample was prepared by iterating the same novel grafting technique that was used to prepare 1sz/ms. This sample together with bulk zirconia, 1z/ms without sulfation, and a commercial $\text{SiO}_2\text{-Al}_2\text{O}_3$ sample were studied. As shown in Fig. 6, the order of reactivity, namely acidity, was as follows: bulk-sz > 3sz/ms > 1sz/ms > $\text{SiO}_2\text{-Al}_2\text{O}_3$ > 1z/ms, consistent with that for the formation of propene. Bulk sulfated zirconia showed higher catalytic activity than supported monolayer sulfated zirconia. However, the latter revealed still higher activity than $\text{SiO}_2\text{-Al}_2\text{O}_3$ (Si/Al = 28), a common strong solid acid catalyst. When more than one monolayer was supported, as in the case with 3sz/ms, enhanced catalytic activity could be obtained, which indicates the appearance of bulk properties of sulfated zirconia. Therefore, iteration of the grafting technique can be one of the solutions if stronger acidity is required. Reduced acidity of sulfated zirconia by Si has been reported previously³³ which was attributed to the potential blocking of active sites by an excess of Si, likely resulting from the one-step preparation method used by these authors. In our study, 1sz/ms and 3sz/ms were prepared by grafting zirconia on previously synthesized mesoporous silica. Therefore, it is less likely that Si blocks sulfated zirconia and causes reduced acidity. We hypothesize that the reduced acidity is due to the interaction between silica and sulfated zirconia which also results in the enhanced thermal stability of sulfated zirconia as discussed above.

Conclusions

A novel grafting technique was used to disperse zirconia with monolayer coverage on mesoporous silica. Sulfated-zirconia on mesoporous silica prepared using this novel method exhibits improved thermal stability but weaker acidity than that of bulk sulfated zirconia, likely due to a strong interaction between silica and sulfated zirconia. Iteration of this grafting technique can lead to higher than monolayer coverage of sulfated zirconia and enhanced acidity.

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Tunable solvents for fine chemicals from the biorefinery†

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Making biorefineries economically and environmentally sustainable is the biggest barrier to the mass commercialization of biofuels in this country. One way to add economic value to the biofuel process is to isolate and extract fine chemicals from waste biomass such as lignin, extractives, and unreacted cellulose and hemicellulose. In this paper we demonstrate a technique for extracting high-value added chemicals such as vanillin, syringaldehyde, and syringol from lignin using a novel CO₂-expanded organic solvent (gas-expanded liquid). This method incorporates many principles of green chemistry while offering several economical advantages to the biorefinery: low operating costs, easy recycling of organic solvents, use of a renewable feedstock, and a way to produce chemicals without wasteful synthesis. Furthermore, this technique demonstrated the ability to produce high-value chemicals (\$5–25 lb⁻¹) from a waste source that is presently being burned for a fuel value of 2–3 cents lb⁻¹. We believe the process presented in this paper will spark interest in developing other sustainable techniques to extract fine chemicals from biorefinery waste.

Introduction

Fuels from renewable resources is an old idea¹ which has become more urgent and may soon be competitive² due to high petroleum prices.^{3,4} Attempts to make biorefineries commercially viable include innovative plant design, improving the efficiency of the bioethanol fermentation, or producing biomaterials from biorefineries.^{1,3,5–8} These methods include increasing the total amount of biomass available by manipulating photosynthesis to increase source strength,⁹ genetically engineering plants to promote plant adaptation to environmental stresses,¹⁰ altering the lignin content of a plant cell wall by coregulation,¹¹ and cost-efficient ways to pretreat biomass, the most expensive step in bioethanol fermentation. Our route for improving the biorefinery economics (and thus sustainability) is producing high-value biomaterials.

In biomass fermentation, naturally-occurring organisms readily break down only six-carbon sugars like glucose, mannose, and galactose,⁸ which make up the cellulose and a fraction of the hemicellulose biomass.¹² Less than 60% of typical biomass consists of components useable for bioethanol production (Table 1), leaving the lignin, extractives or minor components, and unreacted cellulose and hemicellulose as

waste, typically burned for fuel value.² But this “waste” biomass as a source of high-value chemicals is an untapped resource in a biorefinery.³ Vanillin, used frequently in the flavor and fragrance industry, was once commercially extracted from the lignin left as waste from the kraft pulping process of wood.¹³ However, the method created excessive waste, and the last such American plant was closed in 1991.

A more benign and cost-efficient way to extract vanillin from lignin uses a gas-expanded liquid. When a gas, typically CO₂, is added to an organic solvent in which it is soluble, the dissolution of that gas provides the solvent with different and tunable properties. The use of gas-expanded liquids offer several advantages over conventional solvents: ease of separation, use of benign gases to reduce the amount of solvent needed, and the ability to tune properties such as solubility, transportability, and polarity.¹⁴ Furthermore, previous work by our group has shown that the addition of CO₂ to small alcohols forms an *in situ* alkylcarbonic acid.¹⁵

In this paper we use gas-expanded liquids in a gas antisolvent process;¹⁶ as the amount of CO₂ pressure increases, the solubility of some lignin components in methanol decreases and they fall out of solution. Staying in solution are low molecular weight fractions of lignin, which include vanillin, syringol, and syringaldehyde. Vanillin and syringol are commonly used in the flavor and fragrance industry and are sold for many dollars per pound. Syringaldehyde, which sells for tens of dollars per pound, has been patented for use as a

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Table 1 Percent dry weight composition of lignocellulosic feedstocks, adapted from N. Mosier *et al.*⁸

Feedstock	Cellulose	Hemicellulose	Lignin	Extractives/Minor Components
Corn Stover	37.5	22.4	17.6	22.5
Pine Wood	46.4	8.8	29.4	15.4
Switch grass	31	20.4	17.6	31



Fig. 1 Fractionation of organosolv lignin in methanol with increasing CO₂ pressures.

hair and fiber dye as well as a pharmaceutical precursor for obesity and breast cancer treatments.^{17–19} These are high value added chemicals, and their removal from biomass using gas expanded methanol provides an easy and a very cost-efficient way to add sustainability to biorefineries.

Results and discussion

When added to a solution of organosolv lignin dissolved in methanol, CO₂ acts as an antisolvent; the major effect of an antisolvent is to dilute a good solvent with a bad solvent to reduce solubility and cause precipitation of lignin. This precipitation becomes visible with the addition of approximately 10 bar of CO₂ pressure. Fig. 1 shows samples taken from a high pressure cell in which the concentration of lignin dissolved in the liquid phase is clearly decreasing with increasing pressure. We calculated gravimetrically ($\pm 5\%$ error) that 99.95% of the lignin is removed from the gas-expanded liquid phase at 38 bar of CO₂ pressure.

Furthermore, in Fig. 2 the concentrations (normalized to the concentration at ambient pressure) of syringol, vanillin, and syringaldehyde show a synergistic effect. Their concentration increases in the gas-expanded liquid phase as the increasing concentration of a poorer solvent, CO₂, causes lignin to drop out of solution, until between 12–20 bar when the syringol, vanillin, and syringaldehyde also begin to drop out of solution. Table 2 reports the amount of syringol, vanillin, and syringaldehyde removed, by stating the percentage of chemicals extracted based on the initial percentage of lignin in solution in the gas-expanded liquid at 13 bar. For example, from a solution containing 100 mg mL⁻¹ lignin in methanol, based on the data in Table 2, the addition of 13 bar CO₂ pressure could result in the extraction from methanol of 1.0,

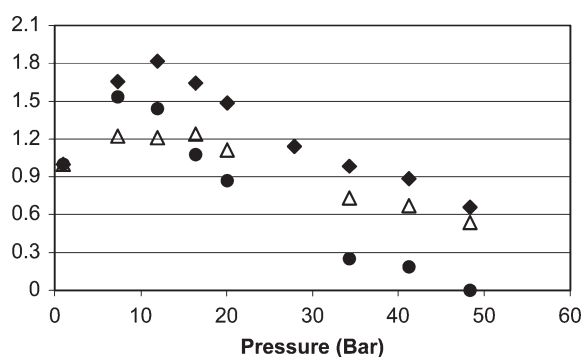


Fig. 2 Normalized concentration in the gas expanded methanol phase versus pressure at 25 °C: ◆, syringol; ●, vanillin; △, syringaldehyde.

Table 2 Percent value-added chemical removed based on initial lignin concentration at 13 bar and 25 °C

Chemical	Percent removed	Error (%)
Syringol	1.00	0.17
Vanillin	0.82	0.42
Syringaldehyde	1.96	0.31

0.82, and 1.96 mg of syringol, vanillin, and syringaldehyde, respectively, per mL of methanol.

The results shown here support our claim that using gas-expanded liquids to remove high value added chemicals from biomass is a viable way to add sustainability to biorefineries. We believe the ability of gas-expanded methanol to precipitate lignin is a result of both the decreased solubility with the addition of CO₂ and the acid-insoluble nature of lignin.²⁰ It therefore makes sense that with an increase in CO₂ concentration and a decrease of pH in the gas-expanded methanol solution, more lignin precipitates. Vanillin, syringol, and syringaldehyde are present in the lignin–methanol solution before the addition of CO₂ pressure. However, as the lignin begins to precipitate, the chemicals become more concentrated in the liquid phase. We believe this is due to the larger molecular weight components of lignin precipitating and allowing additional extraction of the lignin units containing high value added chemicals. Once the pressure becomes higher than 13 bar, the chemicals begin to precipitate as well. We determined the cloud point of both vanillin and syringaldehyde to be 23 and 20 bar, respectively, which would explain the precipitation of those chemicals. A cloud point test was also performed for syringol, but no cloud point was observed within the studied pressures (0–50 bar). We attribute the precipitation of syringol, and the precipitation of vanillin before its cloud point, to the chemicals settling with the lignin. However, we see this phenomenon as a great opportunity to find the most cost efficient way to run this process. We will be able to optimize the process based on cost; we can choose to either remove the chemicals from the liquid phase at a low pressure with a slightly more difficult lignin recovery or to remove them from the solid phase at a higher pressure but with a more difficult solvent recovery. Either way we will have extracted extremely valuable chemicals with a self neutralizing catalyst, no hazardous waste, and without the need of a lengthy synthesis, all important principles in green chemistry.²¹

Not only does our extraction remove the need for a lengthy synthesis, once commercialized, our vanillin derived from a renewable resource will replace a six step synthesis using benzene as a feedstock.¹³ Although no recent synthesis of syringaldehyde was found in the literature, early literature described syntheses involving even more toxic chemicals.^{22,23} We found no synthetic route to syringol published; all synthesis involved biomass extraction, most commonly from pyrolysis waste.²⁴ The literature describes the synthesis of vanillin from lignin previously used in industry; they report a higher concentration (as high as 10% of the lignin content) of vanillin recovered than seen in our experiments.¹³ However, this synthesis used nitrobenzene as an oxidant and sodium hydroxide to remove the sulfur from the kraft-based lignin fragment, all of which are undesirable waste products.

Furthermore, extracting too much vanillin from the system will flood the world market and cause a drop in prices. This is exactly what we don't want when trying to promote sustainability by the production of high-value added chemicals.

Future prospects

We have shown a cost efficient way to extract high value added chemicals from lignin, a component of biomass that is removed for waste in bioethanol production. We also mentioned several other components of biomass that are burned as waste, all of which can offer a unique addition to the biomaterials produced from biomass. In petroleum refineries, many other chemicals are produced to help sustain the industry; we need to do the same for biorefineries.³ We are currently looking for additional ways to supply a sustainable contribution to the biofuel industry by researching what valuable biomaterials can be removed or produced by pretreatment with novel solvents, or extraction from the extractives, hemicellulose, and other waste materials.

Conclusion

We have developed a cost efficient technique for extracting fine chemicals from biomass in an effort to add sustainability to the biofuel industry. Biofuels are a necessary part of our future, and when we are able to produce them in an economical way we will be one step closer to ending our dependency on non-domestic, non-renewable resources. Our technique embodies many of the green chemistry principles and we believe that once the process is optimized it will be able to provide large amounts of profit to the biorefinery. It is our hope that this innovation, as well as the research being performed on some of the other techniques discussed, will help provide cheap, readily available biofuel to our nation.

Experimental

Materials

All Chemicals were obtained from Sigma–Aldrich and used as purchased: methanol (HPLC, 99.9%), lignin (organosolv), vanillin (99%), syringaldehyde (98+%), and syringol (99%). The carbon dioxide (SFC/SFE grade) was obtained from Airgas and was filtered prior to use.

Gas-expanded methanol reactions

An excess of organosolv lignin was added to methanol at ambient conditions and allowed to stir overnight to ensure saturation. The solution was filtered to remove all undissolved solid, and a sample was taken to determine the concentrations of vanillin, syringaldehyde, and syringol. All water and methanol were dried from the filtrate and glassware used and these were then weighed on a Deltarange scale (AT261) to determine the amount of lignin in solution. This number was accurate to ± 2 g due to the human error associated with gravimetric determinations. All samples taken throughout the experiment were run through a Hewlett Packard 6890 gas chromatograph with Mass Selective Detector 5973 (GC-MS)

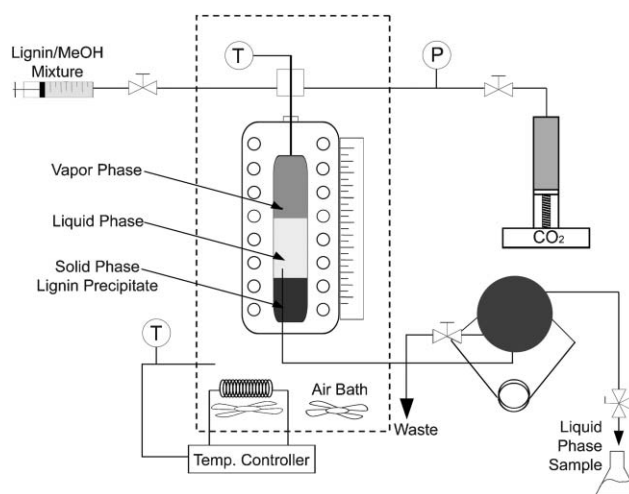


Fig. 3 Schematic of experimental set-up.

for peak identification. Calibration curves, developed using purchased vanillin, syringol, and syringaldehyde, were used to determine the chemical concentrations, with an error of ± 0.01 mg mL⁻¹. The small concentrations of vanillin, syringol, and syringaldehyde present in some of the samples increased the error in concentration due to the limitations of the equipment. The solution was added to a gas tight syringe, and loaded into an equilibrium cell (Jerguson Model 18T-32) that had been evacuated to remove all air from the system. A schematic of the experimental setup is located in Fig. 3. The temperature, although ambient, was monitored with a digital temperature controller (Omega CN 76000) accurate to ± 0.2 K. Throughout experimentation, the temperature of the system stayed within ± 2 K of 298 K. CO₂ was added to the system by an ISCO 500D syringe pump with a series D controller. CO₂ was added until the first signs of lignin precipitate were noted, and then the system was left to equilibrate while periodically being shaken. Once it was ensured that equilibrium was reached (± 2 hour waiting period with periodic shaking until no pressure change was observed for at least 30 minutes), liquid samples were taken *via* a Valco 6-port high pressure sample valve. The sampling apparatus was calibrated to a volume of 535 μ L (± 1 μ L), and after each sample set (three samples at each pressure) the pressure within the system was only reduced by a maximum of 0.2 bar, which we consider to be negligible considering the volume of the experimental solution (>30 mL). Since methanol does expand significantly with the addition of CO₂, the volume of the actual liquid sample removed was determined using previously published methanol–CO₂ binary phase behavior.²⁵ After three samples were taken, more CO₂ was added to the system and the procedure was repeated until the vapor pressure of CO₂ at 298 K was reached. The data reported here is a combination of 3 different runs.

Cloud point measurements

Solutions of known concentration were prepared for each chemical; 1 mg mL⁻¹ of vanillin and 2 mg mL⁻¹ each of syringol and syringaldehyde in methanol. These concentrations were chosen to mimic the amount of respective chemical

in the gas-expanded liquid phase (as reported in Table 2) and were accurate to $\pm 0.01 \text{ mg mL}^{-1}$. Approximately 10 mL of solution was loaded into a variable volume precision-bore sapphire cell (50.8 mm o.d. $\times$ $25.4 \pm 0.0001 \text{ mm i.d.} \times$ 203.2 mm L). This apparatus allowed for the entire sample to be visible during the experiment, making our observation of the cloud point more accurate. CO_2 was added to the system gradually using a 500D Isco syringe pump with a series D controller until there was evidence of precipitation. The pressure at which the precipitation took place was recorded ($\pm 0.1 \text{ bar}$), and the variable volume of the cell (adjusted using an o-ring sealed piston) allowed for the cloud point pressure to be measured several times during one experiment. The cloud points of both vanillin and syringaldehyde were measured using this technique and these data were accurate to within $\pm 2 \text{ bar}$. A cloud point was not observed for the syringol solution over the pressure range studied (0–50 bar).

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Ionic liquids as green electrolytes for the electrodeposition of nanomaterials

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Ionic liquids, especially air and water stable ones, experience much attention, since they have attractive physical properties. We exemplify in this paper the potential of ionic liquids in the electrodeposition of nanocrystalline metals without additives. The results show that nanocrystalline copper and aluminium can be electrodeposited in the air and water stable ionic liquids 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ([BMP]TFO) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([BMP]Tf₂N), respectively, on conventional solid electrodes with sufficient electronic conductivity. Generally, the obtained Al or Cu deposits are shiny, dense and adherent with very fine crystallites with average sizes of about 30 and 40 nm, respectively. The [BMP]⁺ cation might act as a grain refiner, leading to nanosized deposits. The results of first attempts to use plasmas as mechanically contact-free electrodes for the cathodic deposition of nanoscaled metals (glow discharge electrodeposition) are also presented. The relevance of our results for the development of a green process to make nanomaterials as catalysts for fuel processing is briefly discussed.

1. Introduction

Nanocrystalline materials, especially nanocrystalline metals, have found extensive attention since they show unique mechanical, electronic and chemical properties. As the particle size approaches the nanoscale, the number of atoms in the grain boundaries increases leading to dramatic effects on the physical properties as well as the catalytic activity of the bulk materials.

Nowadays, there is a wide variety of methods for the preparation of nanocrystalline metals such as thermal spraying, sputter deposition, vapor deposition, and electrodeposition.¹ The electrodeposition process is commercially attractive since it can be performed at room temperature and the experimental setup is less demanding. Furthermore, the particle size can be adjusted over a wide range by controlling the experimental parameters such as overvoltage, current density, composition, and temperature.

In recent years, ionic liquids have experienced considerable attention, since they have attractive physical properties. They are in many cases nonvolatile, nonflammable, less toxic, good solvents for both organics and inorganics and can be used over a wide temperature range. Moreover, some of the ionic liquids have large electrochemical windows of more than five volts, and hence they give access to elements which cannot be electrodeposited from aqueous or organic solutions. Another advantage of ionic liquids is that problems associated with hydrogen ions in conventional protic solvents can be eliminated in ionic liquids because ionic liquids are normally

aprotic. Therefore, ionic liquids, especially air and water stable ones, are considered to be promising solvents for a wide variety of applications including electrodeposition, batteries, catalysis, separations and organic synthesis.^{2,3} Moreover, the development of ionic liquids has opened the door for the electrodeposition of reactive elements, which can not be obtained from aqueous solutions, such as, *e.g.*, Al, Mg, Ti and Ta, at moderate temperatures.⁴ In particular, Al and its alloys with refractory metals like V, Nb, Ta or the refractory metals alone are of interest for heterogeneous catalysis, especially if nanosized.

As many ionic liquids are environmentally friendly, they are considered as suitable alternatives for many poisonous plating baths. Furthermore, as ionic liquids have very low vapour pressures (often between 10^{−11} and 10^{−10} mbar at or near room temperature, at 100 °C the vapour pressure is—depending on the liquid—in the region of 10^{−6}–10^{−4} mbar), they can be used in open galvanic baths at variable temperatures without releasing harmful vapours, which, in turn, reduces the amount of volatile organic compounds released into the atmosphere. The very small vapor pressure of ionic liquids also allows their use in vacuum experiments even at elevated temperatures, *i.e.* they can be favorably employed in plasma experiments as fluid substrates or solvents. Considering these unique properties, ionic liquids are green solvents for many electrochemical processes—in particular for the cathodic deposition of metals.

In this paper we aim at demonstrating the potential of air and water stable ionic liquids as green electrolytes for the electrodeposition of nanocrystalline metals. We present some recent results on the electrodeposition of nanocrystalline copper and aluminium in the air and water stable ionic liquids 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ([BMP]TFO) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([BMP]Tf₂N), respectively. We also

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summarize the first results on the plasma-electrochemical deposition of Ag and Cu in ionic liquids, which is a new process.

2. Experimental

The ionic liquids 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([BMP]Tf₂N), 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ([BMP]TFO, and 1-butyl-3-methylimidazolium trifluoromethylsulfonate ([BMIm][TFO]) were obtained from Merck KGaA (EMD) in the highest available (ultrapure) quality. The liquids were dried under vacuum for 12 hours at a temperature of 100 °C to water contents below 3 ppm (by Karl–Fischer titration) and stored in an argon filled glove box with water and oxygen below 1 ppm (OMNI-LAB from Vacuum-Atmospheres). Anhydrous AlCl₃-grains (Fluka, 99%), Cu(CF₃SO₃)₂ (Alfa, 99%) and Ag(CF₃SO₃) (Aldrich, ≥99%) were used without further purification.

All conventional electrochemical measurements were performed in the glove box using a Parstat 2263 Potentiostat/Galvanostat (Princeton Applied Research) controlled by PowerCV and PowerStep software. Gold substrates from Arrandee (gold films of 200–300 nm thickness deposited on chromium-covered borosilicate glass) were used as the working electrode. For measurements at room temperature, the electrochemical cell was made of polytetrafluoroethylene and clamped over a Teflon covered Viton o-ring onto the substrate, thus yielding a geometric surface area of 0.3 cm². For variable temperature measurements, a quartz round flask was used as an electrochemical cell. Prior to use, all parts in contact with the solution were thoroughly cleaned in a mixture of 50/50 vol% H₂SO₄/H₂O₂ followed by refluxing in bi-distilled water. A high resolution field emission scanning electron microscope (Carl Zeiss DSM 982 Gemini) was utilized to investigate the surface morphology of the deposited films, and energy dispersive X-ray analysis was used to determine the film composition. The X-ray diffractograms of the deposited samples were recorded using a Siemens D-500 diffractometer with CuKα radiation. A transmission electron microscope (Philips CM30ST, MPI for Solid State Research, Stuttgart) was used for the high resolution study of plasma electrochemical deposits.

The plasma electrochemical experiments were performed in a vacuum glass (tube) reactor (2.5 cm diameter). A 1 cm × 1 cm platinum sheet was used as the anode and a platinum hollow cylinder of about 1.5 cm height and 0.75 cm diameter was used as the cathode, placed in the gas phase above the ionic liquid at a distance of typically 10 cm. The reactor was typically filled with 10 ml of the metal salt containing ionic liquid, fully covering the anode with approx. 2 cm liquid phase. The reactor was then evacuated, and the pressure was controlled to 1 mbar (argon atmosphere). After de-gassing, a current of 10 mA (corresponding to 2 mA cm⁻²) was adjusted under galvanostatic conditions, corresponding to a voltage of typically about 500 V. The formation of a small number of bubbles at the anode could be observed after some time during the electrochemical experiment. Shortly after switching on the current, the creation of a reaction product at the surface

between the ionic liquid and the plasma was observed. After some minutes the originally homogeneous product region started to disperse, and to sediment at the bottom of the ionic liquid in the case of silver. In the case of copper, less product was formed and did not lead to sedimentation. After the deposition process the products were separated from the ionic liquid by using a centrifuge. Re-dispersing the product in water by the help of ultrasound and separating it in the centrifuge several times finally led to a product free of ionic liquid. The reaction products were analyzed by HRSEM/EDX and HRTEM.

3. Results and discussions

3.1. Electrodeposition of nanocrystalline copper

Recently, we have reported that nanocrystalline copper with an average crystallite size of about 50 nm can be obtained without additives in the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([BMP]Tf₂N).⁵ Because of the limited solubility of the tested copper compounds in the ionic liquid [BMP]Tf₂N, copper cations were introduced into the ionic liquid by anodic dissolution of a copper electrode.⁵

In the present study, the electrodeposition of copper was investigated in the ionic liquid 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate [BMP]TFO, with Cu(TFO)₂ as a commercial source of copper. The employed electrolyte was prepared by adding appropriate amounts of Cu(TFO)₂ to the ionic liquid [BMP]TFO until the saturation limit. Fig. 1 shows the cyclic voltammogram of the ionic liquid [BMP]TFO saturated with Cu(TFO)₂ at a gold substrate. In the forward scan, two reduction steps are recorded, c₁ and c₂. The first one might be correlated to an underpotential deposition process, whereas the second one is clearly due to the bulk deposition of copper. Underpotential deposition processes during electrodeposition of copper in chloroaluminate ionic liquids have been formerly reported in ref. 6. The corresponding anodic

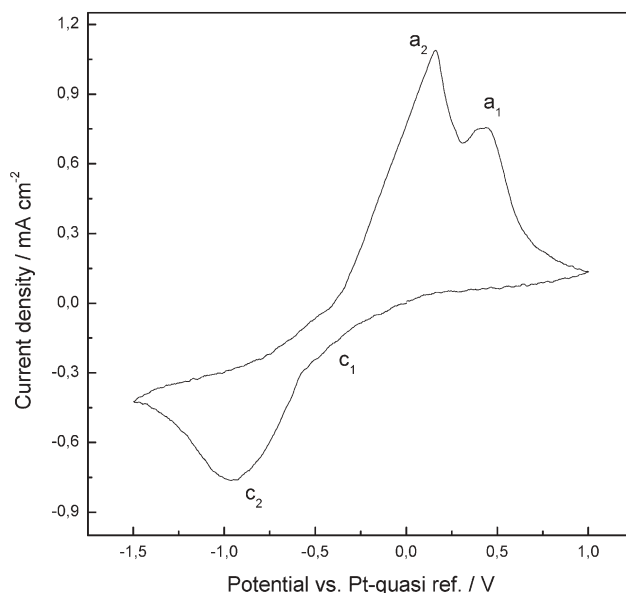


Fig. 1 Cyclic voltammogram of the ionic liquid [BMP]TFO saturated with Cu(TFO)₂ on gold at room temperature. Scan rate 10 mV s⁻¹.

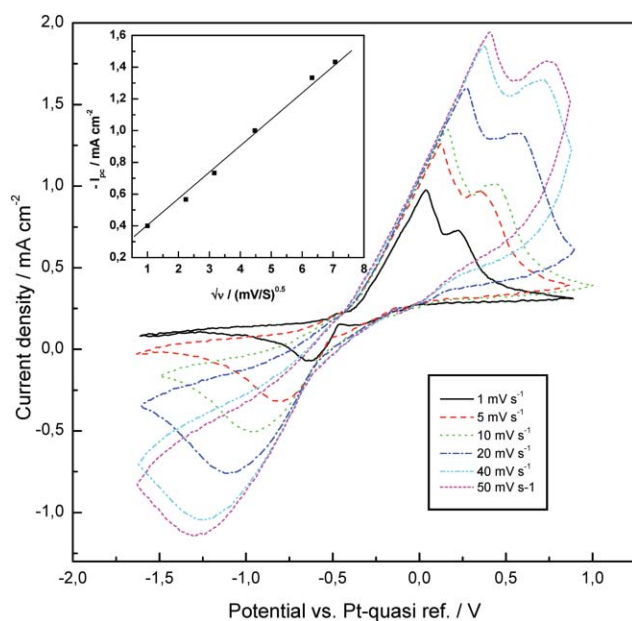


Fig. 2 A set of cyclic voltammograms of the ionic liquid [BMP]TFO saturated with Cu(TFO)₂ on gold at different scan rates. Inset: the absolute value of the cathodic peak currents vs. square root of the scan rate.

peaks, a_1 and a_2 , are recorded in the anodic branch of the cyclic voltammogram. Fig. 2 shows a set of cyclic voltammograms recorded on gold at different scan rates in the ionic liquid [BMP]TFO saturated with Cu(TFO)₂. It is clearly seen that the peak currents of both the reduction and oxidation peaks increase as the scan rate increases. Moreover, the peak potentials of both the reduction and oxidation peaks shift towards the negative and positive directions, respectively, on increasing the scan rate. As shown in the inset of Fig. 2, the current of the cathodic peak of bulk copper deposition rises linearly with the square root of the scan rate, indicating mainly diffusion control. Furthermore, the slope of the $\ln(I_{pc})$ vs. $\ln(v)$ plot is 0.41 ± 0.007 . Based on these results, it can be concluded that the deposition of copper in the employed electrolyte is a quasi-reversible diffusion controlled process.

The SEM micrograph in Fig. 3a shows the surface morphology of an electrodeposited copper layer on gold obtained at a constant potential of -0.6 V (vs. Pt) for 2 hours in the ionic liquid [BMP]TFO saturated with Cu(TFO)₂. As seen, the deposit is dense and contains fine crystallites with average sizes of about 40 nm. The deposit was analysed as metallic copper, as revealed by the corresponding EDX profile, Fig. 3b. Thus, it can be concluded that nanocrystalline copper can be obtained in the employed electrolyte without any additives. This finding is of great interest as nanocrystalline copper is an important catalyst.⁷

3.2. Electrodeposition of nanocrystalline aluminium

Recently, we reported that the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide shows biphasic behaviour on addition of AlCl₃.^{8,9} The lower phase is colourless while the upper one is pale and more viscous. The biphasic behaviour of such liquids was first reported by

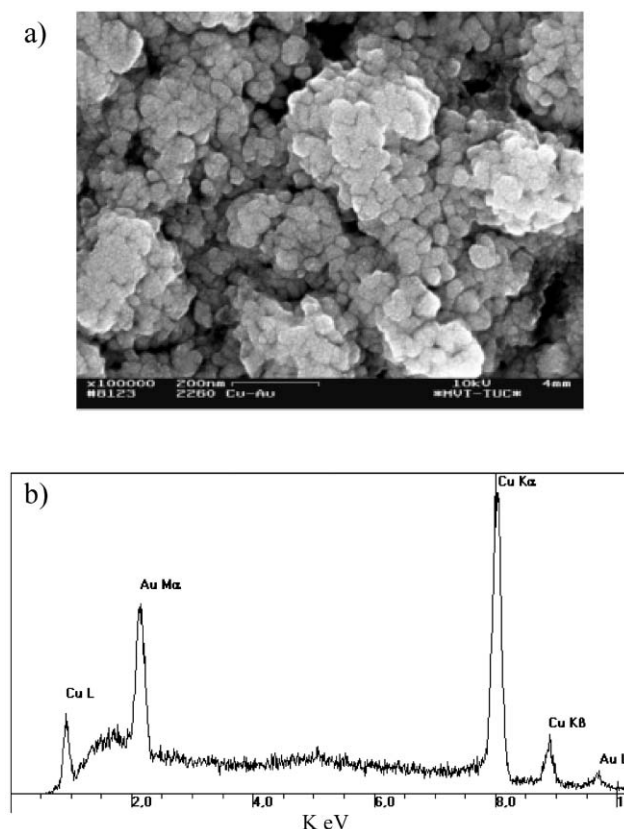


Fig. 3 (a) SEM micrograph of nanocrystalline copper obtained potentiostatically on Au in the ionic liquid [BMP]TFO saturated with Cu(TFO)₂ at a potential of -0.6 V for 2 hours at room temperature. (b) EDAX profile of the area shown in the SEM micrograph.

Wasserscheid.¹⁰ Interestingly, we have found that Al can only be electrodeposited from the upper phase of the biphasic mixture. Moreover, nanocrystalline aluminium with particle sizes ranging from 20–40 nm can be obtained without any additives.^{8,9} Nanocrystalline aluminium in the bulk phase or as a coating is an important precursor to make nanocrystalline Al₂O₃. Fig. 4a shows the cyclic voltammograms of the upper phase of the biphasic mixture of AlCl₃/1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide on a gold substrate at temperatures of 25 and 100 °C. The electrode potential was scanned from the open circuit potential in the negative direction at a scan rate of 10 mV s⁻¹. At 25 °C, the cathodic current rises steeply at a potential of -1.5 V. This reduction process is visibly attributed to the bulk deposition of aluminium. In the reverse scan, the cathodic current continues to flow, forming a current loop, which is presumably correlated with nucleation processes, as Al deposition continues on the developing Al deposits when the potential is scanned to -0.8 V. The anodic scan crosses the cathodic one at a potential of about -0.8 V. The anodic peak recorded on the reverse scan at a potential of about -0.17 V is attributed to the incomplete stripping of the electrodeposited aluminium. At 100 °C there is no evidence for nucleation control in the cyclic voltammogram, and there is only one steeply rising deposition current beginning at -0.2 V. In the reverse scan, the anodic scan does not intersect the cathodic one indicating that the

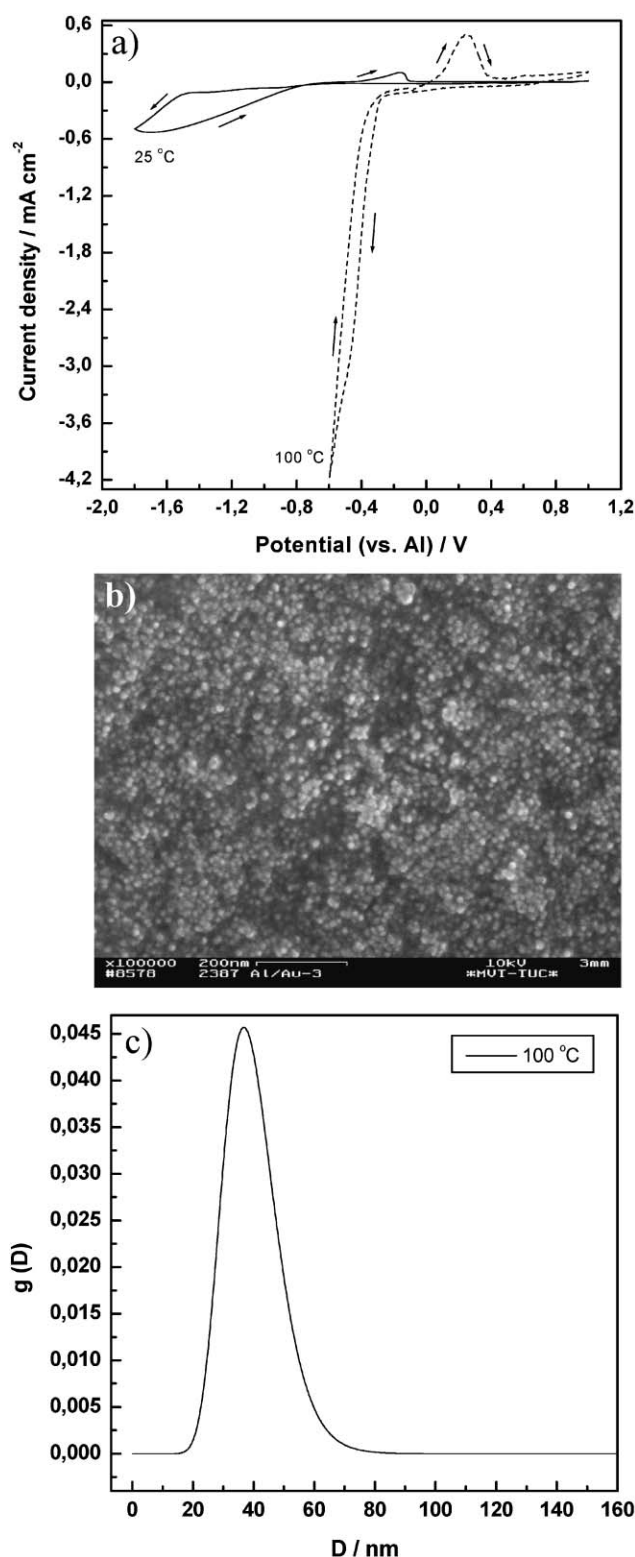


Fig. 4 (a) Cyclic voltammograms recorded at Au substrate in the ionic liquid 1-butyl-1-methyl pyrrolidinium bis(trifluoromethylsulfonfyl)amide containing AlCl_3 1.6 M (from the upper phase of the mixture) at 25 and 100 °C. The scan rate was 10 mV s^{-1} . (b) SEM micrograph of an electrodeposited Al film on gold formed in the upper phase of the mixture $\text{AlCl}_3/[\text{BMP}]\text{Tf}_2\text{N}$ after potentiostatic polarization for 2 hours at 100 °C ($E = -0.45 \text{ V}$). (c) The size distribution of Al nanoparticles determined from the Warren–Averbach analysis.

deposition of Al onto the gold substrate at 100 °C does not require an overpotential to initiate nucleation and growth of bulk deposit. The anodic peak observed on the anodic branch of the cyclic voltammogram is due to the partial stripping of aluminium electrodeposit. As at room temperature, the electrodisolution of Al is not complete in this ionic liquid under the given conditions.

The Al electrodeposits obtained were investigated by means of a high resolution field–emission scanning electron microscopy (SEM). Visually, the deposit appears to be thick, shiny and well adhered to the gold substrate. Fig. 4b shows a high resolution SEM micrograph of an about 5 μm thick layer of Al on gold substrate electrodeposited potentiostatically at 100 °C at -0.45 V (vs. Al) for 2 hours. Generally, the electrodeposited layer contains very fine crystallites in the nanometre regime. The average grain size of Al obtained at 100 °C was determined using Scherrer's equation¹¹ to be 34 nm. A Warren–Averbach analysis was performed in order to get more information on the size distribution of the nanocrystalline aluminium, Fig. 4c. It is clearly seen that the sizes of Al crystallites range from 20 to 65 nm and most of the crystallites have a size of about 40 nm. A detailed study on the electro-deposition of nano- and microcrystalline aluminium in different air and water stable ionic liquids was recently reported.⁹

3.3. Plasma electrochemical deposition of free nanoparticles

As early as 1887, Gubkin used a dc corona discharge in air/water vapour to deposit silver from an aqueous silver salt solution,¹² and recently Koo *et al.* performed the same experiment with an aqueous platinum salt solution and a hydrogen/water plasma—obtaining platinum nanoparticles with diameters in the nm regime.¹³ Recently, we have shown that ionic liquids are even better suited as electrolytes for plasma electrochemical processes, as their vapour pressure is extremely low.¹⁴ This facilitates the generation of much more homogeneous low temperature plasmas which contact the complete surface of the electrolyte, as in the case of solid electrolytes,^{15–17} see Fig. 5a for an example.

Plasma electrochemical deposition may become an efficient route to the continuous production of metal (nano)particles, as the basic process is simple, *cf.* Fig. 5b. The metal particles,

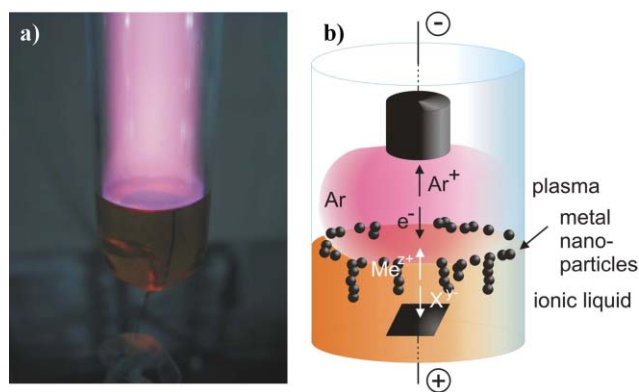


Fig. 5 (a) Photograph of a part of a tubular plasma (glass) reactor showing the ionic liquid in contact with an air plasma. (b) Schematic drawing of a plasma electrochemical set-up.

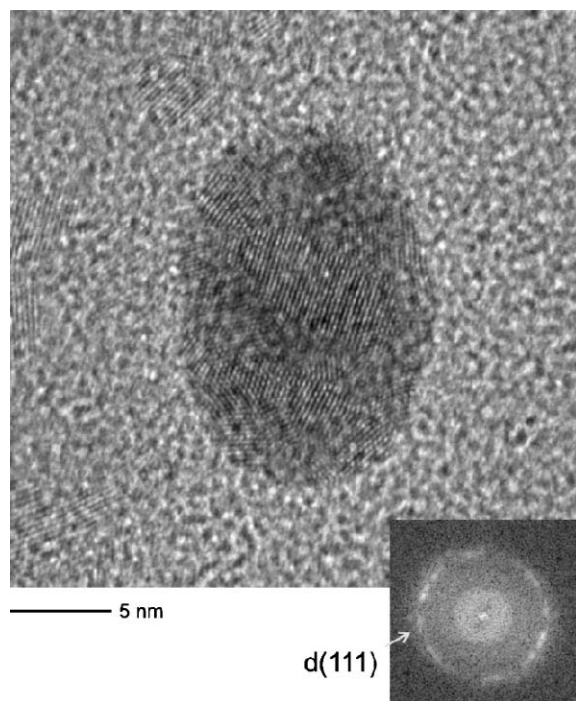


Fig. 6 TEM (transmission electron microscopy) image of a silver nanoparticle (composed of several nanocrystallites) formed by plasma-electrochemical deposition.

once formed, sediment to the bottom of the reactor, and in principle the rate of metal production should only depend on the electric current. Even without immediate sedimentation, the particle size may be controlled easily by stirring the electrolyte solution in order to minimize the growth time for metal nuclei at the electrolyte/plasma interface.

We started with the deposition of silver, as free silver particles are supposed to be less reactive than copper. The products were found to consist exclusively of silver nanoparticles with a narrow size distribution around 20 nm (diameter), see Fig. 6. In the case of copper salts as starting materials, the amount of the product was much smaller and the product itself was less homogeneous than in the case of silver. This may be due to the not yet optimized process. Further exploratory experiments with platinum and palladium are on their way, the corresponding results will be published elsewhere.

At this early point of the development of a well controlled plasma-electrochemical process for the deposition of metal nanoparticles we have no quantitative information on the impurity content and the surface states of the nanoparticles. It appears as if the cathodic and anodic decomposition of the ionic liquid is not a serious side process, but in any case we observed a slow darkening of the ionic liquids, indicating some decomposition reactions. We believe that these can be reduced considerably by adding a second salt with a more easily oxidizable anion. As copper based catalysts are especially highly interesting for fuel processing, we will concentrate on the plasma electrochemical deposition of copper, but will also investigate the deposition of other metals. To our knowledge, the plasma-electrochemical approach is the only

electrochemical route to free nanoparticles, and it may even be developed as a continuous process.

Conclusions

The present paper shows the high potential of ionic liquids in the electrodeposition of nanocrystalline metals without additives or applying pulse plating. It is shown that nanocrystalline Cu and Al can be electrodeposited in the air and water stable ionic liquids [BMP]TFO and [BMP]Tf₂N, respectively, without any additives. Presumably, the [BMP]⁺ cation acts as a grain refiner and it plays its role by adsorption on the substrates and on growing nuclei, thus hindering the further growth of crystallites. Generally, the obtained Al or Cu deposits are shiny, dense and adherent with very fine crystallites in the nanometre regime. Whereas these electrochemical processes at solid electrodes lead to thin nanocrystalline films, we have also developed a process for the electrodeposition of free nanoparticles at the surface of ionic liquids by using low temperature plasmas as fluid electrodes. This plasma-electrochemical route to nanoscaled metals offers several advantages and will be explored in more detail for the preparation of catalyst particles.

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CO₂ reforming of methane over argon plasma reduced Rh/Al₂O₃ catalyst: a case study of alternative catalyst reduction *via* non-hydrogen plasmas

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An argon glow discharge plasma was used to reduce RhCl₃ impregnated Al₂O₃ powder at room temperature. The obtained sample was characterized by chemisorption, X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) equipped with an energy dispersion X-ray spectrometer (EDX). XRD and EDX analyses confirmed that Rh ions were reduced into metallic Rh during the plasma reduction. TEM analysis revealed that the argon plasma reduction induces a high dispersion of Rh nano-particles. The average particle size of Rh is 1.2 nm, estimated by chemisorption. For the CO₂ reforming of methane, the plasma reduced Rh/Al₂O₃ shows comparable activity to a conventional hydrogen reduced catalyst. The value of the standard electrode potential can be employed for the assessment of reducibility of metal ions. The catalyst reduction using argon glow discharge plasma at room temperature will provide a promising alternative to hydrogen reduction for catalyst preparation.

Introduction

The use of catalysts is one of principles of green chemistry. In fact, catalysis plays an extremely important role in present chemical industries and will be even more important in the future. One of the basic operations for catalysis is catalyst reduction, since many reactions require metallic nano-particles as the active species. The catalytic properties of metal species are closely related to morphology and particle size, which are normally determined by the conditions of the catalyst reduction. The catalysts applied now are normally reduced using flowing hydrogen at elevated temperatures or reduced by chemical reductants, such as formaldehyde and hydrazine. Generally, most chemical reducing agents currently used are hazardous to both the human body and the environment, while hydrogen is explosive so special care is required for production, transportation, storage and use. The production of hydrogen and chemical reducing agents is also expensive, with many wastes generated as by-products. It would be useful if an alternative catalyst reduction can be available. In this regard, several alternative catalyst reduction approaches have been reported, including photocatalyst reduction using irradiation^{1,2} and reduction using glucose^{3,4} and vitamin B⁵ as reductants. The photocatalyst reduction is effective and efficient for most cases but the support materials are limited to semiconductors. Other alternative catalyst reduction technologies are mostly employed for applications in liquid. More novel catalyst reduction methods are needed for many other applications.

Recently, catalyst or metal ion reduction using hydrogen plasmas has attracted much attention.^{6–10} The objective for the use of hydrogen plasmas was to obtain a highly dispersed active metal species. As addressed above, the thermal catalyst reduction using hydrogen at elevated temperatures would result in large metal particles due to aggregation at high temperatures. The large particles induce low activity and poor stability in some cases. Catalyst reduction using hydrogen plasmas can even be conducted at room temperature, which has been expected to have a benefit in the improvement of dispersion. As discussed above, the use of hydrogen for the plasma catalyst reduction would need special care. During our investigation on the preparation of Pd/HZSM-5 catalyst using argon glow discharge plasmas, we observed that the supported Pd ions can be totally reduced at around room temperature by this kind of argon plasma.¹¹ Oxygen glow discharge plasmas also show the capability for the reduction of Pd ions.^{11,12} This is interesting because no reducing chemicals are utilized. The activity and stability of argon plasma reduced Pt and Pd catalysts for partial oxidation of methane¹³ and for methane decomposition,¹⁴ respectively, have been confirmed. This result suggests that glow discharge plasmas might provide a green method to prepare supported metal catalyst. Further tests exhibited that not all metal ions can be reduced by glow discharge plasmas. In addition to supported Pd and Pt ions, supported Au,¹² Ag¹² and Ir ions can be easily reduced by argon or oxygen glow discharge plasmas. However, supported Ni²⁺,^{15,16} Fe³⁺ and Co²⁺ cannot be reduced by glow discharge plasmas. Only decomposition was observed during plasma treatment using argon glow discharge.¹⁶ The Ni catalysts treated using argon glow discharge plasmas exhibited a special metal-support interface¹⁶ and showed better low-temperature activity and enhanced stability for methane conversion.¹⁵ Obviously, the reduction ability of glow discharge plasmas is different with different metal ions. For future applications of the non-hydrogen glow discharge plasma catalyst reduction,

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more fundamental investigations are immediately required. In this work, we confirm the argon glow discharge plasma can be applied for the reduction of Al_2O_3 supported Rh catalyst at room temperature. After that, we propose, for the first time, that the value of the standard electrode potential of metal ions can be applied for the judgement of the reducibility of metal ions by non-hydrogen glow discharge plasmas. Moreover, CO_2 reforming of methane over the plasma reduced Rh/ Al_2O_3 catalyst will be tested. CO_2 reforming will be very useful in future fuel synthesis and processing. Rh catalysts have been confirmed to possess an ability to resist coke formation during the reforming reaction, which is very important to reduce waste in the reaction. Rh catalysts also show one of the highest activities in terms of turnover frequency (TOF).^{17,18} It is an excellent catalyst for many reactions,^{17–24} including methane conversion.^{17,19–21} The reported Rh catalysts had to be reduced by hydrogen at high temperatures.^{17,20–24} We aim to develop a non-hydrogen plasma reduction for the preparation of Rh catalysts in this work.

Experimental

Preparation

$\gamma\text{-Al}_2\text{O}_3$ powder ($S_{\text{BET}} = 230 \text{ m}^2 \text{ g}^{-1}$), purchased from Taixing Reagent Plant, Tianjin, China, was calcined at 500°C for 4 h prior to use. It was then impregnated with an aqueous solution of RhCl_3 (Delan Fine Chemical Plant, Tianjin, China) for 12 h, followed by drying at 110°C for another 12 h. Then it was treated with argon glow discharge plasma. The glow discharge plasma setup has been previously described in detail.^{12–14} The sample (about 0.5 g), loaded on a quartz boat, was placed in the glow discharge cell. When the pressure was adjusted in the range of 100–200 Pa, the glow discharge plasma was generated by applying 900 V to the electrode using a high voltage amplifier (Trek, 20/20B). The signal input for the high voltage amplifier is supplied by a function/arbitrary waveform generator (Hewlett Packard, 33120A) with a 100 Hz square wave. Ultra high pure grade argon ($>99.999\%$) was used as the plasma-forming gas. The time of each plasma treatment was 10 min and each sample was treated 5 times. In the end, the color of the catalyst powder had thoroughly changed from light brown to dark, as shown in Fig. 1. The discharge was initiated at room temperature without external heating or cooling. According to the temperature measurements, using IR imaging, the heating effect of the glow discharge can be ignored and the temperature of the catalyst powder is close to room temperature. The sample after plasma treatment is denoted as PT-Rh/ $\gamma\text{-Al}_2\text{O}_3$. PT-Rh/ $\gamma\text{-Al}_2\text{O}_3$ directly calcined at 600°C for 3 h under the protection of argon is referred to as PTAr-Rh/ $\gamma\text{-Al}_2\text{O}_3$. The amount of Rh loaded was 1 wt%. For the purpose of comparison, the catalyst was also prepared by hydrogen reduction thermally (without the use of glow discharge plasma reduction). The catalyst prepared thermally is denoted as C-Rh/ $\gamma\text{-Al}_2\text{O}_3$.

Characterizations

The X-ray powder diffraction (XRD) patterns of the catalyst samples were recorded by a Rigaku D/Max-2500 V/PC



Fig. 1 Catalyst samples before (left) and after (right) argon glow discharge plasma reduction.

diffractometer at a scanning speed of 8° min^{-1} . The diffractometer was equipped with an Ni-filtered $\text{Cu K}\alpha$ radiation source ($\lambda = 1.54056 \text{ \AA}$). The X-ray source was operated at 40 kV and 150 mA. The phase identification was made by comparison with the Joint Committee on Powder Diffraction Standards (JCPDSs).

Transmission electron microscopy (TEM) observations were carried out using a Philips TECNAI G²F20 system equipped with energy dispersion X-ray spectroscopy (EDX) operated at 200 kV.

The hydrogen chemisorption measurements were also carried out using an Autosorb-1-C system (Quantachrome).

Activity test

We employed CO_2 reforming of methane as the test system for the assessment of plasma reduced Rh/ Al_2O_3 catalyst. Catalyst assessment was carried out in a quartz tube with an inner diameter of 4 mm at ambient pressure. A catalyst sample of 50 mg (40–60 mesh) was packed in the quartz tube. For the thermally prepared catalyst, C-Rh/ $\gamma\text{-Al}_2\text{O}_3$, it was pre-reduced *in situ* by flowing hydrogen at $50 \text{ cm}^3 \text{ min}^{-1}$ at 600°C for 3 h. For the plasma-reduced sample, it was first purged with an argon flow at $20 \text{ cm}^3 \text{ min}^{-1}$ at 600°C for 3 h. The feed gases of CH_4 , CO_2 and argon with a ratio of 1 : 1 : 2 were introduced into the micro reactor by mass flow controllers. The gases used were ultra high pure grade ($>99.999\%$), and were used without further purification. After reaction, the products passed through an ice trap to remove water, and then were analyzed online by a gas chromatograph (Agilent 4890) equipped with a thermal conductivity detector (TCD) using a Porapak Q packed column. Argon was used as the carrier gas.

Results and discussion

XRD patterns of the argon plasma reduced sample are illustrated in Fig. 2. For the PT-Rh/ $\gamma\text{-Al}_2\text{O}_3$ sample, peaks assigned to $\gamma\text{-Al}_2\text{O}_3$ ($2\theta = 19.7^\circ, 37.1^\circ, 45.4^\circ, 66.2^\circ$) can be clearly observed. Only a weak shoulder peak at $2\theta = 41.06^\circ$ could be assigned to Rh(111), suggesting the plasma reduced Rh would exist in an amorphous phase or highly dispersed on

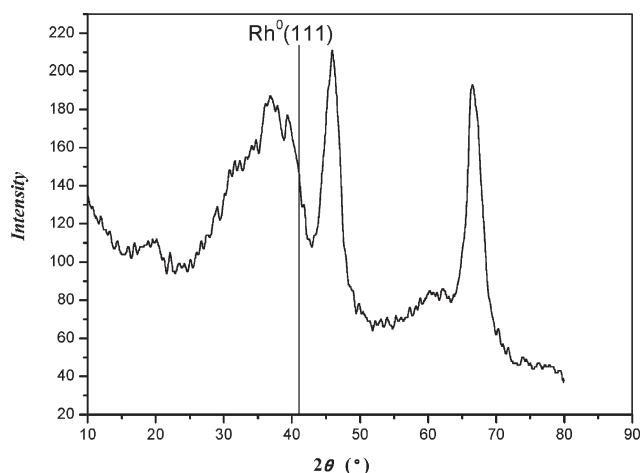


Fig. 2 XRD patterns of PT-Rh/ γ -Al₂O₃.

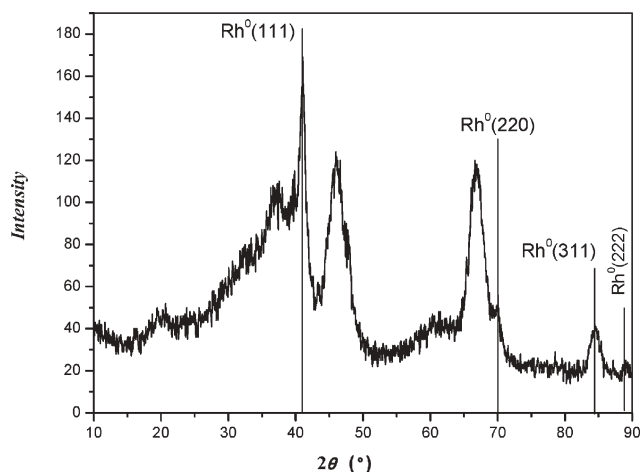


Fig. 3 XRD patterns of PTAr-Rh/ γ -Al₂O₃.

the support. Fig. 3 exhibits XRD patterns of PTAr-Rh/ γ -Al₂O₃. After calcination under the protection of argon, the plasma reduced sample shows intense peaks at $2\theta = 41.06^\circ$, 69.86° , 84.06° and 89.06° . These peaks can be assigned to Rh(111), Rh(220), Rh(311) and Rh(222), respectively. This clearly demonstrates that the Rh ions have been reduced during the argon glow discharge plasma reduction.

The TEM images of PTAr-Rh/ γ -Al₂O₃ are shown in Fig. 4. As shown in Fig. 4, Rh species have been highly dispersed on the support, similar to the sample hydrogen-reduced thermally (C-Rh/ γ -Al₂O₃), as shown in Fig. 5. The Rh particle size is around 1 nm. According to the chemisorption measurements, the average particle size of PTAr-Rh/ γ -Al₂O₃ is 1.2 nm, while it is 0.8 nm for C-Rh/ γ -Al₂O₃. The uniform distribution might be due to static electric repulsion^{11,16} during the plasma treatment. A high resolution TEM image of the particle of PTAr-Rh/ γ -Al₂O₃ is given in Fig. 6. The lattice fringes with $d = 0.219$ nm are clearly visible, which can be assigned to Rh(111). This result is in good agreement with the XRD characterization. The EDX spectrum in Fig. 7 provides further evidence of Rh nanoparticles of PTAr-Rh/ γ -Al₂O₃. It again supports the theory that the argon glow discharge plasma can easily reduce the Rh ions supported on Al₂O₃.

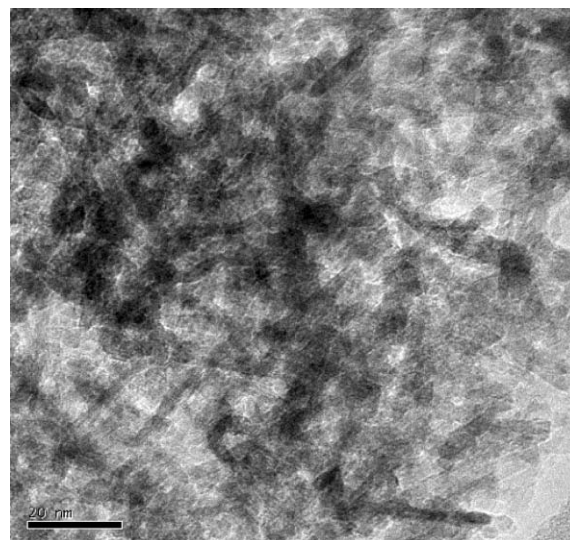


Fig. 4 TEM image of PTAr-Rh/ γ -Al₂O₃.

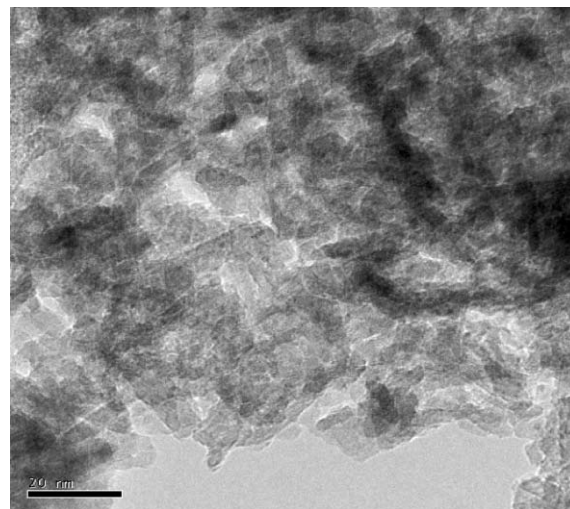


Fig. 5 TEM image of C-Rh/ γ -Al₂O₃.

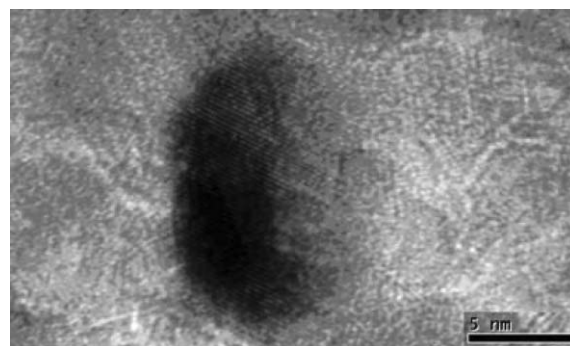


Fig. 6 A high resolution TEM image of PTAr-Rh/ γ -Al₂O₃, (a) PTAr-Rh/ γ -Al₂O₃, (b) C-Rh/ γ -Al₂O₃.

The possible mechanism for the argon glow discharge plasma reduction of Rh ions into metallic Rh nano particles probably involves two processes. One is a direct process. The high-energy electrons generated by the plasma directly reduce

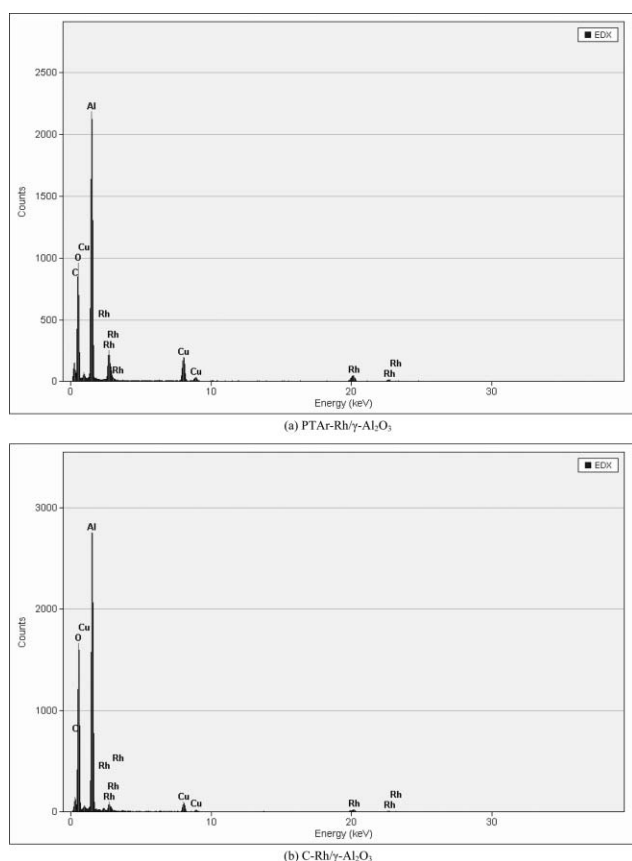


Fig. 7 EDX spectra, (a) methane conversion, (b) CO₂ conversion, (c) hydrogen selectivity, (d) CO selectivity.

the Rh ions through a recombination process. This process has been suggested for the reduction of palladium ions using a glow discharge.^{11,12} The high-energy species in the plasma may also induce the dissociation and ionization of chemisorbed water molecules to generate active species, such as hydrated electrons e_{aq}^- , which are very strong reducing species,¹³ and can act as reducing agents to reduce Rh ions. Thus, the second process is an indirect one involving the excitation of chemisorbed water. In both processes, the reduced Rh could retain some electric charge and repel each other, resulting in the uniform distribution of Rh on the Al₂O₃ support. From the present and previous investigations, the reducibility of metal ions by non-hydrogen plasmas should be determined by the ability of metal ions to adsorb electrons, which can be evaluated by the value of the standard electrode potential (SEP) of metal ions. Table 1 shows the SEP value of metal ions

Table 1 Standard electrode potential of metal ion pairs

Ion pairs	Electrode potential/V	Reduced by non-hydrogen plasma?
[PtCl ₄] ²⁻ /Pt	0.73	Yes
Pt ²⁺ /Pt	1.18	Yes
Pd ²⁺ /Pd	0.92	Yes
Ag ⁺ /Ag	0.80	Yes
Ir ³⁺ /Ir	1.156	Yes
[AuCl ₄] ⁻ /Au	1.00	Yes
Au ⁺ /Au	1.69	Yes
Au ³⁺ /Au	1.50	Yes
Rh³⁺/Rh	0.76	Yes
Co ²⁺ /Co	-0.29	No
Fe ²⁺ /Fe	-0.45	No
Fe ³⁺ /Fe	-0.04	No
Ni ²⁺ /Ni	-0.25	No

tested so far. Obviously, those metal ions with positive potential can be easily reduced by non-hydrogen plasmas, while those with negative SEP cannot be directly reduced by non-hydrogen plasmas. The SEP for Rh³⁺ is 0.758. Rh³⁺ can be easily reduced by non-hydrogen plasmas, as demonstrated in this work.

The argon glow discharge plasma reduced Rh/Al₂O₃ catalyst was tested for CO₂ reforming of methane. The effect of reaction temperature on conversions and selectivities are exhibited in Table 2. Compared to the hydrogen-reduced sample, the plasma-reduced sample shows the same activity at all the reaction temperatures tested. Fig. 8 presents the results of the stability test. Both PTAr-Rh/γ-Al₂O₃ and C-Rh/γ-Al₂O₃ catalysts are stable during the 48 h tests. Fig. 8 also shows the same activities with both catalysts. It confirms that the argon glow discharge plasma catalyst reduction is as effective and efficient as the same catalyst produced by hydrogen reduction at elevated temperatures.

Conclusions

An argon glow discharge plasma was successfully used to reduce an Al₂O₃ supported Rh catalyst for CO₂ reforming of methane. The average Rh particle size of 1 wt% Rh/Al₂O₃ estimated by chemisorption was 1.2 nm. Such a plasma-reduced catalyst exhibits a significantly high activity, as high as that obtained with a hydrogen thermally reduced Rh/Al₂O₃ catalyst. The plasma-reduced catalyst also shows excellent stability. The argon glow discharge plasma catalyst reduction can be easily operated at room temperature. The operation is fast, simple and efficient. The plasma catalyst reduction will provide us a very promising alternative to the conventional

Table 2 Effect of reaction temperature on the activities (reaction conditions: CH₄ : CO₂ : Ar = 1 : 1 : 2; space velocity = 48 000 ml h⁻¹ gcat⁻¹)

Temp./°C	Catalyst	CH ₄ conversion (%)	CO ₂ conversion (%)	H ₂ selectivity (%)	CO selectivity (%)	H ₂ /CO
550	PTAr-Rh/γ-Al ₂ O ₃	21.7	29.1	76.6	93.2	0.70
	C-Rh/γ-Al ₂ O ₃	22.8	30.2	74.8	92.8	0.70
600	PTAr-Rh/γ-Al ₂ O ₃	31.6	40.2	87.3	99.8	0.77
	C-Rh/γ-Al ₂ O ₃	32.5	41.7	85.5	98.4	0.76
650	PTAr-Rh/γ-Al ₂ O ₃	46.9	56.6	90.7	99.2	0.83
	C-Rh/γ-Al ₂ O ₃	47.2	56.9	89.6	99.0	0.82
700	PTAr-Rh/γ-Al ₂ O ₃	61.5	69.9	92.8	99.7	0.87
	C-Rh/γ-Al ₂ O ₃	61.9	70.8	91.9	98.8	0.87

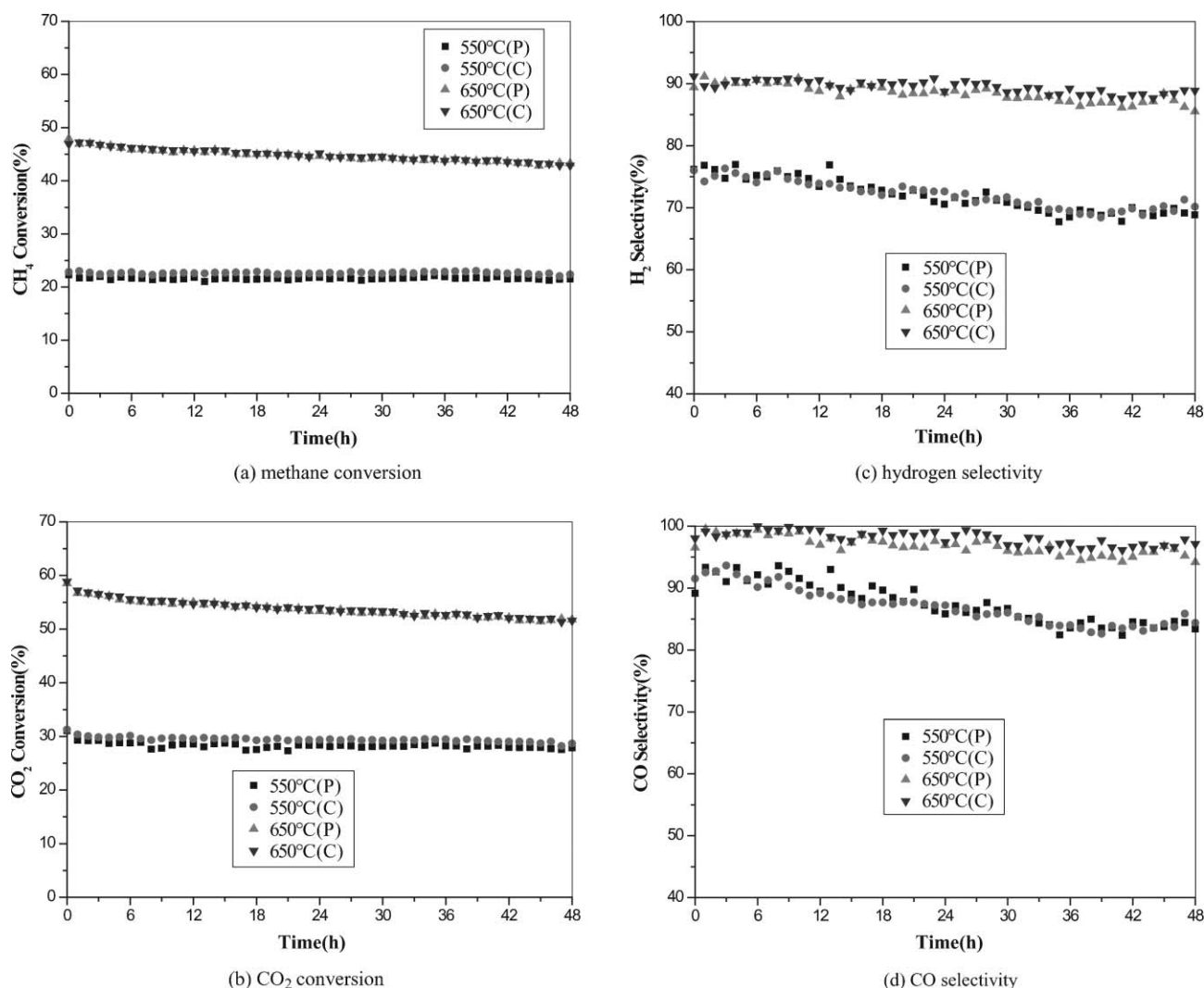


Fig. 8 The stability test (reaction conditions: $\text{CH}_4 : \text{CO}_2 : \text{Ar} = 1 : 1 : 2$; space velocity = $48\,000\text{ ml h}^{-1}\text{ gcat}^{-1}$).

catalyst reduction using hydrogen or other hazardous chemicals. The reducibility of metal ions by non-hydrogen plasmas can be determined by the value of standard electrode potential of metal ions. Those metal ions with positive standard electrode potential can be easily reduced by non-hydrogen plasmas.

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Environmentally friendly refining: Fischer–Tropsch *versus* crude oil†

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Projected changes in crude oil refinery design to meet future fuel specifications require that intermediates are produced that are already present in Fischer–Tropsch syncrude. A qualitative comparison is made between syncrude and crude oil, and the refinery designs needed to convert these raw materials into transportation fuels. Syncrude is sulfur free, nitrogen free and contains no heteroatom rich residues, making its purification and separation less complex than that of crude oil. The conversion units needed to produce motor-gasoline, jet fuel and diesel from syncrude are of similar complexity to that of crude oil, but crude oil residue conversion is much more involved. Furthermore, cleaner conversion technologies can be used to upgrade syncrude. A Fischer–Tropsch refinery consequently has a smaller environmental footprint than a crude oil refinery.

Introduction

The demand for transportation fuel inexorably drives crude oil production, which already reached 83 million barrels per day in November 2005.¹ To counter the environmental impact of increasing fuel use, a reduction in vehicle emissions has been a key driver in determining fuel specifications. This in turn requires refineries to produce fuels with properties that are increasingly divergent to that of crude oil. Refiners might have to invest in technologies that are environmentally unfriendly to produce these fuels that would reduce the pollution caused by the end-users. Although refiners are not absolved from keeping their environmental footprint as small as possible, processes that are energy intensive or deal with hazardous substances are, for the time being, tolerated.

Refinery designs continually change, mostly to keep pace with new fuel specifications. However, it is not unreasonable to expect that the same environmental pressures driving fuel specifications will eventually affect refinery designs too. It is therefore interesting to look at projections dealing with crude oil refineries of the future, since they all have four aspects in common.²

(a) Residue upgrading, albeit being expensive, will drive refining economics by upgrading cheaper heavier crudes and making more naphtha range olefins available for refining.

(b) Hydrogen is key to producing low sulfur paraffinic fuels of the future and refineries will require on-purpose hydrogen generation.

(c) Refinery complexity and cost will increase.

(d) Fuels will become increasingly synthetic in nature, since the molecules needed to meet stringent fuel specifications are not naturally abundant in crude oil.

The projected requirements for future crude oil refineries are surprisingly similar to the properties offered by Fischer–Tropsch technology.³ In Fischer–Tropsch refineries, residue upgrading is comparatively easy, the naphtha is rich in olefins ($\geq 35\%$), hydrogen is available from the gas loop and the fuels are by nature synthetic and sulfur free. This begs the question: if Fischer–Tropsch refineries are ready to produce the fuels of the future, are they not also more environmentally friendly than crude oil refineries?

The refinery needs to process Fischer–Tropsch syncrude and crude oil will be compared. The focus will be on aspects that differentiate the refineries in general terms, rather than dealing with specific refinery configurations.

Syncrude and crude oil properties

Syncrude and crude oil are collective terms used for mixtures of hydrocarbons showing significant variations in properties. Different classification systems can be adopted, with crude oil typically being classified as paraffinic, naphthenic or mixed depending on the compound class that is dominant, or light, medium or heavy, depending on its density. Fischer–Tropsch syncrude is classified as either high temperature Fischer–Tropsch (HTFT) or low temperature Fischer–Tropsch (LTFT). Despite the variations with each type, Table 1 gives some idea of the main differences between syncrude and crude oil.

Table 1 Comparison of syncrude and crude oil composition

Property	HTFT ^a	LTFT ^b	Crude oil
Paraffins	>10%	major product	major product
Naphthenes	<1%	<1%	major product
Olefins	major product	>10%	none
Aromatics	5–10%	<1%	major product
Oxygenates	5–15%	5–15%	<1% O (heavy)
Sulfur species	none	none	0.1–5% S
Nitrogen species	none	none	<1% N
Organometallics	carboxylates	carboxylates	phorphyrines
Water	major by-product	major by-product	0–2%

^a Sasol Advanced Synthol (Secunda); Synthol CFB (Mossel Bay).

^b Shell Middle Distillate Synthesis (Bintulu); Sasol Slurry Phase Distillate process (Ras Laffan and Sasolburg); Arge (Sasolburg).

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The absence of sulfur and nitrogen compounds in syncrude is immediately apparent. Much energy and effort is expended to remove these heteroatoms from crude oil. Syncrude contains oxygenates, and although not all oxygenates are desirable, there are also useful oxygenates in syncrude, such as lubricity-giving long chain carboxylic acids and high octane motor-gasoline components like ethanol.

Another significant difference is the presence of olefins in syncrude, a compound class that is absent in crude oil. This gives syncrude a synthetic capability. In a crude oil refinery, similar synthetic capability is only obtained after olefins are produced in units like fluid catalytic crackers (FCC).

The highly olefinic nature of HTFT syncrude and presence of some aromatics, give HTFT syncrude a better straight run octane than either LTFT or crude oil (Table 2). The octane number of straight run HTFT syncrude can easily be improved by double bond isomerisation, which is a facile acid catalysed reaction that can be done at low temperature (<150 °C). Since HTFT syncrude is rich in linear α -olefins that have a much lower octane number than the corresponding linear internal olefins, significant octane improvement is possible. For example: 1-hexene has a research octane number (RON) of 76.4 and motor octane number (MON) of 63.4, while *trans*-2-hexene has a RON of 92.7 and a MON of 80.8.⁴ Double bond isomerisation to improve the octane number can also be performed at higher temperatures over alumina-rich materials to remove unwanted oxygenates.⁵ This is no longer Fischer–Tropsch refinery practice, but illustrates the quality difference between HTFT syncrude and crude oil naphtha fractions.

A difference that is not apparent from Table 1, is the carbon number distribution. There is significant variation in crude oil, with very light crudes, such as Nigeria Light, having a residue content (>360 °C boiling material) of <30%, while heavy Venezuelan crudes like Tia Juan have a residue content of >80%.⁶ In this respect there is also a significant difference between HTFT and LTFT syncrude (Fig. 1). There is almost no residue fraction in HTFT syncrude, while the carbon number distribution of LTFT syncrude resembles that of crude oil.

The hydrogenated distillate from LTFT syncrude has a high cetane number due to its high linear paraffin and low aromatic content (Table 3), while the distillate of HTFT and crude oil are comparable.

From Tables 2 and 3 it can be concluded that syncrude has inherently better properties for transportation fuel production than crude oil. It therefore stands to reason that if this advantage can be exploited by the refinery design, a Fischer–Tropsch

Table 2 Comparison of the straight run naphtha properties of syncrude and crude oil

Property	HTFT ^a	LTFT ^b	Arabian light crude	
Boiling range/°C	20–105	20–100	20–80	80–180
Fraction of total (%)	30	10	5	15
RON	68	43	61	24
Density/kg m ⁻³	680	680	660	750
Olefins (%)	85	55	0	0
Aromatics (%)	2	0	2	14

^a Synthol stabilised light oil. ^b SSDP cold condensate with oxygenates removed.

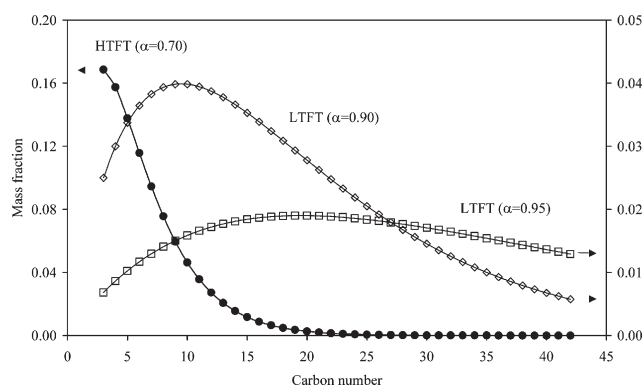


Fig. 1 Carbon number distribution of HTFT and LTFT syncrude with different Fischer–Tropsch chain propagation probabilities (α -values).

Table 3 Comparison of the hydrogenated straight distillate properties of syncrude and crude oil

Property	HTFT ^a	LTFT ^b	Arabian mix ^a
Boiling range/°C	190–380	150–335	250–360
Fraction of total (%)	15	35	25
Cetane	55	72	56
Viscosity, 40°C/cSt	2.2	2.0	2.8
Density/kg m ⁻³	805	770	830
Aromatics (%)	25	<1	25

^a Distillate hydrotreater product. ^b Hydrocracker distillate product.

refinery should be less costly, less complex and possibly more environmentally friendly than a crude oil refinery. This hypothesis will be explored by looking at the details of syncrude and crude oil refinery designs.

Refining requirements

Refining requirements are determined by the prevailing fuel specifications. Since fuel specifications keep on changing, refineries also have to keep on changing, and over the years have moved from topping–reforming designs to refineries that also included vacuum distillation, residue upgrading, aliphatic alkylation and hydroisomerisation. Optionally, a refinery may also have an etherification unit, but the debate on which oxygenates are permissible has become political. Depending on the location of the market, either alcohols or ethers may be included.

It is important to look at the trends in fuel specifications to keep the present discussion general. The sulfur content of fuels is being reduced, with $\leq 10 \mu\text{g g}^{-1}$ sulfur being the norm or becoming the norm. In motor-gasoline the benzene content is decreasing to $\leq 1\%$, the octane requirements are increasing ($\text{RON} \geq 95$ and $\text{MON} \geq 85$) and the composition is becoming more paraffinic. In diesel fuel the cetane index is increasing (≥ 45), the density range narrowing and distillation end point decreasing. The use of heavier fuel oil fractions is declining and refiners have to convert most of their feedstock to material in the 20–360 °C boiling range.

From Table 2, it can be seen that straight run naphtha requires a lot of refining to meet current motor-gasoline specifications, while it is equally apparent from Table 3 that

Table 4 Qualitative indication of refining effort required for various fractions and the abundance of C₃+ hydrocarbons and oxygenates in the aqueous phase of syncrude and crude oil

Fraction	Effort to refine	HTFT ^a	LTFT ^b	Arabian Light
LPG	Easy	30	10	1
Naphtha	Difficult	40	19	20
Distillate	Easy	16	22	33
Residue	Difficult	6	46	46
Aqueous	Easy	8	3	0

^a Synthol, Secunda: ref. 15. ^b Arge, Sasolburg: ref. 16.

straight run distillates requires little refining. To convert residue fractions to lower boiling components requires energy, and most residue conversion processes operate at temperatures of 350 °C and higher. Table 4 gives a qualitative indication of the refining cost and energy requirements to upgrade different feed materials to transportation fuels. This indicates that HTFT syncrude is the easiest feed material to refine.

Naphtha refining

The main issues to consider when refining naphtha to motor-gasoline are the quality of paraffins, octane number and the benzene content.

The paraffins is the only compound class not limited by fuel specifications, and forms the base stock that must be blended with compound classes that are restricted by specifications, namely aromatics, olefins and oxygenates. Paraffin upgrading can be divided into three ranges: butanes, C₅–C₆ and C₇–C₁₀. The butanes already have a high octane⁴ and direct inclusion in motor-gasoline is only limited by vapour pressure. The C₅–C₆ paraffins are known as light straight run (LSR) naphtha and can easily be upgraded by hydroisomerisation, which is made possible by their resistance to cracking and the low degree of isomerisation that is needed to increase their octane number. There are two types of hydroisomerisation catalysts, namely chlorided Pt/Al₂O₃ and Pt/zeolite,⁷ the latter being more environmentally friendly, achieving long catalyst life and avoiding the use of halogenated chemicals. Presently it is not yet possible to upgrade C₇–C₁₀ paraffins to iso-paraffins, due to their cracking propensity⁸ and the high degree of branching needed to achieve an octane number above 80. For example, *n*-octane (RON < 0), 2-methylheptane (RON = 20.6), 3,4-dimethylhexane (RON = 76.3) and 2,2,4-trimethylpentane (RON = 100).⁴

Catalytic reforming is key to crude oil refining, not only because it upgrades low octane C₇–C₁₀ paraffins to high octane aromatics, but also because it is the main source of hydrogen in an oil refinery. The hydrogen is needed to achieve the low sulfur specifications. Unlike Fischer–Tropsch refineries that do not have a sulfur problem (syncrude is sulfur free) and where hydrogen is available from the synthesis gas, crude oil refineries tend to be hydrogen constrained. Fischer–Tropsch refineries also need to upgrade the C₇–C₁₀ paraffins, but a different type of aromatisation technology is preferred. Crude oil is reformed over chlorided Pt/Al₂O₃-type catalysts, while syncrude is preferably reformed over a non-acidic Pt/L-zeolite catalyst. The Pt/L-zeolite technology is more environmentally friendly, since it does not require

halogenated chemicals as co-feed and it is more selective (less wasteful).⁹

Benzene can become a problem in a crude oil refinery if the feed to the catalytic reforming unit contains C₆ material, but this is generally avoided. However, in a Fischer–Tropsch refinery it is preferable to route the C₆ material to the non-acidic Pt/L-zeolite based reformer, thereby deliberately producing benzene as feed for aromatic alkylation. In this way benzene is not treated as an unwanted motor-gasoline component, but rather as a synthetic building block. For example, benzene can be alkylated with propylene that is available in the syncrude, to produce cumene (RON = 113 and MON = 99.3) that can be used in motor-gasoline or jet fuel. In this respect a Fischer–Tropsch refinery is more complex than a crude oil refinery, because two aromatics units are required.

Refineries would have been able to produce motor-gasoline by only making use of C₅/C₆ hydroisomerisation and catalytic reforming if fuel specifications did not restrict the aromatics content and limit vapour pressure. The high-octane isomers of C₅ and C₆ have vapour pressures of 140 kPa and 50 kPa respectively, which makes it difficult to produce a reasonable fuel blend with only C₅/C₆ paraffins and aromatics.

There is, consequently, a need to synthesise heavier (lower vapour pressure) high-octane paraffins in the refinery, typically by aliphatic alkylation. Iso-butane can be alkylated with C₃–C₅ olefins to produce highly branched C₇–C₉ paraffins, called alkylate. Crude oil does not contain any olefins (Table 1), and to apply this technology olefins must be produced somewhere in the refinery, typically during residue conversion. It may also be necessary to include a C₄ hydroisomerisation unit to convert *n*-butane into iso-butane. Despite progress being made with the development of solid acid catalysts for alkylation, commercial alkylation technology still uses H₂SO₄ or HF catalysts that cannot be considered environmentally friendly.¹⁰ It is therefore clear that alkylate production in a crude oil refinery significantly increases its environmental footprint.

The synthesis of high-octane paraffins from syncrude follows a different approach. Dimerisation of butenes over a solid phosphoric acid (SPA) catalyst, produces a high-octane olefinic motor-gasoline that can be hydrogenated to produce a high-octane “alkylate”.¹¹ Syncrude is rich in olefins and this process does not require an iso-butene rich feed. SPA is also an environmentally friendly catalyst. It is produced from phosphoric acid and kieselguhr, a natural silica source. After use, the spent SPA catalyst can be neutralised with ammonia to produce ammonium phosphate plant fertiliser. In a Fischer–Tropsch refinery the environmental footprint for alkylate production is consequently quite small.

A comparison of the conversion units required to upgrade syncrude and crude oil to motor-gasoline (Table 5) shows that the refining complexity is similar, but that crude oil refining requires two units that are less environmentally friendly.

Distillate refining

Distillate refining to either jet fuel or diesel fuel is easier than refining naphtha to motor-gasoline. The main issues to consider are sulfur removal and polyaromatic content. The

Table 5 Conversion processes required to upgrade syncrude and crude oil to motor-gasoline, with an indication of their environmental friendliness

Conversion process	Environmental considerations	Syncrude	Crude oil
C ₄ hydroisomerisation	Clean	No	Yes
Aliphatic alkylation	H ₂ SO ₄ or HF	No	Yes
C ₅ /C ₆ hydroisomerisation	Clean ^a	Yes	Yes
Etherification	Clean	Possibly	Possibly ^b
SPA olefin dimerisation	Clean	Yes	Possibly ^b
Hydrotreating	Clean	Yes	Yes
Reforming (Pt/Al ₂ O ₃)	Chloroalkanes	No	Yes
Reforming (non-acidic Pt/L)	Clean	Yes	No
Aromatic alkylation	Clean	Yes	No

^a Clean with Pt/zeolite catalyst; chloroalkanes needed with Pt/Al₂O₃.

^b Only if olefins cannot be sold as chemicals or processed differently.

cetane index can be problematic if the feed is highly aromatic, but in general jet fuel and diesel fuel specifications can be met by just hydrotreating the feed. Syncrude has the advantage in that it contains neither sulfur, nor polyaromatics. Syncrude also contains long chain carboxylic acids, giving it lubricity, a property that is lost during deep hydrotreating of crude oil to reduce sulfur. Hydrogenation of syncrude is mainly done to increase its storage stability and less severe hydrotreating conditions are required.

Syncrude and crude oil distillate refining is therefore comparable in complexity† and environmental impact.

Residue refining

Residues have to be upgraded, not only because the market for residue products is declining, but also because dumping of residue is environmentally unacceptable. Some material in the 360–550 °C boiling range can be recovered and refined to lubricating oils and waxes, but in general a significant portion of the residue has to be converted to lighter boiling products.

HTFT syncrude presents a special case in terms of residue upgrading, since its carbon number distribution can be manipulated in such way that a very small residue fraction (<1%) is produced. This can potentially eliminate the need for residue conversion in an HTFT refinery, although in present commercial practise the residue fraction is somewhat larger (Table 4) and a small hydrocracking unit is required.

Syncrude (LTFT and HTFT) residue conversion is fairly easy. The >360 °C boiling fraction consists mainly of linear paraffin waxes, with little metal or heteroatom containing compounds that need to be removed. Hydrocracking is therefore preferred,^{3,12} since it is a clean hydrogen addition technology. However, hydrocracking requires an operating temperature of more than 350 °C. It therefore has a significant environmental footprint from an energy consumption point of view and is an attribute all residue conversion processes have in common.

Hydrocracking can also be used for the conversion of crude oil derived material, but its use is limited by hydrogen availability and the need to produce olefins. Without olefins, it is not

† Strictly speaking the distillates produced by Fischer–Tropsch synthesis contain insufficient aromatics to meet the minimum density requirement of 820 kg m⁻³ required by the current European and World Wide Fuel Charter diesel fuel specifications (see Table 3).

possible to use aliphatic alkylation or etherification to produce motor-gasoline in a crude oil refinery. Olefins are only produced by non-hydrogenating or carbon rejection technologies, like coking, fluid catalytic cracking (FCC) and visbreaking. At least one of these technologies is consequently needed.

The naphtha and distillate range material produced during residue upgrading are not necessarily final products. The naphtha is typically used as feed material for motor-gasoline production and, unless hydrocracking has been used, the distillate must still be hydrotreated before it can be used as jet fuel or diesel fuel. The refining effort associated with residue upgrading entails more than just residue upgrading, since it also contributes to volume processed in the naphtha and distillate refining sections.

A comparison of syncrude and crude oil residue upgrading (Table 6) indicates that the refining complexity needed for syncrude is less than that for crude oil. It also shows that syncrude uses only a hydrogen addition technology, while crude oil upgrading must include at least one carbon rejection technology to produce olefins. This makes syncrude residue refining more environmentally friendly than that of crude oil. It is also worthwhile to note that residue upgrading can potentially be eliminated from a refinery processing HTFT syncrude, thereby confirming the previous observation that HTFT syncrude is the easiest feed material to refine.

Separation processes

There are two valuable refining benefits that are inherent to Fischer–Tropsch syncrude. Firstly, all sulfur is removed during synthesis gas purification and forms part of the cost and complexity of syncrude production. Secondly, syncrude is not available as a single feed material, but is essentially pre-fractionated by stepwise condensation after Fischer–Tropsch synthesis. These benefits are only partially offset by the increased separation complexity introduced by the Fischer–Tropsch aqueous product. This stream is processed in a separate work-up section where the water soluble oxygenates can be recovered and sold as chemicals.¹³ The refinery requires only an atmospheric distillation column. A vacuum distillation unit is just needed for non-fuels applications.

Due to the nature of crude oil, the number of separation steps required is much more. The first step is to remove the associated water from the crude oil in a desalting unit that also removes potentially corrosive salts. The water-free crude oil is then separated in various fractions by atmospheric distillation, vacuum distillation and solvent deasphalting. In addition to these, there are also post-refining treatment steps required to remove the sulfur compounds from the vent gas.

Table 6 Conversion processes required to upgrade syncrude and crude oil residues to material in the <360 °C boiling range

Conversion process	Type	T(°C) ^a	Syncrude	Crude oil
Hydrocracking	H ₂ -addition	350–430	Yes	Possibly
Coking	C-rejection	485–505	No	Yes, at least one
FCC	C-rejection	480–550	No	
Visbreaking	C-rejection	440–500	No	

^a The operating temperature range is for typical units.

Table 7 Separation processes needed by syncrude and crude oil refining

Separation process	Syncrude	Crude oil
Desalting	No	Yes
Atmospheric distillation	Yes	Yes
Vacuum distillation	No	Yes
Solvent deasphalting	No	Possibly
Acid gas treatment	No	Yes
Aqueous product work-up	Yes	No

The separation complexity of syncrude is less than that of crude oil (Table 7) partly due to the benefits inherent in the production of syncrude by Fischer–Tropsch synthesis. The cost associated with this benefit is already included in the syncrude production cost, just like the cost of associated gas processing is included in the cost of crude oil production.

Discussion

Fuels refining

Refining is an energy conversion process and, like all other energy conversion processes, it is subject to the second law of thermodynamics. Energy must therefore be expended during the refining process to transform the syncrude or crude oil into transportation fuels. The environmental footprint of a refinery is seen as a combination of its energy requirements, inventory and use of hazardous substances and production of waste.

(a) The energy requirements of a refinery can qualitatively be related to the number of units used (conversion and separation processes), the endothermicity of the conversion processes and the temperature of operation. A comparison of syncrude and crude oil refining showed that the number of units required for naphtha and distillate upgrading is similar, but that crude oil required more units for residue upgrading and separation (Tables 6 and 7). This is not only due to differences in the carbon number distribution of syncrude and crude oil, but also due to differences in composition (Table 1). Fischer–Tropsch syncrude contains olefins and oxygenates that are reactive compound classes and capable of highly exothermic reactions. For example, olefin dimerisation has a heat of reaction exceeding 60 kJ mol^{-1} . Crude oil does not contain such reactive compound classes, making crude oil conversion on average more endothermic than syncrude conversion. This is exemplified by the high temperatures ($\geq 440^\circ\text{C}$) needed by the carbon rejection processes typical of crude oil refining. It can therefore be said that the energy requirements of syncrude refining is less than that of crude oil refining.

(b) The use of hazardous substances during refining does not imply that these substances are causing pollution, but they do pose an environmental risk and may cause pollution during a plant upset. Having an inventory of hazardous substances is seen as a deferred waste disposal problem, and technologies that require such substances should be kept to a minimum. None of the conversion processes used during syncrude refining requires hazardous substances, but crude oil refineries typically have aliphatic alkylation and catalytic reforming units (Table 5). An inventory of concentrated liquid acid and

chloroalkanes makes crude oil refineries less environmentally friendly than syncrude refineries.

(c) Waste disposal and refinery emissions are limited by law, and all refineries are subject to the same restrictions.[§] There is, nevertheless, not much difference in solid waste generation between syncrude and crude oil refineries. Solid waste is reduced by regenerating spent catalysts or, in the case of SPA, the spent catalyst is converted into something useful such as fertiliser. The black products from residue upgrading in a crude oil refinery can also find use in products such as road binders. Crude oil refineries generate more gaseous emissions and are therefore required to invest in acid gas treatment facilities to remove sulfur from vent gas streams. Syncrude refineries in turn generate much more aqueous effluent, since water is a major product of Fischer–Tropsch synthesis. Syncrude refineries therefore require an aqueous product work-up section, as well as treatment facilities to process the unrecovered organic waste dissolved in the water. In terms of waste generation syncrude and crude oil refineries are comparable and the environmental footprint is not much different, although the nature of the waste products differs.

Chemicals extraction

The comparison of syncrude and crude oil refineries has thus far focused only on transportation fuel. The possibility to extract chemicals from a refinery could simplify the refinery design and reduce its environmental footprint.[¶]

In a crude oil refinery it is possible to recover propylene from the FCC unit, which could improve the alkylate quality or avoid the construction of a dimerisation unit. Recovery of waxes from residue, or the production of lubricating oils could reduce the size of residue conversion units.

In comparison to crude oil, Fischer–Tropsch syncrude presents more opportunities for chemicals extraction.^{13,14} It has been shown that it is possible to recover 37% of the product from an HTFT process as commodity chemicals with little additional capital expenditure and that about 50% of the product can be recovered as chemicals with additional capital expenditure. LTFT can also be used as a platform for chemicals production, and presently the Sasol 1 LTFT refinery at Sasolburg in South Africa produces only chemicals.

The impact of “chemicals” production on the simplification of a refinery design is illustrated by the two most recent LTFT gas-to-liquids facilities, Shell Bintulu in Malaysia and Oryx in Ras Laffan, Qatar. The only conversion unit in the refinery is a hydrocracker. The naphtha is not further refined to produce motor-gasoline. Such hydrocracker-only LTFT refinery designs do not produce transportation fuels that meet international fuel specifications and should rather be seen as “chemicals” or blending component refineries.

[§] The present investigation focuses only on refineries. Emissions generated during the production of Fischer–Tropsch syncrude (like CO_2 and sulfur that are removed during synthesis gas purification) and crude oil (like associated gas that are either flared or converted to liquid products) are therefore deliberately excluded from the analysis. [¶] It is also possible to reduce the environmental footprint of both Fischer–Tropsch syncrude and crude oil refineries by product exchange between these two refinery types. These and other synergistic integration methodologies have been described previously.³

Conclusions

The environmental footprint of syncrude and crude oil refineries has been compared based on energy requirements (number of units, endothermicity of conversion and operating temperature), inventory and use of hazardous substances and production of waste. This led to the following observations:

(a) Syncrude has inherently better properties than crude oil for the production of transportation fuel.

(b) The carbon number distribution of HTFT syncrude is such that it is the easiest feed material to refine.

(c) Motor-gasoline production from syncrude and crude oil derived naphtha has similar refinery complexity, but crude oil refining is less environmentally friendly. Crude oil upgrading uses aliphatic alkylation and catalytic reforming technologies that require liquid acids (H_2SO_4 or HF) and halogenated compounds (chloroalkanes).

(d) Distillate refining from syncrude and crude oil is of comparable complexity and environmental impact.

(e) The conversion of crude oil residue requires significantly more effort than the conversion of syncrude residue. Since crude oil does not have olefins, which are required for motor-gasoline production, a crude oil refinery has to include at least one carbon rejection technology. Such a unit operates at high temperature ($\geq 440^\circ\text{C}$), and is not needed for syncrude. This makes syncrude residue conversion more environmentally friendly from an energy consumption perspective.

(f) The separation complexity of syncrude is less than that of crude oil.

(g) Extraction of chemicals can simplify the design of a refinery to reduce its environmental footprint. In comparison to crude oil, Fischer–Tropsch syncrude has more opportunities for chemicals extraction to reduce its environmental footprint.

It can therefore be concluded that the refining of Fischer–Tropsch syncrude is more environmentally friendly than crude oil refining.

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Efficient synthesis of dimethyl carbonate from methanol, propylene oxide and CO₂ catalyzed by recyclable inorganic base/phosphonium halide-functionalized polyethylene glycol†

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The cycloaddition of propylene oxide and CO₂ to form propylene carbonate promoted by a phosphonium salt covalently bound to polyethylene glycol (PEG), and the transesterification of propylene carbonate with methanol to dimethyl carbonate (DMC) mediated by PEG-supported K₂CO₃, were separately investigated. Inorganic base/phosphonium halide-functionalized PEG (K₂CO₃/BrBu₃PPEG₆₀₀₀PBu₃Br) was shown to be active for DMC synthesis from propylene oxide, CO₂ and methanol under mild reaction conditions, even under low CO₂ pressure (2 bar). The effects of various reaction variables on the activity and selectivity performance are discussed in detail. The catalyst was readily separated and reused, without catalyst leaching being detected by ³¹P NMR. Notably, excellent yields of DMC and complete conversion of propylene carbonate were reached under the optimized reaction conditions. This procedure was successfully applied to the synthesis of other dialkyl carbonates.

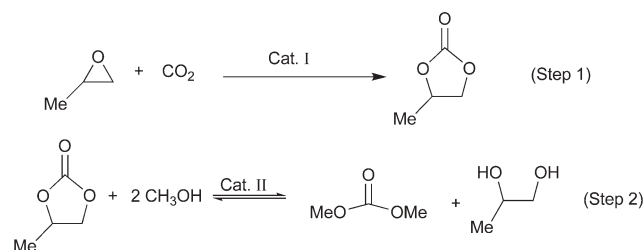
Introduction

Dimethyl carbonate (DMC) has been drawing much attention as a safe, non-corrosive, and environmentally friendly building block for the production of polycarbonate and other chemicals.¹ Also, DMC is of interest as an additive to fuel oil owing to a high octane number, reducing particulate emission from diesel engines.² In addition, it has been used as an electrolyte in lithium batteries due to its high dielectric constant.³ Therefore, development of DMC production technology and fuel properties has become important for the oil and chemical industries.

Currently, there are three processes commercialized for the large-scale production of DMC:⁴ the phosgene process, the oxidative carbonylation of methanol process, and the two-step transesterification process (Scheme 1). A considerable effort has been devoted to the non-phosgene routes to DMC.^{1b–d,5,8b} In this context, the two-step transesterification process is very attractive in view of the so-called “sustainable society” and

“green chemistry”.⁶ However, the major disadvantages of this process are high energy consumption and high investment and production costs, due to the requirement of separation of the intermediate, *i.e.* cyclic carbonate. In other words, this two-step manipulation is one of the main drawbacks of this process. To eliminate the separation process of cyclic carbonate in the two-step manufacture, it is very desirable to integrate the cycloaddition of CO₂ with epoxide and the transesterification of cyclic carbonate with methanol into a one-pot reaction, which could be regarded as the third access to DMC from CO₂.^{7a} Various catalysts^{7a,8} have been used in this process. However, these catalysts are not highly effective from a practical point of view, or are difficult to recycle, and a significant amount of the by-product from the methanolysis of epoxide is produced.

To simplify the preparative procedure for DMC synthesis based on the two-step process from CO₂, namely, to eliminate the separation of the cyclic carbonate and realize catalyst recycling, we separately explored in detail the cycloaddition of propylene oxide and CO₂ to form propylene carbonate (step 1) and the transesterification reaction of propylene carbonate with methanol to DMC (step 2). The coexistence of all reactants (epoxide, methanol, and CO₂) could cause several side reactions, such as methanolysis of epoxide, and optimal reaction conditions for step 1 and step 2 are not always compatible with each other, as reported by Y. Kishimoto.^{8m} Accordingly, developing efficient catalysts for both steps and the optimization of reaction conditions are crucial to the one-pot synthesis of DMC. Our strategy is a so-called “monophase reaction, two-phase separation” one, such that supporting the active homogeneous catalyst *e.g.* phosphonium halide, which could be easily detected by ³¹P NMR, onto CO₂-philic polymer PEG is expected to enhance the catalytic activity and enable recovery of the catalyst. We delightedly found that PEG-supported phosphonium salt demonstrated excellent activity



Scheme 1 Two-step process for DMC synthesis.

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towards step 1 and complete conversion of epoxide was reached. It is important to note that a product purity of over 99% was obtained after separation by filtration after reaction through cooling, without any other purification process. Hence, there is no need to separate the intermediate (cyclic carbonate) by distillation. Moreover, the PEG-supported K_2CO_3 was shown to be highly effective towards step 2. Consequently, another strategy is that DMC synthesis can be conducted in sequence through step 1 and step 2 without separation of the cyclic carbonate.

As a consequence, the recyclable binary catalyst system, $BrBu_3PPEG_{6000}PBu_3Br$ and K_2CO_3/PEG_{6000} had good performance for DMC synthesis from propylene oxide, CO_2 and methanol. Finally, the recyclable single catalyst $K_2CO_3/BrBu_3PPEG_{6000}PBu_3Br$ displayed high activity for this process under mild reaction conditions, even under low CO_2 pressure (2 bar). It is worth mentioning that the catalyst was readily separated and reused, without catalyst leaching being detected by ^{31}P NMR. Notably, an excellent yield of DMC and complete conversion of propylene carbonate were reached under optimized reaction conditions.

Results and discussion

In the framework of our continuous effort on developing a simple and efficient route to organic carbonates,⁷ such as cyclic carbonate, DMC, from CO_2 , we previously reported the one-pot synthesis of DMC catalyzed by homogeneous binary catalyst system $n-Bu_4NBr/n-Bu_3N$.^{7a} A novel process for DMC synthesis from epoxide, CO_2 and methanol employing the recyclable single catalyst is discussed here.

Cycloaddition of CO_2 with propylene oxide

The carboxylation of propylene oxide with CO_2 to propylene carbonate in the presence of 1 mmol% of quaternary phosphonium salts was conducted in a batch wise⁷ operation under various conditions as shown in Table 1. In the presence of PEG_{6000} alone, the reaction did not occur at all (Table 1, entry 1). Whereas, phosphonium salt ($n-Bu_4PBr$) exhibited a

Table 1 Synthesis of propylene carbonate from propylene oxide and CO_2 catalyzed by quaternary phosphonium salts^a

Entry	Cat. I (1 mol%)	P/MPa	t/h	PC ^c (%)
1	PEG_{6000}	8	6	0
2	Ph_3PBuBr	8	6	62
3	$n-Bu_4PBr$	8	6	80
4	$n-Bu_3PC_{12}H_{25}Br$	8	6	99
5	$n-Bu_4PBr/PEG_{6000}$	8	6	90
6	$BrPh_3PPEG_{6000}PPh_3Br$	8	6	80
7	$BrBu_3PPEG_{6000}PBu_3Br$	8	6	99
8	$BrBu_3PPEG_{6000}PBu_3Br$	3	6	99
9 ^b	$BrBu_3PPEG_{6000}PBu_3Br$	1	6	83
10	$BrBu_3PPEG_{6000}PBu_3Br$	1	6	99
11	$BrBu_3PPEG_{6000}PBu_3Br$	0.2	6	98
12	$BrBu_3PPEG_{6000}PBu_3Br$	1	4	96
13	$BrBu_3PPEG_{6000}PBu_3Br$	1	3	85
14	$BrBu_3PPEG_{6000}PBu_3Br$	1	1	53
15	$BrBu_3PPEG_{6000}PBu_3Br$	1	0.5	28

^a Reaction conditions: propylene oxide, 28.6 mmol (2 ml); cat. I, 1 mol%; reaction temperature, 393 K. ^b Reaction temperature, 373 K.

^c PC: propylene carbonate.

moderate catalytic activity (entry 3) under supercritical conditions (393 K, 8 MPa, 6 h). Notably, the order of the catalytic activity among quaternary phosphonium salts was found to be $BrBu_3PPEG_{6000}PBu_3Br \approx n-Bu_3PC_{12}H_{25}Br > BrPh_3PPEG_{6000}PPh_3Br \approx n-Bu_4PBr > Ph_3PBuBr$, while the selectivity remained over 98% for all the cases (entries 2–4, 6–7, Table 1). As a result, the catalytic activity is influenced by the substituents on the phosphorus atom, which could presumably be responsible for the electrophilic reactivity of the phosphonium cation and nucleophilicity of the counter-anion bromide. The $BrBu_3PPEG_{6000}PBu_3Br$ displayed higher catalytic activity than the unsupported salt ($n-Bu_4PBr$), and was even more effective than the simple physical mixture of $n-Bu_4PBr$ and PEG_{6000} under the same conditions (entries 3, 5, 7). Accordingly, the phosphonium salts can be considered as the active species for the reaction, and supporting $n-Bu_4PBr$ on soluble polymer (PEG_{6000}) improves the catalytic activity. The enhancement of catalyst performance by supporting $n-Bu_4PBr$ on soluble PEG is presumably attributed to the benefits from changes in the physical properties^{9,10} of the reaction mixture, such as lower melting points, lower viscosity, high diffusion rates, and increased solubility for propylene oxide and CO_2 through the ‘ CO_2 -expansion of a liquid’ effect.^{7d,11} Indeed, as judged by visual inspection through a window-equipped high-pressure reactor, we found that PEG and its derivatives are expandable with CO_2 as reported in the literature.¹¹ Obviously, simple addition of PEG_{6000} can accelerate the reaction (entry 3 vs. 5), probably due to the enhancement of the solubility of phosphonium salts because of PEG’s high affinity to the cation.

As shown in Fig. 1 and entries 10, 12–15 (Table 1), the yield of PC increased with reaction time within 6 h. The results indicated that the reaction proceeded rapidly within the first 4 h. It is amazing to note that within 4 h, almost quantitative yield (96%) could be achieved with 99% selectivity, which is comparable to the result for the reaction time of 6 h. In other words, a reaction time of 4 h is required for complete conversion of propylene oxide. Notably, selectivity remains 99% for the entire course of the reaction. Furthermore, reaction temperature has a large impact on the catalytic performance. The yield significantly decreased to 83% when the reaction was conducted at 373 K (entry 9 vs. 10, Table 1).

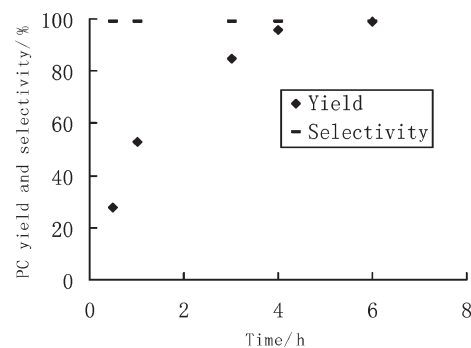


Fig. 1 Reaction time dependence of the yield of propylene carbonate for $BrBu_3PPEG_{6000}PBu_3Br$. Reaction conditions: propylene oxide, 28.6 mmol (2 ml); cat., 1 mol%; reaction pressure, 1 MPa, reaction temperature, 393 K.

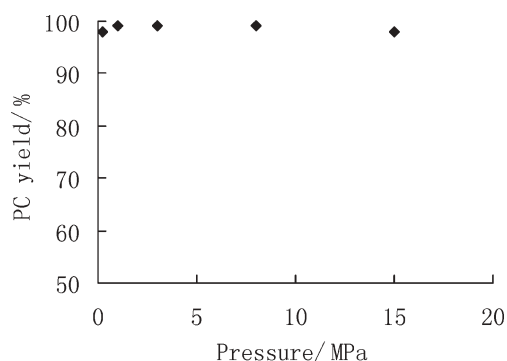


Fig. 2 Effect of CO₂ pressure on the yield of propylene carbonate for BrBu₃PPEG₆₀₀₀PBu₃Br. Reaction conditions: propylene oxide, 28.6 mmol (2 ml); cat., 1 mol%; reaction time, 6 h, reaction temperature, 393 K.

A significant drawback associated with using CO₂ as a reagent and a reaction medium in organic synthesis is the potential danger of operating at high pressure. As shown in Fig. 2, a remarkable feature of the reaction is that the carbon dioxide pressure shows no effect on the PC yield in the range of 0.2–15 MPa (entries 7–8, 10–11, Table 1). The observed zero order on CO₂ is presumably caused by high solubility of carbon dioxide, less mass-transfer limitation and high diffusion rate due to PEG's affinity towards CO₂.^{7d,11} Furthermore, propylene carbonate is produced in quantitative yield and excellent selectivity at CO₂ pressure as low as 2 bar (entry 11, Table 1).

A series of catalytic cycles were examined to test the catalyst recycling. In each cycle, the catalyst (BrBu₃PPEG₆₀₀₀PBu₃Br) was solidified by adding ether and cooling after the reaction, and recovered by a simple filtration, without catalyst leaching detected by ³¹P NMR (Fig. 3), and then subjected to a second run of the reaction by charging with the same substrates. The 5 runs (Fig. 4) are almost consistent in yield and selectivity. Moreover, a high purity (>99%) of the product was obtained in each cycle without any additional purification process. Hence, immobilization of a phosphonium salt on a soluble polymer (*e.g.*, PEG) provides an alternative pathway for realizing homogeneous catalyst recycling.

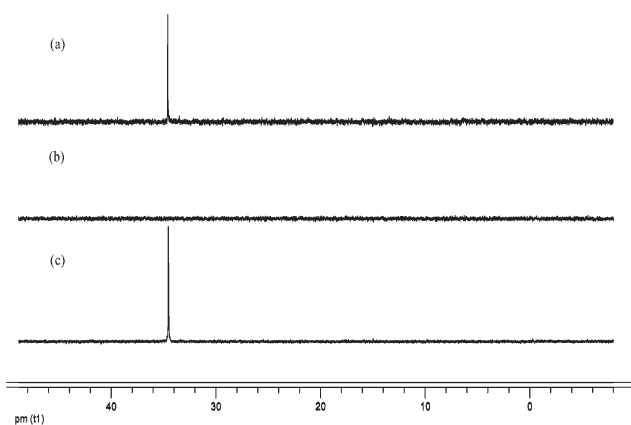


Fig. 3 ³¹P NMR (161.7 MHz, CDCl₃): (a) the fresh BrBu₃PPEG₆₀₀₀PBu₃Br; (b) the filtrate after reaction; (c) the separated catalyst after the third run.

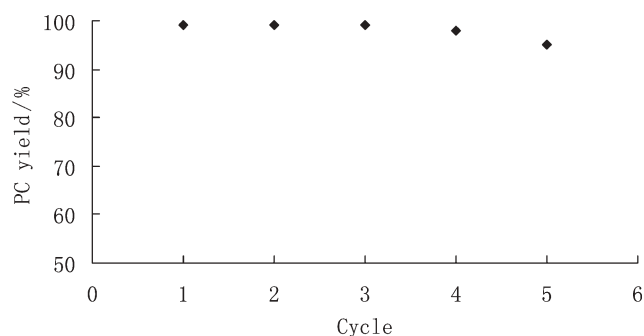


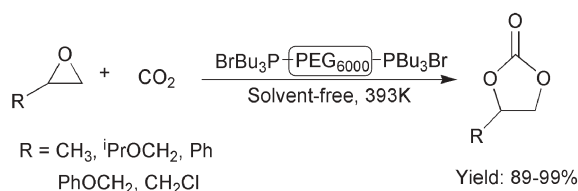
Fig. 4 Catalytic activity of the reused BrBu₃PPEG₆₀₀₀PBu₃Br. Reaction conditions: propylene oxide, 28.6 mmol (2 ml); cat., 1 mol%; reaction temperature, 393 K; reaction pressure, 8 MPa; reaction time, 6 h.

Encouraged by the high activity and selectivity of BrBu₃PPEG₆₀₀₀PBu₃Br for the carbonylation of propylene oxide with CO₂ into propylene carbonate at low CO₂ pressure, we sought to determine the applicability of viable substrates to this process. Table 2 shows the results from the carbonylation of a variety of epoxides using 1 mol% of BrBu₃PPEG₆₀₀₀PBu₃Br at 393 K, 1 MPa, 6 h. The PEG-supported catalyst, BrBu₃PPEG₆₀₀₀PBu₃Br, was found to be applicable to a variety of terminal epoxides, providing the corresponding cyclic carbonates in 89–99% yields and with excellent selectivities (Scheme 2). Propylene oxide (**1a**), and glycidyl phenyl ether (**1c**) were found to be good substrates to obtain the corresponding cyclic carbonates in nearly 100% yield, while isopropyl glycidyl ether (**1b**), epichlorohydrin (**1d**), and styrene oxide (**1e**) exhibited relatively low yields among the epoxides surveyed.

Table 2 Various carbonates synthesis using BrBu₃PPEG₆₀₀₀PBu₃Br as a homogeneous catalyst^a

Substrate	Product	Yield (%)	Selectivity (%)
1a	2a	99	99
1b	2b	90	98
1c	2c	>99	>99
1d	2d	93	97
1e	2e	89	98

^a Reaction conditions: epoxides, 28.6 mmol; cat. **1**, 1 mol%; reaction pressure, 1 MPa; reaction temperature, 393 K; reaction time, 6 h.



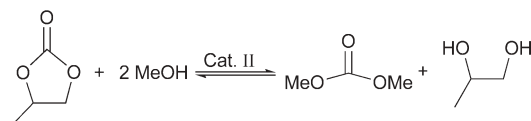
Scheme 2 Synthesis of various carbonates catalyzed by BrBu₃PPEG₆₀₀₀PBu₃Br.

Transesterification of propylene carbonate with methanol

Transesterification of propylene carbonate with methanol is one of important routes to produce DMC (Scheme 3). Cheap inorganic bases were screened for this process. The results are summarized in Table 3. The order of catalytic activity was found to be NaOH > MeONa > K₂CO₃ > Ca(OH)₂ > KOH, (Entries 1–5, Table 3). The variations of the DMC yield with reaction time in the presence of NaOH are illustrated in Fig. 5. Obviously, the rate of DMC production was faster in the beginning and remained unchanged after 0.5 h. This implies that the transesterification reaction reaches equilibrium after *ca.* 0.5 h under the reaction conditions.

Considering the strength of the bases for the cycloaddition reaction, the PEG (MW = 6000) supported K₂CO₃ was chosen as a model to investigate catalytic activity and catalyst recycling. PEG (MW = 6000) supported K₂CO₃ was proved to be active towards transesterification with 68% conversion and 100% selectivity (entry 6, Table 3). It is worth mentioning that K₂CO₃/PEG is readily recovered by a simple filtration, and reused four times without loss of activity (entries 6–9, Table 3).

The influence of the feed molar ratio of methanol to propylene carbonate is summarized in Fig. 6. The DMC yield increases with increasing molar ratio of methanol to propylene carbonate. In order to overcome the thermodynamic limitation



Scheme 3 Transesterification of propylene carbonate with methanol to produce dimethyl carbonate and propylene glycol.

Table 3 Transesterification of propylene carbonate and methanol^a

Entry	Cat. II	Conv. (%)	Yield (%)	
			DMC	PG
1	KOH	46	47	46
2	MeONa	68	68	67
3	Ca(OH) ₂	55	55	55
4	NaOH	83	82	82
5	K ₂ CO ₃	67	67	67
6	K ₂ CO ₃ /PEG ₆₀₀₀	67	68	67
7 ^b	K ₂ CO ₃ /PEG ₆₀₀₀	68	67	67
8 ^c	K ₂ CO ₃ /PEG ₆₀₀₀	68	68	68
9 ^d	K ₂ CO ₃ /PEG ₆₀₀₀	68	68	68

^a Reaction conditions: propylene carbonate, 25 mmol (2.1 ml); methanol, 0.25 mol (11 ml); cat. II, 5 mol%; reaction temperature, 373 K; reaction time, 3 h. ^b The second run of the catalyst recovered after the run in entry 6 (fresh catalyst). ^c The third run of the catalyst. ^d The fourth run of the catalyst.

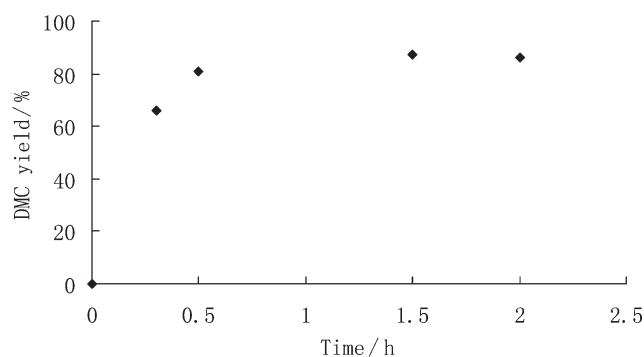


Fig. 5 Time dependence of the yield of dimethyl carbonate for NaOH. Reaction conditions: propylene carbonate, 25 mmol (2.1 ml); methanol, 0.25 mol (11 ml); catalyst, 5 mol%; reaction temperature, 373 K.

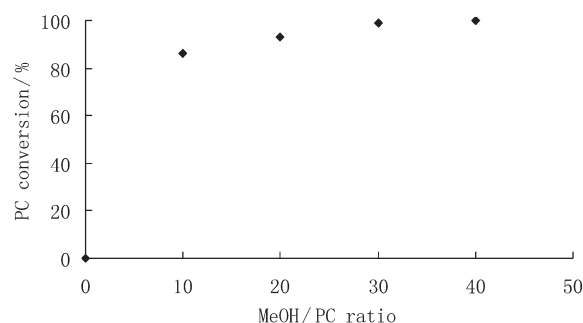


Fig. 6 The ratio of MeOH/PC dependence of the conversion of propylene carbonate for K₂CO₃/PEG₆₀₀₀. Reaction conditions: propylene carbonate, 25 mmol (2.1 ml); catalyst (K₂CO₃/PEG₆₀₀₀), 5 mol%.

of the transesterification and to realize the complete conversion of propylene carbonate, after the reaction reached equilibrium, we further carried out the reaction for 1 h while simultaneously removing the product DMC through distillation under atmospheric pressure. Indeed, propylene carbonate was completely converted to DMC with a molar ratio of methanol to propylene carbonate of 30 (Fig. 6), determined by GC analysis.

Simple process for DMC synthesis from CO₂, propylene oxide and MeOH with no need for cyclic carbonate separation

It is desirable to integrate these two reactions into a one-pot reaction. The crucial points to realize the one-pot process are the choice of active catalysts for both the cycloaddition (step 1, Scheme 1) and the transesterification (step 2, Scheme 1), and tuning of reaction parameters to suppress the side reactions, such as methanolysis of propylene oxide. As discussed above, PEG-supported phosphonium salt displayed excellent activity towards step 1, and complete conversion of epoxide with over 99% of purity of propylene carbonate was reached. Moreover, the PEG-supported K₂CO₃ was shown to be highly effective towards step 2.

We developed a simple process in which step 1 and step 2 took place in sequence with no need for separation of cyclic carbonate, as described in the Experimental. The recyclable binary catalyst system, comprising BrBu₃PPEG₆₀₀₀PBu₃Br and K₂CO₃/PEG₆₀₀₀ had good performance for DMC synthesis from propylene oxide, CO₂ and methanol (entry 1,

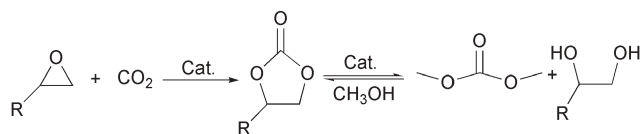
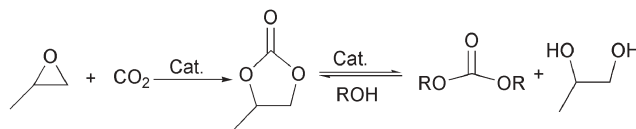
Table 4 The process for DMC synthesis and the corresponding 1,2-diols using different epoxides without cyclic carbonate separation^a

Entry	Substrate	Yield (%)	
		DMC	1,2-Diol
1 ^b		98	98
2		99	99
3		99	99
4 ^c		99	99
5 ^d		98	98
6 ^e		97.5	99

^a Reaction conditions: epoxide, 14.3 mmol; cat. ($K_2CO_3/BrBu_3PPEG_{6000}PBu_3Br$), 1.1344 g; methanol, 16 ml. Operation procedures: synthesis of cyclic carbonates at 393 K, 1 MPa, 6 h, and then methanol was added, and the mixture was refluxed for 30 min at 100 °C, finally the reaction was continued for another 1 h while simultaneously removing the product DMC through distillation under atmosphere pressure. ^b Binary catalyst: $BrBu_3PPEG_{6000}PBu_3Br$ (0.4678 g) and K_2CO_3/PEG_{6000} (0.5290 g) ^c The second run of the catalyst recovered after the run in entry 1 (fresh catalyst). ^d The third run of the catalyst. ^e The fourth run of the catalyst.

Table 4). Moreover, the single supported catalyst ($K_2CO_3/BrBu_3PPEG_{6000}PBu_3Br$) was investigated as the catalyst for this process. The results were given in Table 4. DMC and the corresponding 1,2-diols were obtained in excellent yield (99%) (entries 2–3, Table 4). A series of catalytic cycles were examined to test the catalyst recycling. In each cycle, the catalyst ($K_2CO_3/BrBu_3PPEG_{6000}PBu_3Br$) was solidified by adding ether and cooling after the reaction, and recovered by a simple filtration, without catalyst leaching detected by ^{31}P NMR, and then subjected to a second run of the reaction by charging with the same substrates. The 4 runs (entries 2, 4–6, Table 4) are almost consistent in yield and selectivity. Moreover, a high purity (>99%) of the product was obtained in each cycle without any additional purification process. It is obvious that the single supported catalyst ($K_2CO_3/BrBu_3PPEG_{6000}PBu_3Br$) displayed high activity for this process for DMC synthesis (Scheme 4). It is important to note that this catalyst was easily recovered compared with other catalysts.⁷

The effect of various alcohols was also investigated for this process for the synthesis of dialkyl carbonate (Scheme 5). The

**Scheme 4** The one-pot process for the synthesis of DMC and the corresponding 1,2-diols using different epoxides.**Scheme 5** The one-pot process for dialkyl carbonate synthesis using different alcohols.

results obtained for methanol, ethanol, and isopropanol are given in Table 5. The tested alcohols can be transformed to the corresponding dialkyl carbonates with high conversion and selectivity. This procedure was successfully applied to the synthesis of other dialkyl carbonates.

Conclusions

We developed a simple process for DMC synthesis from propylene oxide, CO_2 and methanol. Inorganic base/phosphonium halide-functionalized PEG ($K_2CO_3/BrBu_3PPEG_{6000}PBu_3Br$) was shown to be active for this process under mild reaction conditions, even under low CO_2 pressure (2 bar). Notably, an excellent yield of DMC and complete conversion of propylene carbonate were reached under the optimized reaction conditions. The catalyst was readily separated and reused without catalyst leaching detected by ^{31}P NMR. This process eliminates the requirement for toxic and wasteful feedstocks such as phosgene and carbon monoxide and has successfully been applied to synthesize the other symmetric dialkyl carbonates and 1,2-diols. The effects of the counter anion, the chain length of PEG, *etc.* on the catalytic activity for DMC synthesis from CO_2 are currently under investigation in our laboratory.

Experimental

Chemical reagents

Methanol (99.5%) was purified using magnesium and stored under a nitrogen atmosphere. PEG_{6000} , inorganic bases and water were blended to gain inorganic bases/ PEG_{6000} by evaporation under reduced pressure.¹² The $BrBu_3PPEG_{6000}PBu_3Br$ was synthesized according to the published procedures.^{7d,13} Other reagents were of analytical grade and were used without further purification.

Table 5 The process for dialkyl carbonate synthesis using different alcohols^a

Entry	Alcohol	Conv. PC (%)	Yield (%)	
			DAC	PG
1	MeOH	99	99	99
2	EtOH	73	72	73
3	ⁱ PrOH	96	95	96

^a Reaction conditions: propylene oxide, 14.3 mmol; cat. ($K_2CO_3/BrBu_3PPEG_{6000}PBu_3Br$), 1.1344 g; alcohol, 0.43 mol. Operation procedures: synthesis of cyclic carbonates at 393 K, 1 MPa, 6 h, and then alcohol was added, and the mixture was refluxed for 30 min at 100 °C, finally the reaction was continued for another 1 h while simultaneously removing the product DMC through distillation under atmosphere pressure. ^b DAC: dialkyl carbonate. ^c PG: 1,2-propylene diol.

Typical method for the preparation of K_2CO_3/PEG_{6000} and $K_2CO_3/BrBu_3PPEG_{6000}PBu_3Br$ ¹²

$BrBu_3PPEG_{6000}PBu_3Br$ (6.5 g, 1 mmol), K_2CO_3 (1.38 g, 10 mmol) and water were mixed to homogeneous solution, then water was vaporized under reduced pressure, finally the residue was dried under vacuum to gain $K_2CO_3/BrBu_3PPEG_{6000}PBu_3Br$. The method for the preparation of K_2CO_3/PEG_{6000} was the same as $K_2CO_3/BrBu_3PPEG_{6000}PBu_3Br$.

Typical procedure for the synthesis of $BrBu_3PPEG_{6000}PBu_3Br$ ^{7d,7f,13}

A solution of PEG (30 g) in dichloromethane (80 ml) was cooled to 0 °C, then PBr_3 (6 ml) was added. The mixture was stirred for 5 h at 0 °C, then stirred for 10 h at r.t. The solvent was concentrated under vacuum, and then further purified by Et_2O (3 × 50 ml). Finally, it was dried under vacuum to give $BrPEG_{6000}Br$ (26 g, 85%), then the above $BrPEG_{6000}Br$ (22 g, 3.6 mmol) and $n-Bu_3P$ (2.2 g, 10.9 mmol) were dissolved in 50 ml benzene under a nitrogen atmosphere, the mixture was heated for 70 h at 70 °C. The solvent was concentrated under vacuum, and was further washed by ethyl acetate (3 × 50 ml) and dried under vacuum to give $BrBu_3PPEG_{6000}PBu_3Br$ (20 g, 85%).

$BrBu_3PPEG_{6000}PBu_3Br$. ¹H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.96 (t, J = 6.8 Hz, 18 H), 1.50 (m, 24 H), 2.36–2.42 (m, 12 H), 3.44–3.81 (m). ¹³C{¹H}NMR (100.4 MHz, $CDCl_3$) δ (ppm) 70.9, 62.0, 30.5, 24.0, 19.8, 13.7. ³¹P{¹H}NMR (161.7 MHz, $CDCl_3$) δ (ppm) 34.5 (s).

Typical procedure for DMC synthesis from epoxide, CO_2 and methanol

In a typical reaction, the cycloaddition reaction of CO_2 to propylene oxide was carried out in a stainless steel autoclave (25 cm³ inner volume). Propylene oxide (2 ml, 28.6 mmol), catalyst (1 mol%), and biphenyl (80 mg, an internal standard for GC analysis) were charged in the autoclave under nitrogen at r.t., CO_2 (gas, ca. 0.1 MPa) was introduced to the above reactor and the initial pressure was adjusted to 1 MPa at 393 K, then the autoclave was heated at that temperature for 6 h. The vessel was then cooled in an ice–water bath, and the excess gases were vented out. After that, the methanol (34.5 ml, 0.86 mol) was added; the mixture was transferred to a 100 ml flask, and refluxed for 30 min at 100 °C. Finally, the reaction was continued for another 1 h while simultaneously removing the product DMC through distillation under atmosphere pressure. The products were analyzed by a gas chromatograph (Agilent 6890) equipped with a capillary column (HP-5, 30 m × 0.25 μ m) using a flame ionization detector, and further identified by GC–MS (HP G1800A) by comparing retention times and fragmentation patterns with authentic samples.

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A non-phosgene route for synthesis of methyl *N*-phenyl carbamate derived from CO₂ under mild conditions†

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A non-phosgene route for the synthesis of methyl *N*-phenyl carbamate from dimethyl carbonate and *N,N'*-diphenyl urea was studied under the mild conditions of atmospheric pressure. A series of homogenous and heterogenous catalysts were screened, and the homogenous catalyst sodium methoxide exhibited excellent activity in the synthesis of methyl *N*-phenyl carbamate under atmospheric pressure. The parameters of molar ratio of reactants, catalyst concentration, reaction time, number of additions of catalyst, reaction temperature and solvents in the synthesis of methyl *N*-phenyl carbamate were also investigated. A possible reaction mechanism with catalyst sodium methoxide was proposed.

Introduction

Isocyanates are important chemicals for the synthesis of polyurethanes, pesticides and herbicides. The commercial method of isocyanates production is *via* the phosgene route, which is highly toxic and corrosive. Many efforts have continuously been made for non-phosgene routes.^{1,2} Methyl *N*-phenyl carbamate (MPC) is a key intermediate for synthesizing isocyanates. The main non-phosgene methods for synthesizing MPC include oxidative carbonylation of aniline,³ reductive carbonylation of nitrobenzene,⁴ methoxycarboxylation of aniline^{5–8} and alcoholysis of *N,N'*-diphenyl urea.^{9,10}

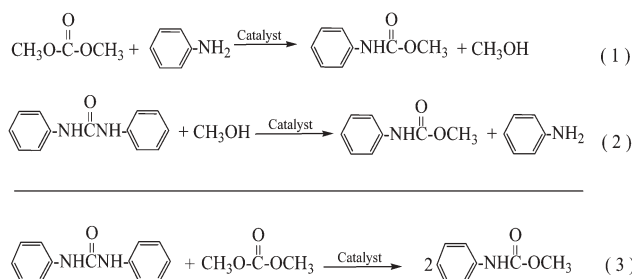
Among the above methods, the two latter ones use dimethyl carbonate (DMC) and *N,N'*-diphenyl urea (DPU) as reactants (see reactions (1) and (2) in Scheme 1), which are commercially synthesized indirectly from CO₂. Moreover, the synthesis of DMC and DPU directly from CO₂ is attractive due to its simple process (see Scheme 2).^{11–14} Therefore, the synthesis of MPC by reactions (1) and (2) will promote CO₂ utilization and the synthesis of important chemicals derived from CO₂.

But reactions (1) and (2) involve poor atom economy, and produce equal molar amounts of aniline or methanol as by-products, which decreases the efficiency of the total functionality of dimethyl carbonate (DMC) or 1,3-diphenyl urea (DPU) (see Scheme 1). To improve the atom economy, reactions (1) and (2) are coupled to reaction (3). By using poisonous chlorobenzene as solvent, reaction (3) was reported under atmospheric pressure.¹⁵ And the reaction between diethyl carbonate and DPU was also reported.^{16,17} But using DMC itself as solvent, reaction (3) has been completed only under high pressure and high temperature,^{18,19} and no-one has studied it under mild conditions of atmospheric pressure. Since the boiling point of DMC is only 90 °C under atmospheric pressure, reaction (3) isn't carried out easily under atmospheric pressure when DMC itself is used as solvent, and it is necessary to choose catalysts with high activities below 90 °C.

In this paper, the synthesis of MPC from DMC and DPU (reaction (3)) was investigated by using DMC itself as solvent under the mild conditions of atmospheric pressure.

Experimental

The preparation of catalyst NaOCH₃ was according to Dong:²⁰ 100 ml liquid NaOCH₃ with methanol solvent (colorless, the content of NaOCH₃: 27%–31% by mass, the content of dissociative alkalis: <0.45% by mass) was distilled in a 200 ml three-neck flask with the protection of nitrogen under atmospheric pressure. When solid NaOCH₃·CH₃OH appeared, the heating was stopped. After the temperature was cooled to room temperature with a stream of nitrogen, 30 ml of solvent, methyl laurate, was added into this flask and was

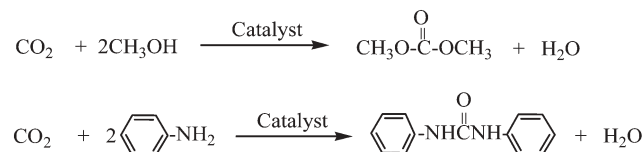


Scheme 1 Synthesis of methyl *N*-phenyl carbamate from dimethyl carbonate and *N,N'*-diphenyl urea.

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Scheme 2 Direct synthesis of DMC and DPU from CO₂.

heated again under a vacuum of 0.01–0.09 MPa. When the methyl laurate was completely distilled out, solid NaOCH₃ catalyst was obtained.

Dimethyl carbonate was distilled and stored with molecular 4 Å sieves. The basic ionic liquid [(CH₃)₂N]₂C=NH₂⁺ CH₃COO[−] was supplied by Institute of Chemistry, Chinese Academy of Sciences. CaO was prepared by the decomposition of calcium carbonate at 900 °C for 2 h. Pb(CH₃COO)₂ and Zn(CH₃COO)₂ were obtained by dehydrating in Pb(CH₃COO)₂·3H₂O at 75 °C for 2 h and Zn(CH₃COO)₂·2H₂O at 100 °C for 2 h, respectively. Other reagents were commercial reagents of AR grade.

The reactions between DMC and DPU under the conditions of atmospheric pressure were carried out in a 100 ml three-neck flask with a nitrogen inlet, a temperature controller, a stirrer, and a reflux condenser connected with a nitrogen outlet. In a typical experimental procedure, DMC (0.7 mol), DPU (0.035 mol), and catalyst (1%, based on total mass of reactants) were added under a stream of nitrogen. The mixture was heated to 90 °C under atmospheric pressure, and refluxing was continued for 4 h. After reaction, the reactor was cooled to room temperature. A 100 ml autoclave was used in the experiments to investigate the reaction temperature, and the typical experimental procedure is as follows: DMC (0.7 mol), DPU (0.035 mol), and catalyst (1%, based on total mass of reactants) were added, the air in the autoclave was replaced by nitrogen, and the reactions were carried out at 130 °C for 4 h at 1 MPa of nitrogen pressure. The resulting solution was analyzed by HPLC (high performance liquid chromatography, Agilent-1100) and characterized by GC/MS (SHIMADZU GCMS-QP2010).

Results and discussion

Activities of various catalysts for the reaction

The results of the reaction of DMC and DPU with a variety of catalysts are presented in Table 1. And the preliminary experiments showed that a non-catalytic reaction between DMC and DPU produced only a trace of MPC after 4 h. The minimal conversion of DPU (see Table 1, entry 1) indicated

Table 1 Activities of various catalysts for reaction of dimethyl carbonate and *N,N'*-diphenyl urea^a

Entry	Catalyst	DPU conversion (%)	MPC yield (%)
1	None	1.1	0.4
2	Bu ₂ SnO	15.4	14.6
3	SnCl ₂	5.2	3.1
4	SnO	2.7	1.9
5	NaOCH ₃	74.7	74.3
6	NaOH	16.1	15.3
7	K ₂ CO ₃	1.6	1.1
8	CaO	2.0	1.7
9	Zn(CH ₃ COO) ₂	0.9	0.8
10	ZnO	2.4	0.7
11	PbO	8.4	8.0
12	Pb(CH ₃ COO) ₂	1.3	1.0
13	(C ₂ H ₅) ₃ N	59.1	54.2
14	Ti(OC ₄ H ₉) ₄	4.8	4.0

^a Dimethyl carbonate (0.700 mol), *N,N'*-diphenyl urea (0.035 mol), catalyst (1%, based on total mass of reactants), reaction time (4 h).

that catalyst was essential for the formation of MPC under atmospheric pressure. Catalysts such as Bu₂SnO,¹⁹ which had good performance for the reaction of DMC and DPU under high pressure and temperature, showed poor activity under atmospheric pressure (entry 2). Tin compounds such as SnCl₂ and SnO were also tested, but showed less activity (entries 3 and 4). The non-catalytic reaction between DPU and methanol (see reaction (2)) easily takes place,^{9,10} but catalysts are necessary for the reaction between DMC and aniline (see reaction (1)).⁵ So some typical catalysts, used in the reaction of DMC with aniline, were used for the reaction of DMC and DPU. The catalyst NaOCH₃, often used in the reaction of DMC with aniline,^{6,7} showed excellent activity for the reaction of DMC and DPU (see Table 1, entry 5) under atmospheric pressure. Basic catalysts such as NaOH, K₂CO₃ and CaO, were also tested, but all showed poor catalytic activity, especially K₂CO₃ and CaO (entries 6–8). Compounds of zinc and lead such as Zn(CH₃COO)₂, Pb(CH₃COO)₂, ZnO and PbO, which had good activity in the reaction of DMC with aniline,⁸ also showed poor activity in reaction (3) under the atmospheric pressure (entries 9–12). Both catalyst (C₂H₅)₃N,¹⁵ used in reaction (3) when chlorobenzene was used as solvent under atmospheric pressure, and catalyst Ti(OC₄H₉)₄,^{16,17} used in the reaction between diethyl carbonate and DPU under atmospheric pressure, showed much lower activity than NaOCH₃, especially catalyst Ti(OC₄H₉)₄ (see entries 13, 14 and 5). From the above results, it could be showed that alkali metal alkylate NaOCH₃ had an excellent activity (entry 2), which could efficiently catalyze the synthesis of methyl *N*-phenyl carbamate under atmospheric pressure.

Therefore, reactions between DMC and DPU were further investigated by using NaOCH₃ as catalyst.

Effect of molar ratio of DMC to DPU

The effect of the molar ratio of DMC to DPU on the reaction was studied with NaOCH₃ as the catalyst, and results are shown in Fig. 1. The molar ratio of DMC to DPU was varied in the range of 10–30. The conversions of DPU increased obviously up to the molar ratio of 20, but the selectivity of

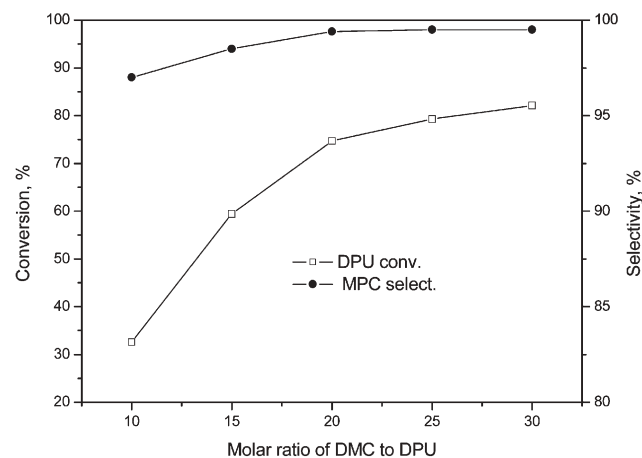


Fig. 1 Effect of molar ratio of DMC to DPU on the reaction between dimethyl carbonate and *N,N'*-diphenyl urea. *N,N'*-diphenyl urea (0.035 mol), catalyst (0.7 g), reaction time (4 h).

MPC remained. With the further increase of molar ratio, the conversions of DPU increased slowly and the selectivity of MPC remained almost constant. One reason is that the increase of DMC amount is favorable to reaction (3) shifting to the right side. Another reason is that the reagent DPU has a little solubility in the reagent DMC, with the increase of molar ratio, the amount of DPU dissolved in DMC increases, which is more favorable to the reaction (3). But with further increase of DMC amount, concentration of catalyst NaOCH_3 decreases which lowers catalytic activity and increase of conversion of DPU. It might be that both reasons affected the change of conversions of DPU with the change of molar ratio of DMC to DPU. And the selectivity of MPC increased with the DMC amount, which indicated that the increase of DMC could decrease side-reactions.

Effect of catalyst NaOCH_3 concentration

The effect of catalyst NaOCH_3 concentration on the reaction between DMC and DPU was investigated in the range 0.3–1.6%, based on the total mass of reagents (see Fig. 2). A series of data showed that DPU conversion increased steadily with an increase of NaOCH_3 concentration up to 1%, and with further increase in NaOCH_3 concentration, DPU conversion showed little change. However, selectivity of MPC was almost constant at all times.

Effect of reaction time

The conversion of DPU and the selectivity of MPC *versus* reaction time using NaOCH_3 catalyst were also studied. As shown in Fig. 3, the conversion of DPU rapidly increased to 40.2% with increasing reaction time up to 1 h, which is almost equal to the amount of increase of conversion of DPU in the remaining 7 h. When the reaction time increased to 5 h, the conversion of DPU increased a little. The two reasons for this might be that reaction was easily carried out at the beginning, but with a decrease in the amount of DPU and an increase in the amount of MPC, the reaction velocity became slow, or that

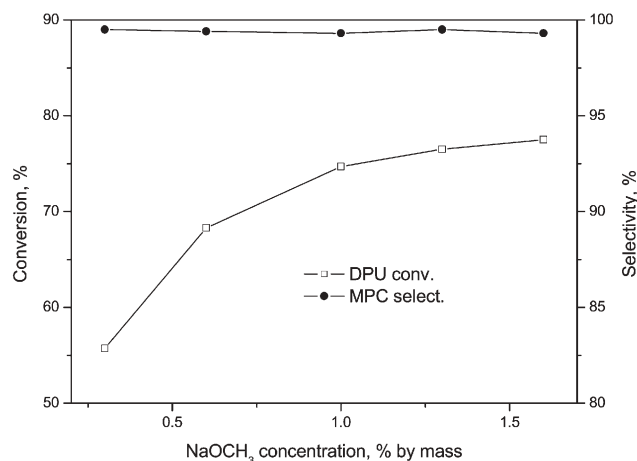


Fig. 2 Effect of catalyst NaOCH_3 concentration on the reaction between dimethyl carbonate and *N,N'*-diphenyl urea. Dimethyl carbonate (0.700 mol), *N,N'*-diphenyl urea (0.035 mol), reaction time (4 h).

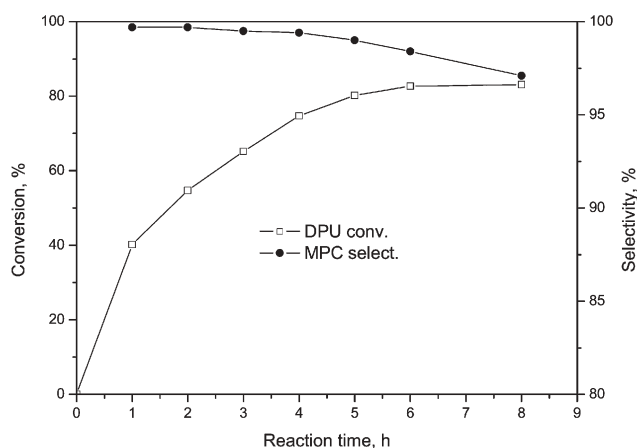
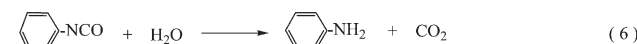
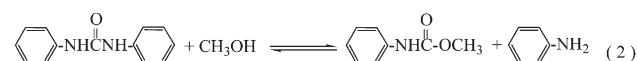


Fig. 3 Effect of reaction time on the reaction between dimethyl carbonate and *N,N'*-diphenyl urea. Dimethyl carbonate (0.700 mol), *N,N'*-diphenyl urea (0.035 mol), catalyst (1%, based on total mass of reactants).



Scheme 3 Possible side-reactions in the reaction of DMC and DPU.

NaOCH_3 catalytic activity was quickly reduced at the beginning of the reaction. The selectivity of MPC decreased slowly with increasing reaction time, and a small amount of by-products, such as methanol, aniline and *N*-methyl aniline, was detected. This might be caused by the decomposition of MPC (see Scheme 3),²¹ which causes side-reactions (2), (5) and (6).²²

Effect of number of additions of NaOCH_3 catalyst

Since it was possible that the catalytic activity of NaOCH_3 was quickly reduced at the beginning of the reaction (see Fig. 3), a series of experiments were carried out as follows: in one reaction, NaOCH_3 catalyst (1%, based on total mass of reactants) was put into a reactor at the beginning, and the same amount of NaOCH_3 catalyst was put into the reactor after a reaction time of 1 h, and in another reaction, the same amount of NaOCH_3 catalyst (1%, based on total mass of reactants) was put into the reactor every 40 min. Reaction time was 2 h. The results are shown in Fig. 4. If NaOCH_3 catalytic activity was quickly reduced at the beginning of the reaction, conversions of DPU would have increased significantly with the increase in the number of additions of NaOCH_3 . However, with the increase of number of additions of NaOCH_3 , the conversion of DPU increased very slowly, which was caused by the increase of NaOCH_3 concentration.

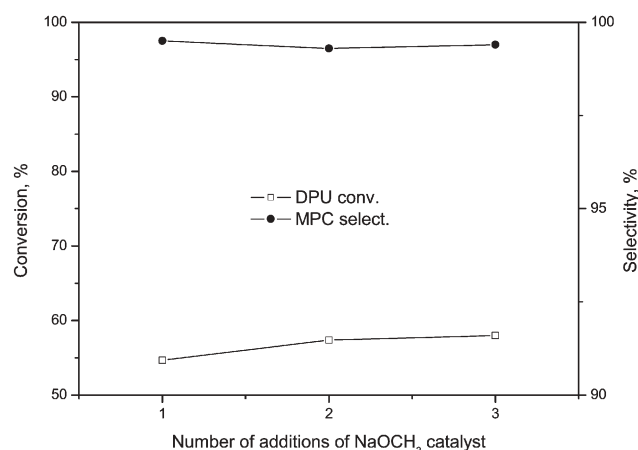


Fig. 4 Effect of number of additions of catalyst NaOCH₃ on the reaction between dimethyl carbonate and *N,N'*-diphenyl urea. Dimethyl carbonate (0.700 mol), *N,N'*-diphenyl urea (0.035 mol), reaction time (2 h).

Effect of reaction temperature

The effect of reaction temperature was also studied with NaOCH₃ catalyst. The results are shown in Fig. 5. Since a higher temperature was favorable to this endothermic reaction, the conversion of DPU increased with the increase of reaction temperature. When it further increased up to 110 °C, the conversion of DPU started to decrease, while the selectivity of MPC decreased continuously. It was suggested that high temperature wasn't always advantageous to the reaction (3) with NaOCH₃ catalyst, which might easily lead to NaOCH₃ catalyst losing its activity and accelerating the side-reactions.

Effect of various solvents

Since DMC has a poor solubility to DPU, the effect of various solvents, such as the basic ionic liquid [(CH₃)₂N]₂C=NH₂⁺ CH₃COO⁻, acetic acid, dimethylsulfoxide and toluene were investigated, and the results are presented in Table 2. From

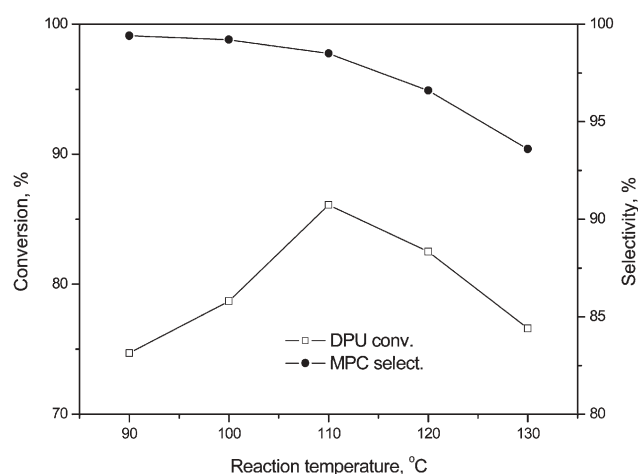


Fig. 5 Effect of reaction temperature on the reaction between dimethyl carbonate and *N,N'*-diphenyl urea. Dimethyl carbonate (0.700 mol), *N,N'*-diphenyl urea (0.035 mol), reaction time (4 h), catalyst (1%, based on total mass of reactants).

Table 2 Effect of various solvents on the reactions of dimethyl carbonate and *N,N'*-diphenyl urea^a

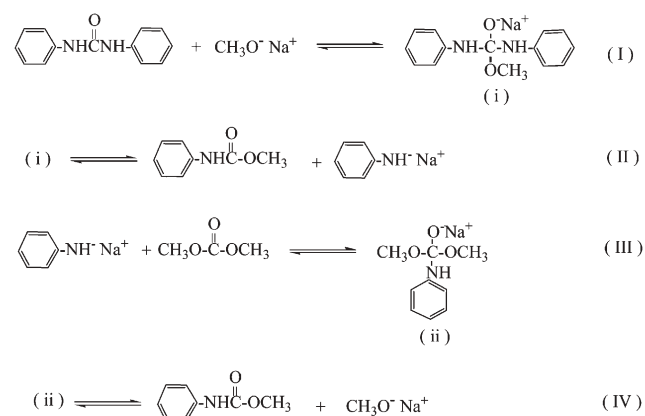
Entry	Solvent	DPU conversion (%)	MPC selectivity (%)
15	[(CH ₃) ₂ N] ₂ C=NH ₂ ⁺ CH ₃ COO ⁻	14.5	0.7
16	Acetic acid ^b	52.7	0.5
17	Dimethylsulfoxide	57.1	72.2
18	Toluene	65.1	86.4
5	Dimethyl carbonate	74.7	99.4

^a Dimethyl carbonate (0.140 mol), *N,N'*-diphenyl urea (0.035 mol), catalyst (1%, based on total mass of reactants), reaction time (4 h), solvents (50 ml), catalyst NaOCH₃, reaction temperature (90 °C).
^b Catalyst Bu₂SnO.

Table 2, strong polar solvents, such as the basic ionic liquid [(CH₃)₂N]₂C=NH₂⁺ CH₃COO⁻²³ and acetic acid,²⁴ which had good solubility for DPU, showed very poor performance (see entry 15 and 16). And weak polar solvents such as dimethylsulfoxide,²⁵ which also have good solubility for DPU, showed better performance than the above strong polar solvents, but showed poorer performance than non-polar solvents such as toluene, which have bad solubility for DPU. It suggests that the polarity of solvents had more effect on the reaction than their solubility for DPU. When weak polar DMC was used as reactant and solvent simultaneously, the optimum result was obtained.

Plausible reaction mechanism (Scheme 4)

Sodium methoxide, a strong alkaline catalyst, is well-known to catalyze the reaction of organic ester with alcohol *via* a nucleophilic substitution mechanism,²⁶ which indicates that the reaction between DMC and DPU with NaOCH₃ catalyst is likely to be a nucleophilic substitution reaction. Firstly, NaOCH₃ as nucleophile attacks DPU to produce transitional compound (i). Then transitional compound (i) produces MPC and $\text{C}_6\text{H}_5\text{-NH}^-\text{Na}^+$, and $\text{C}_6\text{H}_5\text{-NH}^-\text{Na}^+$ as the nucleophile attacks DMC to produce transitional compound (ii). Transitional compound (ii) produces MPC and CH₃O⁻Na⁺, and catalyst CH₃O⁻Na⁺, completing a cycle.



Scheme 4 Mechanism of reaction between DMC and DPU with NaOCH₃ catalyst.

Conclusions

The synthesis of methyl *N*-phenyl carbamate from dimethyl carbonate and *N,N'*-diphenyl urea has been investigated under the mild conditions of atmospheric pressure. The screening of various homogenous and heterogenous catalysts shows that sodium methoxide is an excellent catalyst, and can efficiently carry out the synthesis of methyl *N*-phenyl carbamate under atmospheric pressure. Under the experimental conditions of atmospheric pressure and 90 °C, the yield of MPC exceeds 80% with the low-toxicity homogenous catalyst NaOCH₃, which is more than 77%, the yield of MPC with high poisonous homogenous catalyst Bu₂SnO under the conditions of 3.4 MPa and reaction temperature 150 °C.¹⁹ Since reactants DMC and DPU can be synthesized from the greenhouse gas CO₂, the study on synthesizing MPC from DPU and DMC under mild conditions will accelerate CO₂ utilization and promote the synthesis of important chemicals derived from CO₂.

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Mixed-conducting oxygen permeable ceramic membranes for the carbon dioxide reforming of methane†

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Due to the high economic, environmental, and safety costs associated with pure oxygen, mixed-conducting oxygen-permeable ceramic membranes are being explored as an alternative oxygen source for hydrocarbon conversion reactors. This work reports a dramatic improvement in catalyst performance when an oxygen-permeable $\text{SrFeCo}_{0.5}\text{O}_x$ ceramic membrane is used in conjunction with a conventional powder Pt/ZrO_2 catalyst for the CO_2 reforming of CH_4 . Experiments comparing catalyst performance with up to 2% co-fed oxygen to catalyst performance with oxygen from the ceramic membrane demonstrated a conversion three times higher with the membrane than with any amount of co-fed oxygen. The results suggest that membrane oxygen is more beneficial for catalyst activity and stability than molecular gas-phase oxygen.

Introduction

With the increasing global demand for cleaner energy, fuel cell hydrogen and ultraclean gas-to-liquid (GTL) fuels are receiving a great deal of attention as alternative energy sources. Mixtures of H_2 and CO , known as synthesis gas, serve as the intermediate between hydrocarbon feedstocks and both hydrogen and GTL fuels. Synthesis gas can be produced by reforming reactions (steam, CO_2 , and autothermal) or partial oxidation reactions, all of which either require or can benefit from pure oxygen as a reactor feed. Among these, partial oxidation of hydrocarbons requires the greatest amount of oxygen and the energy-intensive air separation unit represents a significant fraction of both the operating and capital costs of such a synthesis gas facility.^{1–4}

Because of the high economic, environmental, and safety costs associated with pure oxygen, oxygen-permeable ceramic membranes have been explored as an alternative oxygen source for hydrocarbon conversion reactors.^{1–10} These non-porous ceramic materials allow the conduction of oxygen ions through the lattice of the solid material resulting in a 100% selectivity for oxygen regardless of the source gas. The mixed-conducting materials of interest for membrane reactor applications conduct electrons as well as oxygen ions, so they require only high temperature (typically 700 °C or higher) and an imposed oxygen potential gradient to transmit oxygen. Unlike solely ionic conducting materials such as those used in solid oxide fuel cells (SOFC's), mixed-conducting ceramics require no external circuitry. Like SOFC ceramics, they exhibit oxygen fluxes that generally increase with temperature above some

threshold temperature. A single membrane material was studied in this work: the non-perovskite $\text{SrFeCo}_{0.5}\text{O}_x$ mixed oxide referred to henceforth as SFC.

Mixed-conducting ceramics have typically been investigated for use with the partial oxidation of methane (POM) because of its appropriately high operating temperatures and the strongly reducing environment created by the POM reactions. The high reactor temperature allows effective membrane oxygen transport with no additional energy requirement, while the reducing POM environment provides a large oxygen potential gradient even with atmospheric pressure air on the oxygen source side. POM is a desirable commercial reaction because its stoichiometric $\text{H}_2 : \text{CO}$ ratio of 2 is ideal for Fischer–Tropsch synthesis of liquid hydrocarbons (F–T liquids) and, unlike steam and CO_2 reforming, it is an exothermic reaction. These incentives, coupled with the expense of the conventionally-produced oxygen required by POM, have led to its dominance of the membrane reactor field of inquiry.

Although many materials have been identified with measurable oxygen transport ability, only minimal success fabricating membranes that could satisfy the requirements of commercial POM applications has been achieved to date. With these circumstances in mind, it is proposed that lower oxygen fluxes that are currently easy to attain could benefit other reactions that do not require oxygen as a primary reactant yet meet the necessary operating condition requirements of oxygen-permeable ceramic membranes. The high operating temperature and reducing reaction environment of CO_2 reforming satisfy these constraints. Furthermore, some studies of oxygen-permeable ceramic membranes have shown that including CO_2 on the reaction side or diluting the methane with small amounts of inert gas or oxygen generates a less reducing environment that can prolong membrane lifetime.^{11,12} Thus, membranes that might not be capable of withstanding the severe reducing conditions of the POM reaction could still be acceptable candidates for the CO_2 reforming reaction.

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In addition to the possible benefits to catalyst performance, membrane-supplied oxygen incorporates several significant environmental advantages over gas-phase oxygen supplies for synthesis gas operations: (1) the aforementioned substantial reduction in process energy consumption; (2) safer oxygen (no hotspots or flammability concerns);^{3,8} (3) inherently distributed oxygen introduction which can produce a more uniform and predictable reactor temperature profile and increase the selectivity of oxidation reactions;⁹ and (4) minimized occurrence of homogeneous thermochemical reactions involving O₂ which can produce soot-forming precursors.¹³ Furthermore, if the resulting synthesis gas is used to produce F–T liquids (or oxygenated hydrocarbons *via* hydroformylation), CO₂ reforming itself fits under the green chemistry heading through its utilization of two greenhouse gases as a feedstock.

Experimental

Reaction and flux tests were performed in the two-sided concentric quartz tube membrane reactor depicted in Fig. 1. The reactor was sealed at high temperatures using gold ring seals between the outer quartz tubes and the membrane surfaces and an external pneumatic press to maintain constant compressive force. The gold seals soften as the reactor system approaches its 800 °C reaction temperature and the seal is fully formed within 30 min at 800 °C. In all cases, the leak around the gold rings during operation was estimated as less than 0.2% of the reactor feed flowrate based on N₂ in the reactor effluent. However, it is important to note that leakage during reactor heat-up is unavoidable before the gold seals soften sufficiently near 800 °C. The air content of the effluent during heat-up averages approximately 5% of the reactor's pretreatment argon feed.

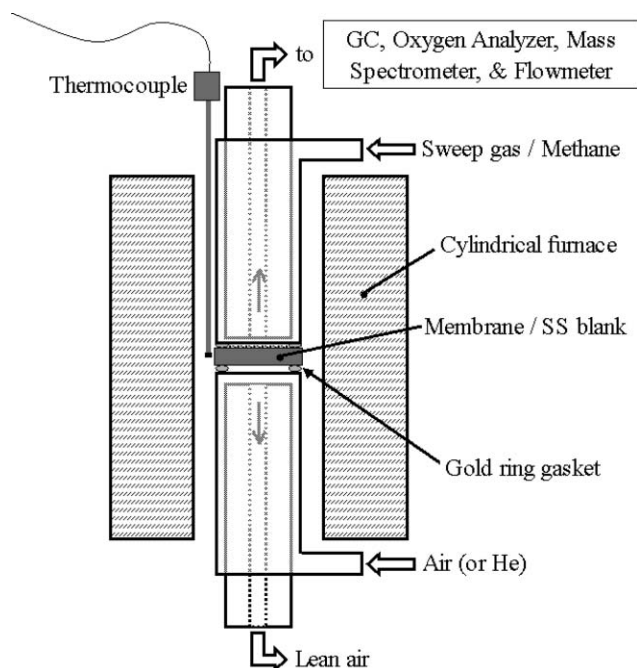


Fig. 1 Schematic of membrane reactor system.

As shown in Fig. 1, reactants flow into the top part of the reactor through the annular space between the two concentric quartz tubes, and effluent leaves the reactor through the inner tube after passing through the catalyst layer on the membrane's top surface. The inner tube has a very thick wall and is positioned as close to the membrane surface as possible (within 1 mm) to maximize contact of the gas stream with the catalyst layer.

In addition to the SFC ceramic membranes, a stainless steel "blank" membrane was coated with an inert boron nitride (BN₃) paint to prevent reaction on the steel surface. This blank membrane was used to examine the effect of co-fed molecular oxygen on catalyst performance and to provide baseline data for the ceramic membrane experiments. The SFC ceramic membranes were pressed at 5000 lb force for 3 min in a uniaxial press and then sintered at 1180 °C in flowing air for 10 h. The SFC powder, which was obtained from Praxair Specialty Ceramics, was passed through a 60-mesh sieve and coated with 1 wt% ethylcellulose binder prior to pressing. The ethylcellulose binder burns off entirely between 350 and 450 °C and does not affect the density of the finished SFC membranes, which is consistently about 94% of the theoretical density.

In all reaction tests, the CH₄ : CO₂ ratio was 1 : 1 and the CH₄ and CO₂ comprised 80% of the feed. During the SFC membrane experiments, the remaining 20% of the feed was pure argon while specific percentages of O₂ in Ar were used for experiments with the stainless steel blank membrane. In addition to true CO₂ reforming (*i.e.*, no oxygen), the co-fed oxygen amounts tested with the blank were 0.2%, 1%, and 2% O₂ of the total volumetric feed flowrate. The feed flowrate corresponded to a space velocity of 150 L h⁻¹ g_{cat}⁻¹ in all tests. Atmospheric pressure air was used as the oxygen supply at the bottom membrane surface and the SFC membranes were tested for cracks or porosity at the reaction temperature of 800 °C using slightly pressurized He. No quantifiable He penetration was detected at 800 °C before or after reaction.

Catalyst from the same batch of 0.5 wt% Pt/ZrO₂ catalyst was used in every test. This catalyst was chosen because it has been studied previously in conventional quartz tube PFR reactors^{14,15} and has shown relatively quick deactivation. The catalyst was prepared by depositing Pt on commercially available ZrO₂ support material using the incipient wetness impregnation technique with an aqueous solution of H₂PtCl₆·6H₂O. Prior to deposition, the substrate was calcined at 800 °C; after deposition it was dried overnight at 120 °C and then calcined at 400 °C for 2 h in flowing air. BET single point surface area analysis indicated a support surface area of 29 m² g⁻¹, and Pt dispersion was determined to be 21% by TEM particle size analysis. With two exceptions (described in the "Catalyst pre-treatment effects" section), no catalyst reduction step was performed.

For all membrane reactor experiments, 10 mg of powder Pt/ZrO₂ catalyst was spread in a thin layer (~1 mm) across the entire portion of the membrane surface (SFC or blank) that was within the reactor's outer quartz tube. This ensured good proximity between the membrane and the entire catalyst bed and minimized transport resistance within the catalyst layer on both the SFC membrane and the blank. Fig. 2 provides a

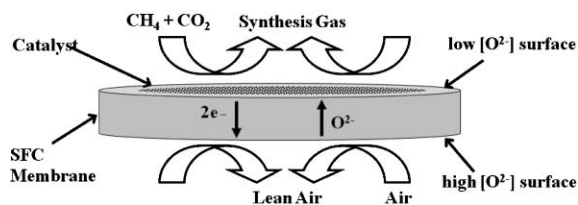


Fig. 2 Schematic of SFC membrane under reaction conditions.

schematic depiction of the SFC membrane under operating conditions.

The reactor was heated to 800 °C with an argon-only feed and then held at this temperature while the gold seals formed and the membrane equilibrated under the {air : argon} oxygen potential gradient. To ensure comparable pre-reaction conditions for the catalyst, this 2 h hold at 800 °C was also imposed during all experiments with the stainless steel blank membrane. Steady state oxygen production from the SFC membranes under these conditions was assessed using mass spectrometer data and found to be 0.008 mL min⁻¹ O₂ for the membranes used in this study. This corresponds to an O₂ flux of 0.005 sccm cm⁻² at 800 °C.

The reactor effluent composition was quantified using an SRI 8100 gas chromatograph with FID for carbon-containing compounds and TCD for H₂ and N₂. The effluent was also monitored continuously with a Balzers OmniStar mass spectrometer both to provide important additional information including pre-reaction oxygen flux data and to confirm and interpolate trends observed in the GC data. In addition, effluent flowrate and oxygen concentration were monitored continuously using an Agilent ADM2000 flowmeter and an AMI Model 60 oxygen sensor. Effluent water was calculated from a hydrogen atom balance (trends were confirmed by mass spectrometer results), membrane oxygen flux was calculated from an oxygen atom balance, and carbon deposition was determined from a carbon atom balance.

Results and discussion

Catalyst pre-treatment effects

The relatively high oxygen atmosphere experienced by the catalyst during reactor heat-up because of seal leakage undermines the effectiveness of any low temperature catalyst reduction strategy with the membrane reactor. Additionally, catalyst reduction at or near the reaction temperature is not an effective alternative on the SFC membrane because the membrane surface itself reduces readily on exposure to H₂ and evolves oxygen in the absence of H₂. Because catalyst pre-treatment options are limited in the membrane reactor, a conventional quartz tube PFR was used to provide relative catalyst activity data for a selection of catalyst pre-treatment and reactor feed options.

These PFR pre-treatment effect tests were performed for 12 h at 800 °C using a catalyst bed that was diluted 40 : 1 by mass with SiO₂ powder to minimize thermal effects in the bed. With no co-fed O₂, the initial CH₄ conversion rate of a reduced catalyst was more than twice the initial rate of the unreduced catalyst. However, as shown in Table 1, this activity

Table 1 Plug flow reactor catalyst pre-treatment test results. Reaction conditions: $T = 800$ °C, 1 : 1 ratio of CH₄ and CO₂, space velocity of 150 L h⁻¹ g_{cat}⁻¹, 0.5 wt% Pt/ZrO₂ catalyst, 12 h time-on-stream

Catalyst pre-treatment			Final CH ₄ conversion/ mmol min ⁻¹ g _{cat} ⁻¹
Heating environment	Reduction	Co-fed oxygen	
Inert	H ₂ at 400 °C	None	9.0
Inert	None	None	6.7
Inert	None	1%	8.3
1% O ₂ in Ar	None	1%	1.9

discrepancy had diminished significantly after 12 h of CO₂ reforming and the reduced catalyst's activity was still declining, approaching the activity of the unreduced catalyst.

Table 1 also presents the baseline effect of co-fed O₂ on CH₄ conversion using 1% O₂ as a first-pass approximation of the oxygen supplied by an SFC membrane under the applicable reaction conditions. With unreduced catalyst, CH₄ conversion increased when co-fed oxygen was included in the reactor feed although the deactivation trends with and without co-fed O₂ were parallel. For the final PFR pre-treatment test, the catalyst bed was heated to the reaction temperature in 1% O₂ in Ar rather than pure Ar to simulate the leak during membrane reactor heat-up, before the gold softened and sealed; CO₂ reforming with 1% co-fed O₂ followed. These results confirm that heating in even a small amount of oxygen has a negative effect on the activity of this catalyst. The unreduced catalyst tests all exhibited stable CH₄ conversion after 6–7 h of reaction time while the lone reduced catalyst test exhibited declining catalyst activity through the end of the 12 h experiment. These trends confirm the relevance of the final unreduced catalyst activity data from these tests and also imply that the benefits of a preliminary catalyst reduction step provides only a short-term benefit with this Pt/ZrO₂ catalyst.

One last investigation on the effect of catalyst pretreatment on its performance in the membrane reactor was performed. Catalyst was pre-reduced in the PFR system before a 10 mg sample was tested in the membrane reactor on the stainless steel blank with 1% co-fed O₂. The pre-reduction step involved heating the catalyst in the PFR to 400 °C under flowing H₂, holding for 1 h, then cooling to room temperature in Ar. The pre-reduction had no effect on the initial or final catalyst activity in the membrane reactor, so no other pre-reaction catalyst reduction steps were performed in this study. However, *in situ* reduction appears to occur during the onset of CO₂ reforming in the membrane reactor to an extent that depends on the amount of co-fed O₂.

Membrane reactor results

In the membrane reactor with the stainless steel blank membrane the first-pass estimate of 1% co-fed O₂ exhibited a similar relationship to the no oxygen case as in the PFR tests. The initial CH₄ conversion was higher with 1% O₂ than without O₂, but the deactivation trend was the same in both cases and minimal changes in conversion were observed after 7 h of reaction. As shown in Fig. 3, a dramatic difference in both rate and extent of deactivation was observed with the same catalyst loading on the SFC membrane, and these results

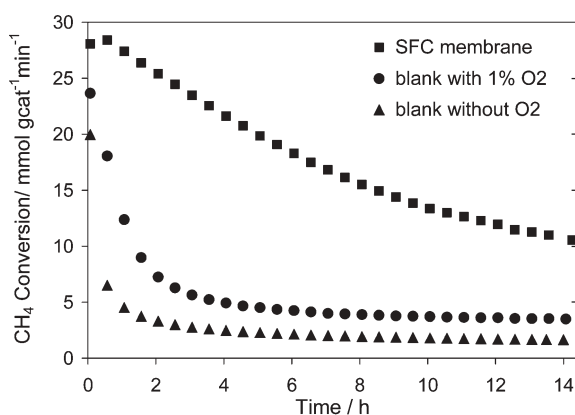


Fig. 3 Membrane reactor test results for the SFC membrane and the stainless steel blank (with and without co-fed O₂). Reaction conditions: $T = 800\text{ }^{\circ}\text{C}$, 1 : 1 ratio of CH₄ and CO₂, and a space velocity of $150\text{ L h}^{-1}\text{ g}_{\text{cat}}^{-1}$ with 0.5 wt% Pt/ZrO₂ catalyst.

imply that oxygen supplied *via* a ceramic membrane both enhances and preserves the activity of the Pt/ZrO₂ catalyst. Similar catalyst preservation results have been reported for a Ni/ γ -Al₂O₃ catalyst in a POM membrane reactor system.⁴

Other co-fed O₂ levels of interest were identified from estimates of membrane oxygen production during the reaction depicted in Fig. 3. These oxygen production values were calculated from GC data and indicate that membrane oxygen production stabilized at a value of $\sim 0.02\text{ mL min}^{-1}$ (gas-phase O₂ equivalent) after 6 h of exposure to the reaction conditions. This amount of O₂ would represent 0.08% of the feed if it were co-fed, and it is also 2.5 times the steady state oxygen production observed prior to reaction under the {air : argon} oxygen potential gradient. Table 2 provides four additional membrane oxygen production estimates at times spanning the reaction period, with the second row presenting the equivalent feed percentage if the membrane oxygen had been co-fed in the gas phase and the third row displaying the multiple of the pre-reaction membrane oxygen production represented by the oxygen produced under reaction conditions.

The first two values in the third row of Table 2 do not represent true oxygen flux through the membrane but rather a “dumping” of oxygen from the membrane as it equilibrates with its new environment. Because the environment over the top surface of the membrane is changed from argon to a much more reducing syngas-containing environment, membrane oxygen production is initially high. It then drops quickly as the membrane begins to equilibrate with the reaction environment. Since the amount of oxygen produced by the membrane was not constant throughout the test period, two additional levels of co-fed O₂ were selected to test with the stainless steel blank: 2% co-fed O₂ to reproduce the high initial oxygen production and 0.2% to represent the low steady state production.

Table 2 Membrane oxygen production estimates during reaction

Time on stream/h	0	2	7	14
Equivalent co-fed O ₂ (%)	2.0	0.47	0.07	0.06
Multiple of {air : argon} flux	64	15	2.1	1.9

Table 3 Membrane reactor test results for all tests. CH₄ conversion units = $\text{mmol min}^{-1}\text{ g}_{\text{cat}}^{-1}$. Reaction conditions: $T = 800\text{ }^{\circ}\text{C}$, 1 : 1 ratio of CH₄ and CO₂, and a space velocity of $150\text{ L h}^{-1}\text{ g}_{\text{cat}}^{-1}$ with 0.5 wt% Pt/ZrO₂ catalyst

Oxygen addition	Initial CH ₄ conversion	CH ₄ conversion after 14 h
Membrane	28.0	10.3
2% Co-fed	13.4	2.6
1% Co-fed	23.5	3.4
0.2%	25.4	2.9
None	19.8	1.6

These final two tests were performed to determine whether catalyst activity enhancement or preservation effects could be achieved with co-fed oxygen. However, they exhibited the same deactivation trend as the previous tests using the stainless steel blank. Table 3 presents the initial and final CH₄ conversion values for all of the membrane reactor tests described in this work. Although the 0.2% co-fed O₂ experiment showed an initially higher CH₄ conversion than the 1% O₂ test, this was the only point at which its activity exceeded that of the 1% O₂ case. Surprisingly, the 2% O₂ test showed the lowest initial activity of any of the tests, which removed the possibility that an initial release of gas-phase oxygen from the SFC material was responsible for the high catalyst activity with the SFC membrane. By the second GC injection (*i.e.*, 35 min of reaction time) CH₄ conversion with 2% co-fed O₂ had exceeded that of the no oxygen case, but it remained significantly below the lower co-fed O₂ cases throughout the test period. These observations are consistent with the possibility that *in situ* catalyst reduction can be hampered by co-fed O₂.

The results of this study suggest that membrane oxygen is more reactive than co-fed molecular oxygen. It should be noted that CH₄ conversion on the membrane without catalyst was less than 1% at all times. Thus, the combination of catalyst and SFC membrane is needed to produce the observed benefit from membrane oxygen; the SFC surface alone has minimal activity with the CO₂ reforming feed gases. The stainless steel blank without catalyst also produced conversions less than 1%, confirming that gas-phase reactions are negligible under these operating conditions.

While the exact role of oxygen in the reaction mechanism has not yet been determined, several possibilities are being explored. The first is that oxygen ions recombine to form molecular oxygen after they diffuse through the membrane material and then desorb from the membrane surface before reacting. This molecular oxygen would be introduced at the bottom of the catalyst bed and would thus compete less with CH₄ for active Pt sites than in the co-fed O₂ cases. Although this scenario is consistent with the increased activity with the ceramic membrane, it is unlikely that oxygen ions on the surface of the membrane would preferentially recombine to form molecular oxygen and desorb from the surface before reacting with the readily available hydrogen in the highly reducing reaction environment.

An alternate explanation is that the oxygen ions on the surface of the membrane react directly with hydrogen produced by methane decomposition. Membrane oxygen is not expected to react directly with CH₄ in significant quantities

since, as previously stated, CH₄ conversion in the absence of catalyst is negligible. However, water produced by the oxidation of hydrogen at the membrane surface could increase CH₄ conversion by participating in steam reforming as it passes out through the catalyst layer.

The final explanation is that oxygen could migrate from the membrane surface to the catalyst *via* the oxygen ion conducting ZrO₂ support. The oxygen species on the catalyst could then participate in the reactions. While these results do not differentiate between oxygen species spillover onto the Pt/ZrO₂ catalyst or oxygen species reacting on the membrane surface, they do confirm that SFC alone does not activate methane and demonstrate that the catalyst and the membrane work in concert to achieve the observed improvement.

Conclusions

Dense ceramic SrFeCo_{0.5}O_x membranes have been investigated as a means of adding small amounts of distributed oxygen to the CO₂ reforming of CH₄ reaction in a planar membrane reactor. These membrane reactor experiments revealed two distinct phenomena. The first phenomenon, the effect of small amounts of co-fed O₂ on unreduced catalyst activity, should apply to any conventional catalytic reactor system. As observed from the set of four co-fed O₂ levels with the stainless steel blank (including the no oxygen case), the effect of gas-phase oxygen on the activity of the unreduced Pt/ZrO₂ catalyst depends on the amount of oxygen supplied. As expected, co-fed O₂ increases CH₄ conversion over the no oxygen scenario, but above some optimum concentration it also appears to hinder *in situ* reduction and thereby reduce catalyst performance. For this Pt/ZrO₂ catalyst in the unreduced condition, the optimal co-fed oxygen amount falls somewhere between 0.2 and 1%.

The second phenomenon is the dramatic effect of the SFC membrane on the Pt/ZrO₂ catalyst's activity. While this effect requires further study to elucidate the specific role of membrane oxygen, the results presented herein indicate the

substantial promise of this novel application for oxygen-permeable ceramic membranes. The combination of the enhanced catalyst performance with the significant environmental advantages of membrane oxygen encourages further exploration of ceramic membrane reactors for CO₂ reforming.

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Catalytic performance of Rh/SiO₂ in glycerol reaction under hydrogen†

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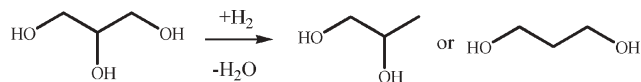
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Glycerol is a main byproduct in the biodiesel production process, and the effective utilization of glycerol can contribute to biodiesel promotion. One of the possible methods is the catalytic conversion of glycerol to valuable chemicals, and this can also agree with the concept of green chemistry in terms of the utilization of renewable resources. Catalytic performance of supported metal catalysts (metal: Rh, Ru, Pt, Pd support: active carbon, SiO₂, Al₂O₃) was evaluated in the reaction of glycerol aqueous solution under H₂. It is found that Rh/SiO₂ exhibited higher activity and higher selectivity to hydrogenolysis products such as propanediols and propanols than Ru/C catalysts at low temperature (393 K). We also investigated the additive effect of ion-exchange resin (Amberlyst). Regarding the reaction route in the reaction of glycerol, it is suggested that the consecutive hydrogenolysis of propanediols to propanols on Rh/SiO₂ can proceed *via* 1,2-propanediol, while it can proceed on Ru/C *via* 1,3-propanediol.

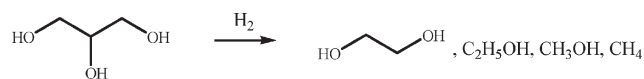
1. Introduction

Catalytic conversion of renewable feedstock and chemicals becomes more and more important in terms of green chemistry. Such conversion to hydrogen can promote the utilization of renewable energy sources,^{1–5} and conversion to petrochemicals can facilitate the replacement of petroleum by renewable resources.^{6–8} It has been proposed that commodity chemicals derived from fossil resources at present will be producible in future biorefineries from renewable resources, such as plant-derived sugar and other compounds.⁹ Glycerol is regarded as one of the building blocks in the biorefinery feedstock.⁹ It is also a main byproduct in biodiesel production by transesterification of vegetable oils.¹⁰ Attention has been recently paid to the conversion of glycerol to petrochemicals, such as propanediols¹¹ and acrolein.^{12,13} Various catalysts have been attempted for the reaction of glycerol to propanediols. The reaction formula is described below. The reaction corresponds to the substitution of the OH group with H₂, which is called here hydrogenolysis.



Using CuO/ZnO catalysts along with a sulfided Ru catalyst, the reaction of glycerol has been carried out at 15 MPa and 513–543 K.^{14,15} Raney Cu,^{16,17} Cu/C¹⁸ and Cu–Pt and Cu–Ru bimetallic catalysts¹⁹ at 1.0–4.0 MPa and 493–513 K have also been investigated. The catalysts containing Co, Cu, Mn, Mo, and an inorganic polyacid were applied at the reaction conditions of 25 MPa and 523 K.²⁰ In the case of homogeneous catalysts containing W and group VIII transition metals, the

reaction conditions were 32 MPa and 473 K.²¹ Hydrogen pressures around 6–10 MPa and reaction temperatures of 453–513 K have usually been applied when supported metal catalysts were used.^{22–25} In addition, it has also been reported recently that copper chromite was effective for the hydrogenolysis of glycerol to 1,2-propanediol at 1.4 MPa and 473 K,²⁶ which corresponded to mild reaction conditions in terms of hydrogen pressure. On the other hand, they also demonstrated that the copper chromite catalyst exhibited lower activity below 453 K. It has been known that Ru/C showed rather high activity in the glycerol reaction in the presence of H₂, even at lower reaction temperature compared to the copper chromite catalysts.²⁷ One of the weak points of Ru/C is that the degradation reaction as well as the hydrogenolysis can also be catalyzed in the glycerol reaction. The degradation reaction can be due to the cracking of the carbon–carbon bond. The reaction formula is shown below.



Since glycerol is regarded as a renewable source of C₃ compounds, the aim of this study is catalyst development for the hydrogenolysis reaction. Therefore, the degradation reaction is undesirable because it causes the decrease of the selectivity to the hydrogenolysis products. In this article, it is reported that Rh/SiO₂ gave a higher yield of hydrogenolysis products and higher selectivity than Ru/C in the glycerol reaction in the presence of H₂. In addition, the additive effect of Amberlyst to Rh/SiO₂ was compared to the case of Ru/C. We also discuss the formation routes of hydrogenolysis and degradation products based on the catalytic performance when the products in the glycerol reaction were used as reactants.

2. Experimental

Active carbon supported noble metal catalysts (Rh/C (BET surface area 557 m² g^{−1}), Ru/C (485 m² g^{−1}), Pt/C (478 m² g^{−1}))

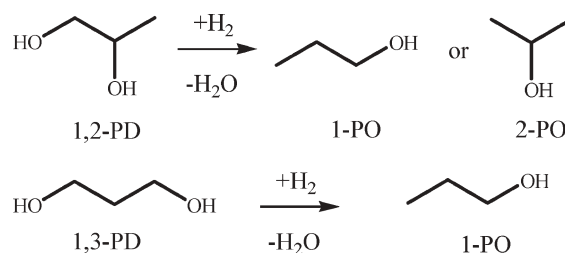
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and Pd/C (348 m² g⁻¹) were purchased from Wako Pure Chemical Industries; the loading amount of metal on these catalysts was 5 wt%. Noble-metal catalysts supported on Al₂O₃ and SiO₂ were prepared by impregnating the support materials with an aqueous solution of metal precursor such as RhCl₃·3H₂O, RuCl₃·5H₂O, H₂PtCl₆·6H₂O, and Pd(NO₃)₂. These chemicals were supplied from Soekawa Chemical Co., Ltd. The loading amount of metal was 4 wt%. After the impregnation procedure and drying at 383 K for 12 h, they were calcined in air at 773 K for 3 h. The SiO₂ (G-6) (BET surface area 535 m² g⁻¹) was supplied from Fuji Silysia Chemical Ltd. In addition, another SiO₂ (380) (380 m² g⁻¹, Aerosil) was also used as a support material. The Al₂O₃ (JRC-ALO-1, 110 m² g⁻¹) was supplied from Japan Reference Catalyst. The cation-exchange resin Amberlyst 15 (4.7 eq. per kg-resin dried, particle size 0.4–1.2 mm, highest operating temperature 393 K; MP Biomedical) was used as a solid acid catalyst. All catalysts were used in powdery form with granule size of <100 mesh.

The reaction of glycerol under an H₂ atmosphere was carried out in a 70 ml stainless steel autoclave; a 20 ml aqueous solution of glycerol was used. The reaction was conducted under the following standard conditions: 393 K reaction temperature, 8.0 MPa initial hydrogen pressure, 10 h reaction time, 20 mass% glycerol aqueous solution, 150 mg supported metal catalyst with or without 300 mg Amberlyst. Catalysts were reduced in the reactor at 393 K for 1 h under 1.0 MPa H₂ pressure just before the activity test. Reaction conditions were changed for investigation of the reaction condition effects. Details of the reaction conditions are described for each result. In addition, we also carried out the reaction test of 1,3-propanediol (1,3-PD) and 1,2-propanediol (1,2-PD) in order to discuss the reaction routes of glycerol hydrogenolysis and degradation. The concentration of these reactants in the aqueous solution was 2 mass%.

In all the experiments, the aqueous solution of the reactant, the catalyst powder and a spinner were put into the autoclave; then the reactor was purged with H₂ (99.99%; Takachiho Trading Co., Ltd.). After purging, the reactor was heated to the reaction temperature, and the H₂ pressure was increased. The temperature was monitored using a thermocouple that was inserted in the autoclave and connected to the thermo-controller. Although the hydrogen pressure decreased with reaction time, the decreased hydrogen pressure was 1/10 of the initial pressure at most. After the reaction, the gas-phase products were collected in a gasbag and the liquid phase products were separated from the catalyst powder through filtration. These products were analyzed using a gas chromatograph (Shimadzu GC-8A) equipped with an FID. A Stabilwax capillary column (diameter 0.53 mm Ø, 60 m) was used for the separation. Products were also identified using GC-MS (QP5050, Shimadzu). As the products of the hydrogenolysis reaction, 1,2-PD, 1,3-PD, 1-propanol (1-PO) and 2-propanol (2-PO) were observed. As the products of the degradation reaction, ethylene glycol (EG), C₂H₅OH, CH₃OH and CH₄ were detected. Propanols were formed by the hydrogenolysis reaction of propanediols as below.



Conversion of the reactants in all reaction tests were calculated based on the following equation.

Conversion of reactant (%) =

$$\frac{(\text{Sum of C - based mol of all products})}{\text{Sum of C - based mol of reactant and all products}}$$

The conversion can also be defined as (reactant before – reactant afterwards)/(reactant before) × 100. In the present case, it is necessary to determine the conversion and the selectivity even when the conversion level is very low. In addition, since all the products in the reaction tests were identified, each value of the product amount was utilized, and the equation above was applied for the estimation of the conversion. It should be noted that the conversions calculated by this method and the method based on the latter definition agree well when the conversion was beyond around 5%. The mass balance was also confirmed in each result and the difference in mass balance was always in the range of the experimental error.

Selectivity of the products in all reaction tests were also calculated based on the following equation.

$$\text{Selectivity (\%)} = \frac{(\text{C - based mol of the product})}{(\text{Sum of C - based mol of all products})}$$

As a result of the reaction tests, ethylene glycol, ethanol, methanol and methane were detected as degradation products. The degradation of glycerol can give the C₂ and C₁ compounds in some cases. However, it can give only the C₁ compounds in other cases. Since the degradation can proceed in various ways, it is difficult to determine the formation route of each degradation product precisely. Therefore, we simply assume that each degradation product is formed from glycerol, *i.e.* C₃ → 3/2C₂ and C₃ → 3C₁, in the determination of the selectivity. The yield is calculated from conversion (%) × selectivity (%) / 100. The details are referred to in our previous report.⁷ The surface areas of the supported metal catalysts were measured using the BET method (N₂ adsorption) with a Gemini (Micromeritics) apparatus. Temperature-programmed reduction (TPR) was carried out in a fix bed reactor equipped with a thermal conductivity detector using 5% H₂ diluted with Ar (30 ml min⁻¹). The amount of catalyst was 0.05 g, and the temperature was increased from room temperature to 1123 K at a heating rate of 10 K min⁻¹. Transmission electron microscope (TEM) images were taken for determination of the particle size using equipment (JEM 2010; JEOL) operated at 200 kV. After reduction with H₂, the samples were stored under vacuum until measurements were made. Supersonic waves dispersed the samples in 2-propanol, and dispersed

samples were placed on Cu grids under air atmosphere. Average particle size was calculated by $\Sigma n_i d_i^3 / \Sigma n_i d_i^2$ (d_i : particle size, n_i : number of particles with d_i).²⁸

3. Results and discussion

The results of the glycerol reaction over various supported noble metal catalysts at 393 K are described in Fig. 1. All the supported Pd and Pt catalysts exhibited very low activity in the glycerol reaction, and all the Al₂O₃ supported metal catalysts showed low activity. In the case of Ru catalysts, active carbon is a much more suitable support than SiO₂ and Al₂O₃. This is also supported by the previous reports that Ru/C is an effective catalyst for glycerol hydrogenolysis.^{7,17,23–25,27} However, Ru/SiO₂ showed much lower activity than Ru/C. It should be noted that both Rh/SiO₂ of 380 and G-6 and Ru/C exhibited high activities for the glycerol reaction; in particular, Rh/SiO₂ (G-6) gave a much higher yield of hydrogenolysis products than other catalysts, and the selectivity to hydrogenolysis products on Rh/SiO₂ (G-6) was higher than that on Ru/C. The product distribution is shown in detail later. Furthermore, the activity of Rh/Al₂O₃ was as low as that of other Al₂O₃ supported metal catalysts. In order to discuss the low activities of Al₂O₃ supported catalysts, the TPR profiles of SiO₂ and Al₂O₃ supported catalysts were compared, as shown in Fig. 2. The H₂ consumption peak of Rh/SiO₂ was clearly observed at 350 K, and, in contrast, that of Rh/Al₂O₃ was observed in the wide temperature range beyond 350 K. Here, we have to pay attention to the H₂ consumption behavior below the reduction pretreatment temperature and the reaction temperature of the glycerol reaction (393 K). The reduction degree below 393 K on the basis of $\text{Rh}^{3+} + 3/2\text{H}_2 \rightarrow \text{Rh}^0 + 3\text{H}^+$ is estimated to be 0.81 and 0.15 on Rh/SiO₂ and Rh/Al₂O₃, respectively. This suggests that the Rh species of Rh/SiO₂ can be reduced during the reduction pretreatment

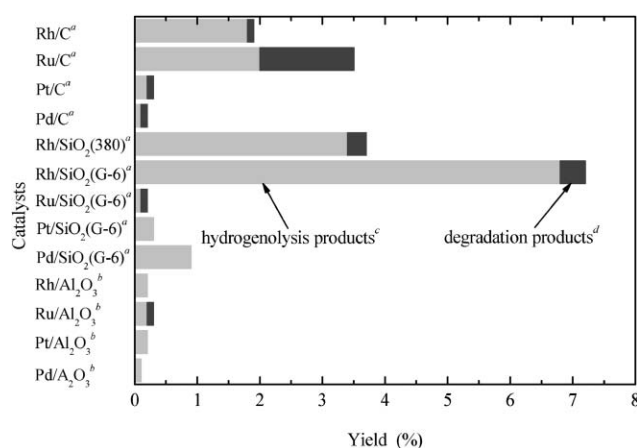


Fig. 1 Results of the glycerol reaction over supported noble metal catalysts at 393 K. Reaction conditions: 20 mass% glycerol aqueous solution 20 ml, 8.0 MPa initial H₂ pressure, 10 h reaction time, 150 mg metal catalyst. ^aCatalysts were reduced *in situ* at 393 K and 1.0 MPa H₂. ^bCatalysts were pre-reduced in the fixed bed reactor at 573 K and 0.1 MPa H₂, and then the samples were transferred to the autoclave under air atmosphere. ^c1,2-propanediol + 1,3-propanediol + 1-propanol + 2-propanol. ^dEthylene glycol + ethanol + methanol + methane.

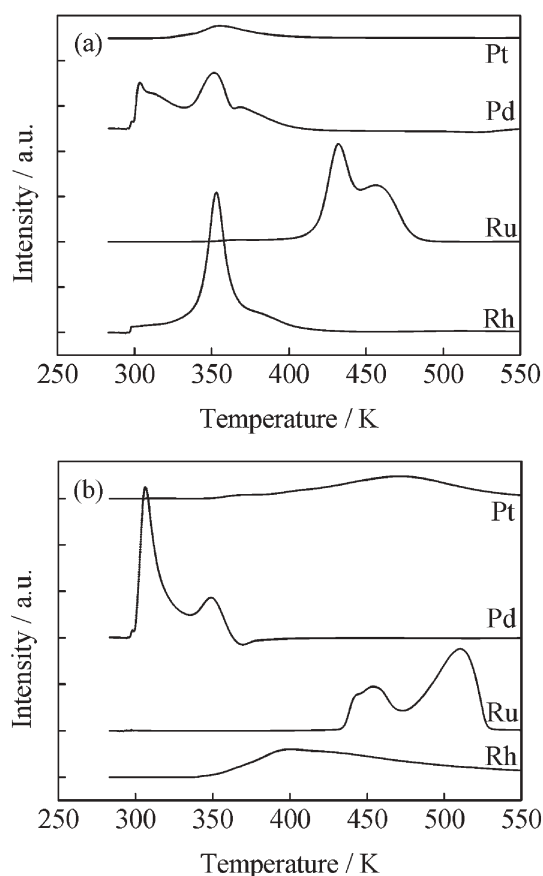


Fig. 2 Temperature-programmed reduction profiles of supported noble metal catalysts. (a) SiO₂ (G-6), (b) Al₂O₃.

and the active metallic species is abundant, however the Rh species of Rh/Al₂O₃ cannot be reduced sufficiently. From the results, the reducibility of Rh species on the support materials can influence the activity of the glycerol reaction strongly. However, the reduction of the Ru species on SiO₂ and Al₂O₃ proceeded above the reduction pretreatment and reaction temperature (393 K). This result suggests that the Ru species is not reduced and the active Ru metal species is not formed, and this can explain the low activity of Ru/SiO₂ and Ru/Al₂O₃. In the case of Pd/SiO₂ and Pd/Al₂O₃, the H₂ consumption peak appeared in the range between room temperature and 400 K. The reduction degree on the basis of $\text{Pd}^{2+} + \text{H}_2 \rightarrow \text{Pd}^0 + 2\text{H}^+$ below 393 K was estimated to be 1.07 and 1.13 on Pd/SiO₂ and Pd/Al₂O₃, respectively. The two peaks observed on the TPR profiles of the Pd catalysts can be assigned to the reduction of Pd species with weak and strong interaction with the support surface. In contrast, the peak intensity on Pt/SiO₂ and Pt/Al₂O₃ was very small. It is suggested that the Pt species on Pt/SiO₂ and Pt/Al₂O₃ are reduced, even at room temperature during the purge of the TPR cell with H₂ containing gas. These results suggest that a major part of Pt and Pd can be reduced under the conditions of the glycerol reaction. On the other hand, all the SiO₂ and Al₂O₃ supported Pt and Pd catalysts showed very low activity in the glycerol reaction. This indicates that metallic Pt and Pd species is not so active. Regarding the active carbon supported catalysts, the metal species on all the catalysts can be reduced during the glycerol

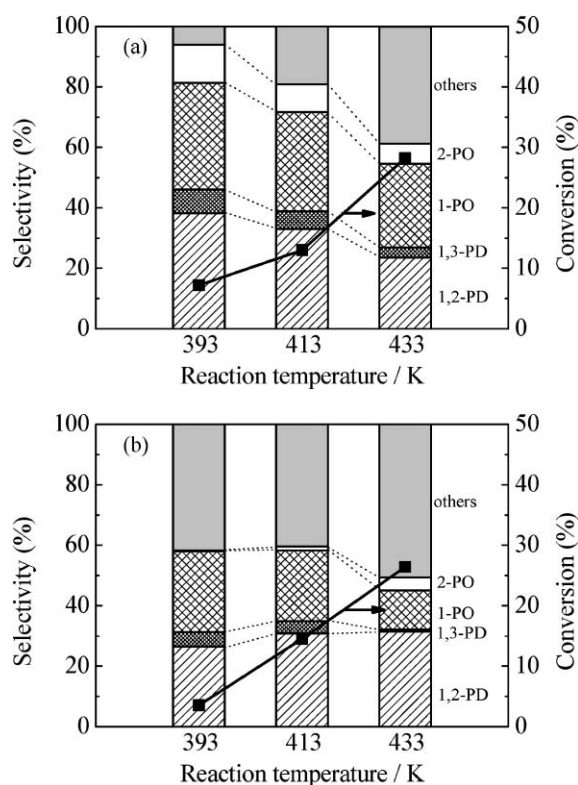


Fig. 3 Reaction temperature dependence of the glycerol reaction over (a) Rh/SiO₂ (G-6) and (b) Ru/C. Reaction conditions: 20 mass% glycerol aqueous solution 20 ml, 8.0 MPa initial H₂ pressure, 10 h reaction time, 150 mg metal catalyst. PD: propanediol, PO: propanol, others: ethylene glycol + ethanol + methanol + methane

reactions because the peaks assigned to metal species were detected by the X-ray diffraction method on the used samples, as reported previously.⁷ This also supports the low activity of Pt and Pd. In contrast, metallic Ru and Rh species are highly active, and these can be formed on Rh/SiO₂, Rh/C and Ru/C. In addition, the difference in the activity over the two Rh/SiO₂ and one Ru/C catalysts can be explained by the number of surface Rh atoms. From here, we focus on the catalytic performance of Rh/SiO₂ (G-6) and Ru/C.

Fig. 3 shows the reaction temperature dependence of the glycerol reaction over Rh/SiO₂ (G-6) and Ru/C. It is characteristic that Rh/SiO₂ (G-6) exhibited a lower selectivity to degradation products under higher glycerol conversion than Ru/C at 393 K. At higher reaction temperatures, the selectivity to degradation products on Rh/SiO₂ (G-6) increased

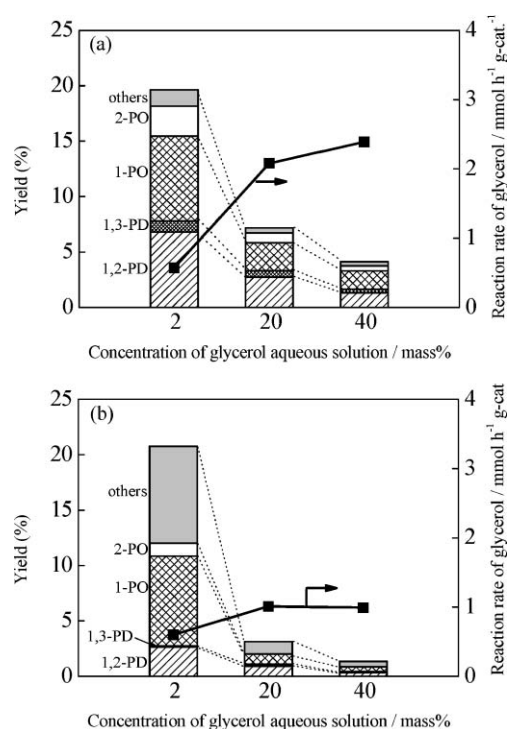


Fig. 4 Effect of glycerol concentration in the glycerol reaction over (a) Rh/SiO₂ (G-6) and (b) Ru/C. Reaction conditions: 20 ml glycerol aqueous solution, 393 K reaction temperature, 8.0 MPa initial H₂ pressure, 10 h reaction time, 150 mg metal catalyst. PD: propanediol, PO: propanol, others: ethylene glycol + ethanol + methanol + methane

significantly. This result recommends that the reaction should be carried out at lower reaction temperature, where Rh/SiO₂ showed much higher activity and higher hydrogenolysis selectivity than Ru/C. The details of the distribution of hydrogenolysis and degradation products are listed in Table 1. The main degradation products on Ru/C were EG and CH₄, and this represents the cracking of the C–C bond in the glycerol to ethylene glycol and methane. In contrast, in the case of Rh/SiO₂ (G-6), the selectivity to EG and ethanol were lower than that to CH₄. This indicates that the degradation reaction route on Rh/SiO₂ is different from that on Ru/C, and this suggests that glycerol is cracked to three methane molecules on Rh/SiO₂.

Fig. 4 shows the effect of glycerol concentration over Rh/SiO₂ (G-6) and Ru/C. On both catalysts, the glycerol conversion decreased with increasing glycerol concentration. However, the difference between Rh/SiO₂ and Ru/C was larger

Table 1 Result of the glycerol reaction over Rh/SiO₂(G-6) and Ru/C catalyst at 393 K^a

Catalysts	Conversion (%)	Total yield of hydrogenolysis products (%)	Total yield of degradation products (%)	Selectivity of each product (%) ^d							
				1,2-PD	1,3-PD	1-PO	2-PO	EG	C ₂ H ₅ OH	CH ₃ OH	CH ₄
Rh/SiO ₂ (G-6) + Amberlyst ^b	14.3	13.0	1.3	26.0	9.8	42.2	12.9	0.2	1.0	0.0	7.9
Rh/SiO ₂ (G-6) ^c	7.2	6.8	0.4	38.1	7.9	35.2	12.6	1.1	1.5	0.1	3.4
Ru/C + Amberlyst ^b	12.9	9.7	3.2	55.4	4.9	14.1	0.9	12.9	3.6	0.3	7.9
Ru/C ^c	3.5	2.0	1.5	26.4	4.9	26.7	0.3	22.0	5.8	2.3	11.6

^a Reaction conditions: 20 mass% glycerol aqueous solution 20 ml, 393 K reaction temperature, 8.0 MPa initial H₂ pressure, 10 h reaction time.

^b 150 mg metal catalyst + 300 mg Amberlyst. ^c 150 mg metal catalyst. ^d C-based selectivity. PD = propanediol, PO = propanol, EG = ethylene glycol.

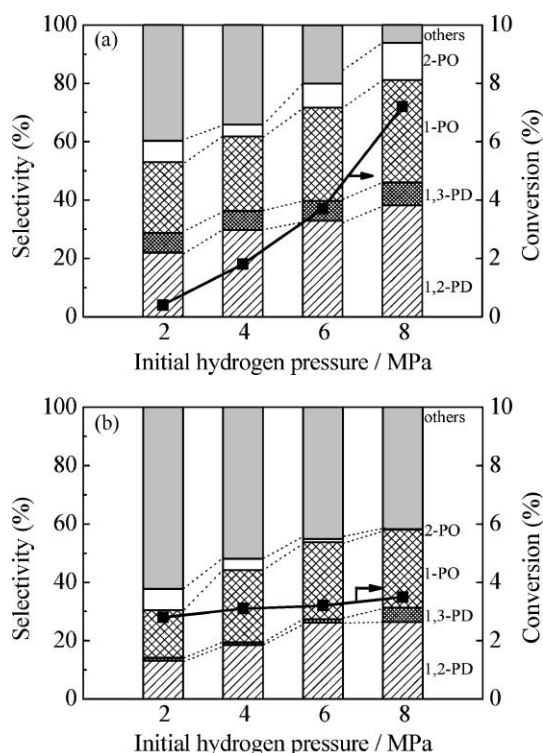


Fig. 5 Effect of hydrogen pressure in the glycerol reaction over (a) Rh/SiO₂(G-6) and (b) Ru/C. Reaction conditions: 20 mass% glycerol aqueous solution 20 ml, 393 K reaction temperature, 10 h reaction time, 150 mg metal catalyst. PD: propanediol, PO: propanol, others: ethylene glycol + ethanol + methanol + methane

at higher glycerol concentrations, and it should be noted that Rh/SiO₂ gave higher glycerol conversion even under high glycerol concentration conditions. Although the details are not shown here, we confirmed that the reaction proceeded under steady-state conditions, judging from the change of H₂ pressure during the test. Therefore, it is possible to estimate the reaction rate from the results of the activity tests. In terms of the reaction rate of glycerol, the rate on Rh/SiO₂ was about twice as high as that on Ru/C under the condition of 40 mass% glycerol aqueous solution, although the difference was small at 2 mass% concentration. In addition, another important point is that Rh/SiO₂ maintained high selectivity to hydrogenolysis products even under high glycerol concentration.

Fig. 5 shows the effect of H₂ pressure. At lower hydrogen pressure, such as 2.0 MPa, Ru/C gave much higher glycerol conversion than Rh/SiO₂. In the case of the Ru/C, the effect of H₂ pressure was very small, and the yield of hydrogenolysis products increased gradually with increasing H₂ pressure. In contrast, in the case of Rh/SiO₂, the conversion and selectivity to the hydrogenolysis products increased remarkably with increasing H₂ pressure, and this means that the yield of hydrogenolysis products is enhanced by the increase of H₂ pressure. It is possible to estimate the reaction order of glycerol with respect to H₂ over Rh/SiO₂ (G-6), and the obtained order is estimated to be second. Further investigations on the promoting mechanism of hydrogen on the hydrogenolysis reaction over Rh/SiO₂ are necessary; however, it is suggested

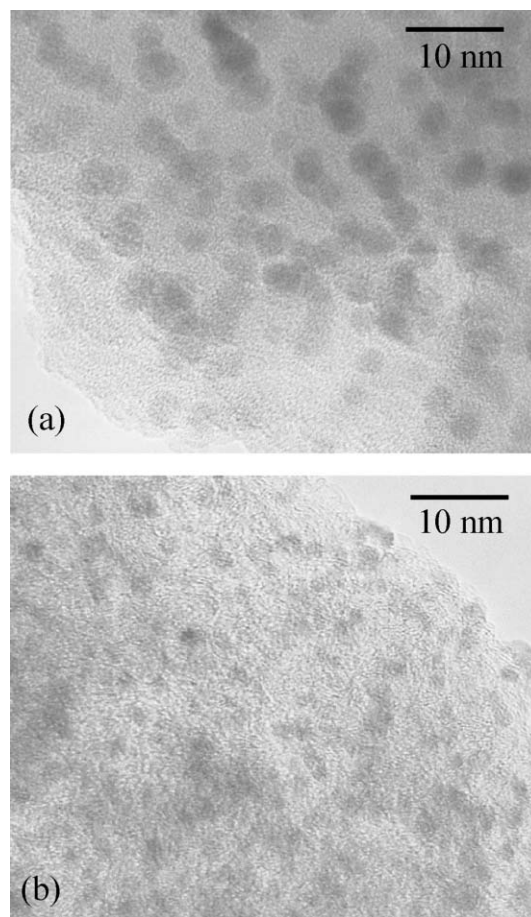


Fig. 6 TEM images of (a) Rh/SiO₂ (G-6) and (b) Ru/C catalysts after the glycerol reaction at 393 K for 10 h.

that the adsorbed hydrogen species on the Rh surface promote the hydrogenolysis reaction.

Fig. 6 shows TEM images of the used Rh/SiO₂ (G-6) and Ru/C catalysts after the reaction at 393 K for 10 h under the standard reaction conditions. The metal particles were observed in both cases, and the average particle sizes of Rh and Ru were determined to be about 3.8 ± 0.2 and 2.5 ± 0.2 nm, respectively. In the case of Ru/C, based on the relationship ($D = 1.32/d$) between particle size (d , nm) and the dispersion (D , %),^{29,30} the dispersion is calculated as $53 \pm 4\%$. In the case of Rh/SiO₂ (G-6), based on the relationship, ($D = 1.10/d$),^{29,31} the dispersion is obtained as $29 \pm 2\%$, which is lower than that of Ru/C. In addition, the average particle size of both catalysts after the reduction pretreatment were almost the same as those of used catalysts, although the details are not shown here. This means that the aggregation of metal particles during the reaction can be neglected, and this is related to the tendency of the decrease of H₂ pressure during the reaction to be almost proportional to the reaction time. In addition, based on the dispersion obtained from the TEM results, the turnover frequency on Rh/SiO₂ (G-6) is estimated to be about five times as high as that on Ru/C under the standard reaction conditions.

Here, we investigated the effect of Amberlyst addition to Rh/SiO₂ (G-6) in comparison with Ru/C. The results are listed

Table 2 Reaction results of various reactants over Rh/SiO₂ and Ru/C under H₂^a

Catalysts	Reactant	Conversion (%)	Selectivity of each product (%) ^d							
			1,2-PD	1,3-PD	1-PO	2-PO	EG	C ₂ H ₅ OH	CH ₃ OH	CH ₄
Rh/SiO ₂ (G-6) +Amberlyst ^b	Glycerol	29.3	22.6	5.4	41.3	17.0	0.0	1.8	0.0	12.0
	1,2-PD	17.5	—	0.0	56.5	21.6	0.0	2.1	0.0	19.7
	1,3-PD	22.6	0.0	—	68.2	0.0	0.0	6.8	0.0	24.9
Rh/SiO ₂ (G-6) ^c	Glycerol	19.6	34.6	5.2	39.1	13.7	0.0	2.9	0.0	4.6
	1,2-PD	9.8	—	0.0	66.5	20.9	0.0	1.0	0.0	11.6
	1,3-PD	19.2	0.0	—	81.3	0.0	0.0	9.3	0.0	9.4
Ru/C +Amberlyst ^b	Glycerol	38.8	28.8	0.8	28.9	2.4	7.4	18.7	1.9	11.2
	1,2-PD	6.3	—	0.0	28.2	30.0	0.0	27.8	0.0	13.9
	1,3-PD	77.7	0.0	—	32.8	0.0	0.0	44.8	0.0	22.4
Ru/C ^c	Glycerol	20.8	12.7	0.4	39.1	5.6	7.6	20.6	1.6	12.4
	1,2-PD	6.3	—	0.0	25.1	37.1	0.0	25.2	0.0	12.6
	1,3-PD	75.1	0.0	—	26.0	0.0	0.0	49.3	0.1	24.6

^a Reaction conditions: 2 mass% aqueous solution of reactant 20 ml, 393 K reaction temperature, 8.0 MPa initial H₂ pressure, 10 h reaction time, 150 mg metal catalyst. ^b 150 mg metal catalyst + 300 mg Amberlyst. ^c 150 mg metal catalyst. ^d C-based selectivity. PD = propanediol, PO = propanol, EG = ethylene glycol.

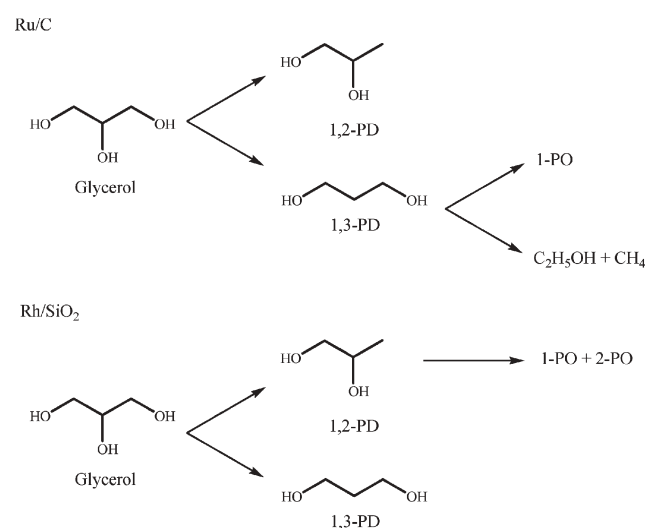
in Table 1. In this experiment, the reaction temperature was chosen to be 393 K. One reason is based on the results of reaction temperature dependence (Fig. 3), and another is due to the highest operating temperature of the ion-exchange resin. As reported previously, under the same reaction conditions, the Amberlyst was stable for at least 60 h.⁷ From the comparison between Ru/C and Ru/C + Amberlyst, it is found that the glycerol conversion was increased by the addition of Amberlyst, and the total hydrogenolysis product yield mainly increased; in particular, 1,2-PD formation was drastically promoted. This behavior can be interpreted by the combination of the dehydration to acetol on Amberlyst and subsequent hydrogenation to 1,2-PD on Ru/C as reported previously.⁷ On the other hand, in case of Rh/SiO₂ (G-6) and Rh/SiO₂ (G-6) + Amberlyst, the addition of Amberlyst enhanced glycerol conversion, and hydrogenolysis product yield; however, 1-PO formation was promoted most significantly. The propanediols are thought to be more valuable than propanols, thus the combination of Amberlyst with Ru/C might be more suitable than that with Rh/SiO₂.

In order to explain the product distribution, the reactions of 1,2- and 1,3-PDs under hydrogen were also tested (Table 2). On Ru/C and Ru/C + Amberlyst, the reaction rate of 1,3-PD was much higher than that of glycerol and 1,2-PD, and this can be related to a very low yield of 1,3-PD in the glycerol reaction. In contrast, the reaction rate of 1,2-PD was much lower than that of glycerol, and this is associated with the high selectivity to 1,2-PD in the reaction of glycerol. In addition, the propanols are also formed by the sequential hydrogenolysis of propanediols. The hydrogenolysis of 1,2-PD can give 1-PO and 2-PO, and the hydrogenolysis of 1,3-PD can give 1-PO. The selectivity ratio of 1-PO to 2-PO is dependent on the catalysts. The selectivity to 1-PO was much higher than that to 2-PO in the reaction of glycerol over Ru/C and Ru/C + Amberlyst. The behavior indicates that 1-PO is mainly formed *via* 1,3-PD, whose amount was very low owing to its high reactivity over Ru/C and Ru/C + Amberlyst. High selectivity to C₂H₅OH on Ru/C and Ru/C + Amberlyst in the glycerol reaction also indicates that ethanol is formed from the degradation of propanediols. However, the reaction rate of 1,3-PD was comparable to that of glycerol over Rh/SiO₂ (G-6),

and this can be related to a much higher yield of 1,3-PD in the glycerol reaction than that on Ru/C, although the selectivity to 1,3-PD was not so high as that reported.²⁰ The selectivity ratio of 1-PO to 2-PO in the glycerol reaction on Rh/SiO₂ and Rh/SiO₂ + Amberlyst seems to be similar to that in the reaction of 1,2-PD. This suggests that 1-PO is mainly formed *via* 1,2-PD, and this is different from that over Ru/C. The formation of 1-PO was enhanced by the Amberlyst addition to Rh/SiO₂. This is because the Amberlyst catalyzes the dehydration of glycerol to acetol, as mentioned above, and Rh/SiO₂ catalyzes the hydrogenation of acetol to 1,2-PD, and furthermore Rh/SiO₂ catalyzes the hydrogenolysis of 1,2-PD to propanols with higher selectivity to 1-PO than 2-PO. Based on the results in Table 2, the model scheme of the glycerol reaction under H₂ over Ru/C and Rh/SiO₂ is described in Fig. 7.

4. Conclusions

Among the various supported noble metal catalysts, it is found that Rh/SiO₂ (G-6) catalyst is effective in the reaction of

**Fig. 7** Model scheme of the glycerol reaction over Ru/C and Rh/SiO₂.

glycerol under H_2 . It is characteristic that Rh/SiO_2 exhibited higher activity and selectivity to hydrogenolysis products (1,2-PD + 1,3-PD + 1-PO + 2-PD) in the reaction of glycerol than Ru/C , which can be regarded as a conventional catalyst. In particular, under higher H_2 pressure and higher concentration of glycerol, Rh/SiO_2 was a more effective catalyst than Ru/C . By the addition of Amberlyst, glycerol conversion increased on the Rh/SiO_2 as well as on Ru/C . In addition, the reaction route of glycerol on Rh/SiO_2 can be different from that on Ru/C . The consecutive hydrogenolysis of propanediols to propanols in the glycerol reaction can proceed mainly via 1,3-propanediol on Ru/C , while the consecutive reactions can proceed mainly via 1,2-propanediol on Rh/SiO_2 . The efficient catalytic conversion of glycerol into valuable chemicals, which is a main byproduct in the biodiesel production, can contribute to the promotion of biodiesel utilization from an economic point of view.

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Greener synthesis route for Jet Propellant-10: the utilization of zeolites to replace AlCl_3 †

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This paper summarizes our recent developments in the utilization of H-type zeolites to replace AlCl_3 in *exo*-tetrahydrodicyclopentadiene production. H-type Y zeolites with large pore size (0.74 nm) had sufficient activities for isomerization of *endo*-tetrahydrodicyclopentadiene (*endo*-THDCPD) to form *exo*-tetrahydrodicyclopentadiene (*exo*-THDCPD). As for acidity strength, the moderate strength of zeolite acidity was favorable. The incorporation of fluorine generated more moderate acids, which improved the catalytic performance of zeolites to *exo* yield = 92.58%, *exo* selectivity = 96.47%, and suppressed the adamantane (ADM) yield = 2.32%. When $\text{NH}_4\text{F}/\text{SSY} = 6.57\%$, calcined at 500 °C, this showed an equivalent performance as AlCl_3 .

1 Introduction

In this contribution, we focus on the synthesis of the single-compound fuel, Jet Propellant-10. Its relatively simple composition of >98.5% *exo*-tetrahydrodicyclopentadiene (*exo*-THDCPD) (freezing point −79 °C) and *endo*-tetrahydrodicyclopentadiene (*endo*-THDCPD) (freezing point 80 °C) is responsible for its very high volumetric energy content (39.6 MJ L^{−1}) due to the strained cyclic geometry (Scheme 1).^{1,2} This property, in combination with its low toxicity and suitable flashpoint (55 °C), explains its success as a fuel for short-range missiles. *Exo*-THDCPD is additionally used in other fuel mixtures (e.g. JP-9 and PF-1), and also as a solvent for paints, etc. The production of *exo*-THDCPD is summarized in Scheme 1.

Hydrogenation of dicyclopentadiene (DCPD) affords selectively *endo*-THDCPD. This compound needs to be isomerized to *exo*-THDCPD to meet the freezing point requirements of a jet fuel. Unfortunately, *exo*-THDCPD can be further isomerized to adamantane (ADM), a side-reaction which needs to be avoided as much as possible because of its high freezing point (above 269 °C). Whereas the isomerization reaction was originally catalyzed by the highly corrosive sulfuric acid,^{3,4} AlCl_3 has been predominantly used for this

purpose since 1960s.⁵ Although the use of $\text{Pd}(\text{acac})_2$ as a catalyst brought the yield up to 99.5%,⁶ the high cost limited its application at an industrial scale. In 1980s, Cheng *et al.*⁷ and Olah and Farooq⁸ catalyzed *endo*-THDCPD to *exo*-THDCPD using liquid super acids. The problems of separation and corrosion are still to be solved. Therefore, there is still a strong need to develop new catalysts at low cost for *exo*-THDCPD production with minimum environmental impact.

The synthesis of ADM from *endo*-THDCPD catalyzed by Y zeolites at the laboratory^{9–11} and industrial scales¹² have been reported. In the synthesis of ADM, *exo*-THDCPD production would be promoted by the use of zeolites. This paper summarizes our recent developments in the utilization of H-type zeolites to replace AlCl_3 in *exo*-THDCPD production.^{13,14} It was shown that H-type zeolites have equivalent yields and better selectivity than AlCl_3 , which could make *exo*-THDCPD production greener.

2 Experimental

2.1 Materials

Commercially available zeolites were used. All Y zeolites were produced by the Wenzhou Catalyst Co., China. H-ZSM-5 and H-β were provided by the Nankai Catalyst Co., China. The characteristics of these zeolites are given in Table 1. All zeolites in the ammonia form were activated for 2 h at T_f (ca. 450–600 °C) in air to form the corresponding H-type before catalytic runs. The H-type ZSM-5, β and ReY were calcined at 200 °C to eliminate adsorbed water molecules.

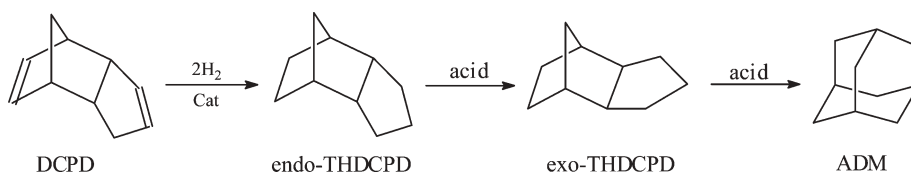
The fluorine loading of zeolites into H-type Y zeolites was carried out as follows: about 1 g of $\text{NH}_4\text{-SSY}$ zeolites were

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Scheme 1

Table 1 Characteristics of zeolites provided by producer

Zeolite	Si : Al ratio	Unit cell structure/ 10^{-10} m	Crystallinity (%)	Na ₂ O (wt%)
NH ₄ Y	5.0	ca. 24.65–24.69	≥90	≤2.0
ReY	5.0	ca. 24.64–24.68	≥90	≤2.0
NH ₄ -USY	≥5.2	ca. 24.52–24.58	≥80	≤0.2
NH ₄ -SSY	ca. 9.0–12.0	ca. 24.49–24.53	≥78	≤0.2
H-β	ca. 28.0–29.0	^a	≥90	^a
H-ZSM-5	50.0	^a	≥90	^a

^a No data are available from vendor.

impregnated with 1.50 mL of an aqueous solution of NH₄F (Tianjin Chem Reagents Co.). After drying at 120 °C overnight, the catalysts were activated stepwise in air at 250 °C for 4 h to decompose NH₄F, and at T_f for a further 2 h. The subsequent activation at T_f helped fluorine to be incorporated into the skeleton of the zeolites, and to decompose NH₄⁺ into NH₃ and H⁺ to form acidic, active H-type Y zeolites.

2.2 Characterization

NH₃-temperature-programmed desorption (TPD) was performed on an Autochem 2910 instrument equipped with thermal conductivity detectors (TCD). The conditions for the analysis were as follows: carrier gas He, absorption temperature 120 °C, linear heating rate 10 °C min⁻¹, temperature range 120–600 °C.

2.3 Apparatus and procedure

The experiments were carried out in a mechanically stirred autoclave at 195 °C. Samples of the reaction mixture were analyzed by a GC HP-4890 equipped with a HP-5 capillary column (length: 30 m; diameter: 0.53 mm; thickness of the film: 0.15 μm) and flame ionization detectors (FID).

3 Results and discussion

3.1 Acidity characterization of zeolites

NH₃-TPD curves of H-USY, ReY and H-SSY calcined at 450, 200 and 450 °C, respectively, are shown in Fig. 1.

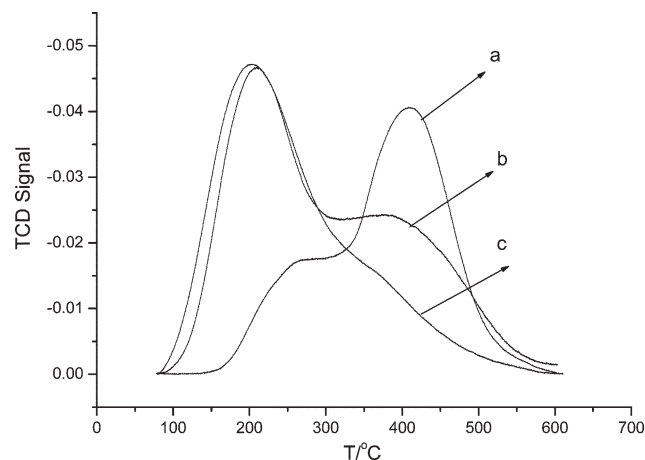


Fig. 1 NH₃-TPD curves of different Y zeolites: (a) H-SSY calcined at 450 °C; (b) H-USY calcined at 450 °C; and (c) ReY calcined at 200 °C.

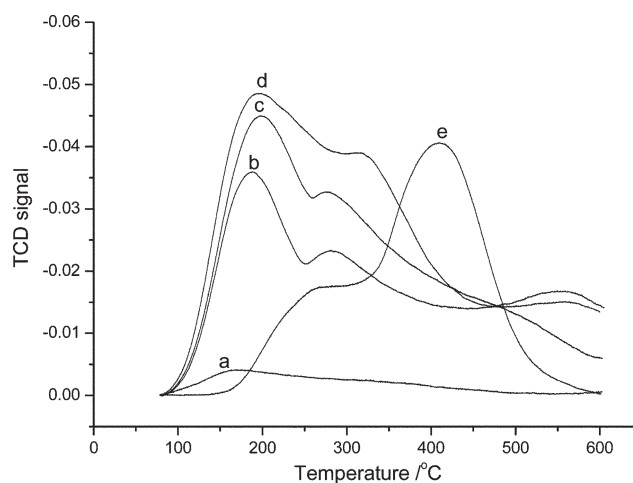


Fig. 2 NH₃-TPD curves of fluorine-modified H-SSY with different NH₄F/SSY and calcination temperatures: (a) NH₄F/SSY = 6.57%, 600 °C; (b) NH₄F/SSY = 9.81%, 450 °C; (c) NH₄F/SSY = 3.28%, 550 °C; (d) NH₄F/SSY = 6.57%, 500 °C; and (e) NH₄F/SSY = 0.00%, 450 °C.

As Fig. 1 shows, the acidity increases in the order ReY < H-USY < H-SSY. Weak acid sites (T_{peak} around 200 °C) dominate the acidity of ReY, with a small number of moderate acids (T_{peak} around 300 °C). On the contrary, H-SSY has much more strong acid sites (T_{peak} around 400 °C) and some moderate acid sites.

NH₃-TPD curves of fluorine-modified H-SSY with different NH₄F/SSY and calcination temperatures are shown in Fig. 2.

As shown in Fig. 2, the addition of fluorine decreases the strong acid sites and increases weak acid sites significantly. As for moderate acids, both NH₄F/SSY and calcination temperature should be suitable to achieve the increase of the moderate acid sites. The formation of large amounts of weak acids can be explained by thermal dealumination to form aluminium oxide species with weak acidity. Although unmodified H-SSY showed high thermal stability during calcination, the involvement of fluorine can decrease the thermal stability of the zeolitic skeleton of H-SSY. It should be pointed out that a higher fluorine content calcined at a higher temperature [Fig. 2(a), NH₄F/SSY = 6.57%, calcination temperature 600 °C] leads to the collapse of the zeolitic skeleton, which results in the almost complete loss of acidity. The complete loss of acidity can be reflected by both NH₃-TPD and pyridine-adsorbed FT-IR. The loss of acidity, especially strong and moderate acid sites, is an indication of the collapse of the zeolitic skeleton. The complete loss of acidity could certainly decrease the catalytic activity of the zeolites, which will be discussed with the catalytic activity data in the following section.

3.2 Activities of different types of zeolites

During the isomerization of large molecules, the pore structure and size of the zeolites are very important parameters. Zeolites H-β, HY and H-ZSM-5 were tested in this study, as shown in Table 2.

All of these three H-types show sufficient acidity, but they have different zeolitic channels and cavities. For the cavities,

Table 2 Influence of zeolite type

Zeolite	Calcination temperature/°C	Endo conversion (%)	Exo yield (%)	Exo selectivity (%)	ADM yield (%)
HY	450	90.00	85.55	95.05	2.63
H-β ^a	200	Almost no activity			
H-ZSM-5 ^b	200	Almost no activity			

^a Reaction times for H-β were 4 and 8 h. ^b Reaction times for H-ZSM-5 were 4 and 8 h.

they are hard to measure and calculate. Combined with the calculated dimensions of the THDCPD isomers, the shape-selectivity of zeolitic catalysts was studied.¹⁴ H-ZSM-5 and H-β showed no activity for this skeleton rearrangement at 195 °C because of their relatively small pore size (H-ZSM-5: 0.53 × 0.56 nm, 0.51 × 0.55 nm; H-β: 0.57 × 0.75 nm, 0.56 × 0.65 nm) when compared with the dimensions of *endo*-THDCPD (cross-section of minimum area 0.67 nm × 0.65 nm; kinetic diameters σ 0.58 × 0.60 nm) (Fig. 3). The reactant needs to be adsorbed onto an acidic site, be protonated, and then be isomerized into the *exo*-THDCPD and ADM, which needs then to be desorbed again. For HY, the large size of the channels (0.74 × 0.74 nm) can provide sufficient windows for *endo*-THDCPD to penetrate into the inner surface of the HY zeolites, and then be adsorbed onto acidic centers to precede skeleton rearrangement for the formation of isomerized products. In conclusion, reactant selectivity can explain why H-β and H-ZSM-5 lack isomerizing activity at 195 °C.

3.3 Acidic Y zeolites

Commercially available HY zeolites with different Si : Al ratios – HY, H-USY and H-SSY – were tested. The experimental results are summarized in Table 3.

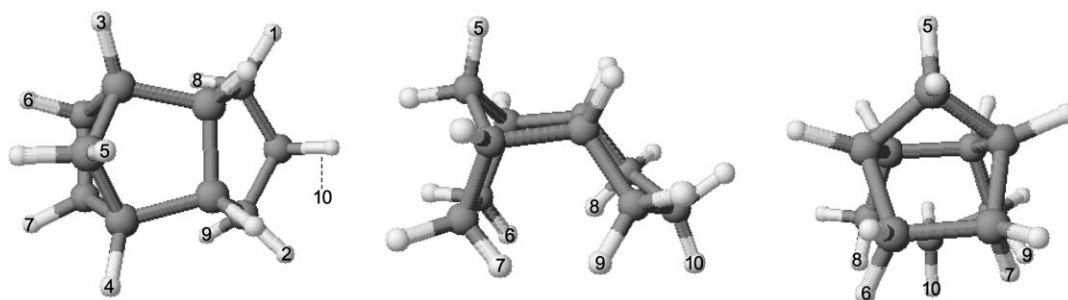
Corma's review¹⁵ showed that a higher Si : Al ratio leads to a smaller unit cell structure (UCS), and thus fewer acidic sites, stronger acidity and longer distance between two neighboring acid sites. Based on the data provided by the zeolite vendor,

the Si : Al ratio increases in the order HY < H-USY < H-SSY; UCS decreases in the order HY > H-USY > H-SSY. So the acidity increases in the order HY < H-USY < H-SSY, and the number of acidic sites decreases in the same order. It is shown that acidity strength is more important than the number of acidic sites to the formation of *exo*-THDCPD. Therefore the modification of Y zeolite should be focused on the change in the acidity strength and acidity distribution rather than on the number of acidic sites.

As an acidic zeolite, ReY showed unsatisfactory activity for *endo*-THDCPD isomerization. The reason will be discussed according to the acidity characterization in Fig. 1. As Fig. 1 shows, the acidity increases in the order ReY < H-USY < H-SSY. The activity (measured by *endo*-THDCPD conversion) increases in the same order ReY < H-USY < H-SSY. In contrast, the selectivity decreases with the increase in acidity, mainly reflected by the yields of ADM (also increasing with acidity strength) and other by-products. In ADM production studies, it has also been proved that strong Brønsted acids favor the formation of ADM and cracking of by-products. In this study it is found that for the formation of *exo*-THDCPD, moderate acids are needed. The low activity of ReY showed that weak acidity contributed insignificantly to the conversion of *endo*-THDCPD.

3.4 Zeolites modified by fluorine

In order to modify the surface acidity of the zeolites, fluorine was introduced as described for H-ZSM-5 modification by

**Fig. 3** Optimized 3D geometry of *endo*-THDCPD.**Table 3** Influence of Si : Al ratio

Zeolite	Si : Al ratio	Calcination temperature/°C	Endo conversion (%)	Exo yield (%)	Exo selectivity (%)	ADM yield (%)
HY	5.0	450	90.00	85.55	95.06	2.63
		550	92.43	87.22	94.36	3.60
H-USY	≥5.2	450	94.93	89.69	94.48	3.03
		550	96.73	89.46	92.48	4.33
H-SSY	ca. 9.0–12.0	450	95.83	87.55	91.36	4.40
		550	95.85	87.58	91.37	4.72

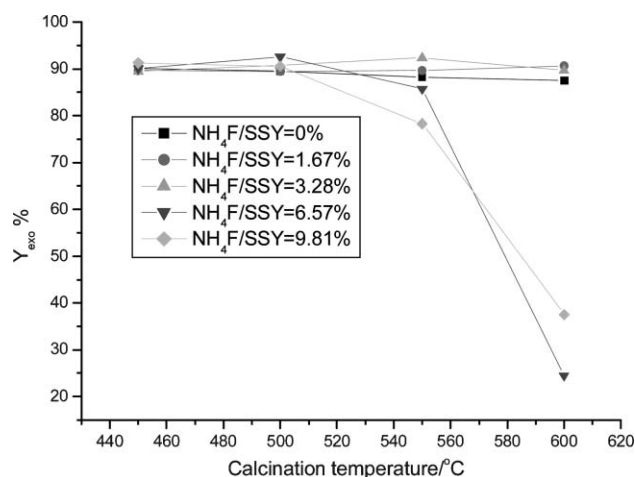


Fig. 4 Influence of $\text{NH}_4\text{F}/\text{SSY}$ and calcination temperature on Y_{exo} .

NH_4F .^{16,17} For fluorine incorporation, the calcination temperature and F content, measured by $\text{NH}_4\text{F}/\text{SSY}$ (mass ratio), were two key factors influencing the catalytic performance. However, $\text{NH}_4\text{F}/\text{SSY}$ is the most influencing factor in determining the content of fluorine incorporated into the zeolitic skeleton. As discussed in Section 3.2, the catalytic activity of fluorine-modified H-SSY is measured by Y_{exo} and S_{exo} , which correspond to the yield and selectivity of *exo*-THDCPD.

The influences of $\text{NH}_4\text{F}/\text{SSY}$ and calcination temperature on Y_{exo} and also on S_{exo} are illustrated in Fig. 4 and Fig. 5, respectively. Generally speaking, the fluorine modification is positive in improving the *exo*-selectivity and suppressing the ADM formation since the addition of fluorine increases moderate acids. As shown in Fig. 5, the low concentration of fluorine shows a hardly noticeable effect on the catalytic performance, especially at lower calcination temperatures (450, 500 °C), while at higher calcination temperatures (550, 600 °C), the fluorine modification leads to an increase in *exo*-THDCPD yield and *exo*-selectivity. As shown in Fig. 5, with the improvement in *exo*-selectivity, suitable fluorine concentration and calcination temperature lead to a better *exo*-yield. The reason is attributed to the strengthening of moderate acids, such as Fig. 2(b), Fig. 2(c) and Fig. 2(d). Moderate fluorine loading

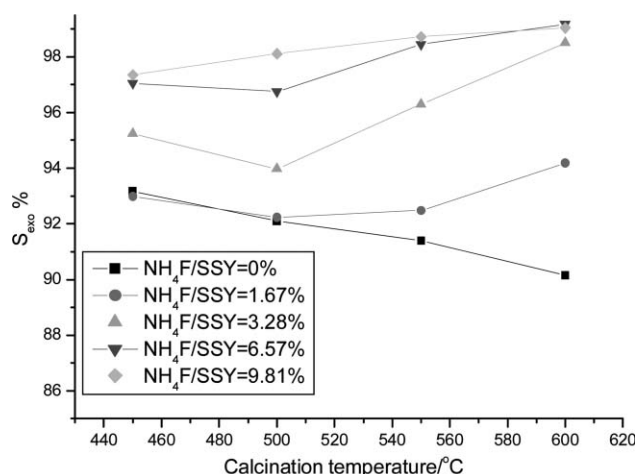


Fig. 5 Influence of $\text{NH}_4\text{F}/\text{SSY}$ and calcination temperature on S_{exo} .

and higher temperature lead to more moderate acids, which favor the formation of *exo*-THDCPD. In all, the best Y_{exo} (92.58%) is achieved for H-SSY with $\text{NH}_4\text{F}/\text{SSY} = 6.57\%$, calcined at 500 °C (Fig. 4). Compared with parent zeolites with the best yield (90.08%), the yield of *exo*-THDCPD is improved by 2.50%.

The involvement of fluorine as an electron-withdrawing component can change the surface acidity of zeolites toward the desired direction, in which moderate acids are needed to achieve better *exo*-yield. On one hand, the amount of moderate acids of fluorine-modified H-SSY [Fig. 2(b)–(e)] decreased in the order 2(d) > 2(c) > 2(b) > 2(e), which was reflected by the decreasing order of *exo*-yield: 2(d) (92.58%) $\approx$ 2(c) (92.34%) > 2(b) (91.28%) > 2(e) (90.08) (Fig. 4). The best catalyst is obtained with a calcination temperature of 500 °C and $\text{NH}_4\text{F}/\text{SSY} = 6.57\%$. Compared with unmodified H-SSY zeolites (best performance occurred at 450 °C, with $X_{\text{endo}} = 96.66\%$, $Y_{\text{exo}} = 90.08\%$, $S_{\text{exo}} = 93.18\%$, $Y_{\text{ADM}} = 3.60\%$), the conversion decreased by 0.19%. However Y_{exo} and S_{exo} were improved by 2.50 and 3.29% respectively, suppressing the formation of ADM by 1.28%. This desired tendency is achieved through forming more moderate acids with the addition of fluorine into the zeolitic skeleton.

In order to test the thermal durability of fluorine-modified zeolites, the best catalysts were regenerated for at least eight times and showed no noticeable decrease in yield and selectivity.

USY zeolites modified by fluorine were also tested, which showed improved performance.

3.5 Proposed mechanism of isomerization

Scheme 1 shows the traditional mechanism of THDCPD isomerization. Although there are hundreds of $[\text{C}_{10}\text{H}_{15}]^+$ isomers, because of thermodynamic and kinetic unfavorable factors, other $\text{C}_{10}\text{H}_{16}$ isomers could hardly be detected. All isomers detected are *exo*-THDCPD, *endo*-THDCPD and ADM. With the assumption that other $[\text{C}_{10}\text{H}_{15}]^+$ are thermodynamically unstable or kinetically unfavorable, a simple mechanism for the isomerization of THDCPD is proposed, as shown in Fig. 6. The key scheme is the isomerization of $[\text{C}_{10}\text{H}_{15}]^+$. Although the yield of *exo*-THDCPD could reach 99% with liquid super acids as catalysts below room temperature, the purified *exo*-THDCPD (99%) could be partly isomerized to *endo*-THDCPD (Table 4), which means that the steps are reversible. According to Olah and Farooq,⁸ 100% of $[\text{ADM}]^+$ could exist in liquid super acids, which shows that step 4 and step 5 were irreversible. Also, heating ADM in the presence of zeolites does not lead to the formation of *endo*-THDCPD and *exo*-THDCPD, but to ring-opening products. Total conversion of *endolexo*-THDCPD to ADM can be achieved,^{7–11} which also shows the step 5 was irreversible.

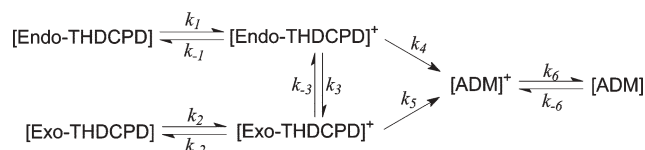


Fig. 6 Mechanism of isomerization.

Table 4 Equilibrium mixture at 200 °C

Reactant	The composition of reaction mixtures (wt%)			
	<i>Endo</i> -THDCPD	<i>Exo</i> -THDCPD	ADM	Others
<i>Endo</i> -THDCPD	3.20	87.55	4.24	5.01
<i>Exo</i> -THDCPD	3.24	86.71	4.56	5.49

Generally speaking, step 3 is kinetically favorable, which could proceed very quickly even at very low [*endo*-THDCPD]⁺ concentration. Steps 4 and 5 are thermodynamically favorable, which means higher [THDCPD]⁺ will lead to more thermodynamically stable [ADM]⁺.

Based on the isomerization mechanism, low concentration of [*endo*-THDCPD]⁺ will favor the formation of *exo*-THDCPD until the equilibrium is established. Because Step 3 is exothermic, the reactions should proceed at low temperature to achieve high equilibrium yields. In all, the *exo*-THDCPD should be carried out with strong acids at low concentration and low temperature. For the formation of ADM, higher reaction temperature, more acidic numbers and stronger acidity are needed to convert [*endo*-THDCPD]⁺ to [ADM]⁺.

According to the above mechanism, the best condition for *exo*-THDCPD production should be strong acids at low concentration and low reaction temperature. Although the use of liquid super acids can achieve higher yield and selectivity, the difficulty in separation and corrosion are the major problems. That is why Y zeolites are used at higher temperatures to achieve almost equivalent yield and selectivity as AlCl₃ does. For the ADM, strong acids at high concentration and higher reaction temperature will be needed. In some cases, even HCl is needed to improve the acidity of catalysts for ADM. In all, strong acidity, high concentration and high reaction temperature favor the formation of ADM.

4 Conclusion

The synthesis of *exo*-THDCPD by isomerization of *endo*-THDCPD on commercially available zeolites is studied. It is shown that pore size and acidity are the most important factors to influence the activity and selectivity of the zeolitic catalysts. HY zeolites (0.74 nm) are the most active with smaller pore sizes (H-β and H-ZSM-5). Besides pore size, acidity is the other key factor. Based on the proposed mechanism, the surface acidity of zeolites is modified toward the desirable direction. It is possible to enhance the moderate acids of H-type Y zeolites by incorporation of ammonium fluoride in relatively low concentrations and, subsequently, by stepwise activation at high temperature. The strengthening of moderate acids favors the *exo* yield, the decrease in strong acids leads to improved *exo* selectivity and suppressed ADM yield, which is desirable in *exo*-THDCPD production.

Fluorine-modified H-SSY (NH₄F/SSY = 6.57%, calcination temperature 500 °C) shows the best isomerizing activity for *endo*-THDCPD, with a maximum *exo* yield of 92.58%, an improved *exo* selectivity of 96.74% and a suppressed ADM yield of 2.32%.

It can be concluded that fluorine-modified H-SSY shows potential use for the production of *exo*-THDCPD to take the place of AlCl₃ as the isomerizing catalyst for *endo*-THDCPD. The fluorine-modified zeolites show similar activities as AlCl₃ under solvent-free conditions. Catalyst recycling and reuse causes almost no harm to the environment or little corrosion. The easy separation appears more promising for commercial use in *exo*-THDCPD production.

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Removal of carbon dioxide by absorption into blended amines: kinetics of absorption into aqueous AMP/HMDA, AMP/MDEA, and AMP/piperazine solutions†

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The emissions of anthropogenic carbon dioxide (CO₂) are believed make a significant impact on global climate change. Hence, amine chemical absorption technology has been suggested to separate and recover CO₂. In this study, reaction rate constants between CO₂ and blended amines were determined by measuring their absorption rate for CO₂. The experiments were carried out to investigate the characteristics of CO₂ absorption by using additional absorbents such as hexamethylenediamine (HMDA), *N*-methyldiethanolamine (MDEA) or piperazine blended into 2-amino-2-methyl-1-propanol (AMP) in an agitated vessel. The absorption rates of CO₂ into aqueous blended amine solutions were measured. Additive concentrations of 1, 3, and 5 wt% were added for each 30 wt% AMP solution. The results showed that the addition of HMDA, MDEA or piperazine into AMP increased the absorption rate as compared to AMP alone. Of these additives, HMDA showed the most enhancement in the reaction rate of AMP. The reaction rate constants of HMDA, MDEA and piperazine blended into AMP at 303–343 K were given by $k_H = 3.84 \times 10^{10} \exp(-5361/T)$, $k_M = 6.60 \times 10^9 \exp(-4959/T)$, and $k_P = 9.09 \times 10^9 \exp(-5058/T)$, respectively.

Introduction

The Inter-governmental Panel on Climate Change (IPCC) reported that human activities result in the production of greenhouse gases (CO₂, methane (CH₄), chlorofluorocarbon (CFCs), and nitrous oxide (N₂O)), which significantly contribute to global warming, and global warming is one of the most serious environmental problems.¹ Of these gases CO₂ has the greatest impact on the global warming, causing approximately 55% of the observed global warming.¹ According to the United Nations Framework Convention on Climate Change (UNFCCC) in Kyoto,² a commitment to reduce CO₂ emissions by 6% below the 1990s level was made by several countries. Industrialized countries should take the lead in combating climate change and the adverse effects. They were responsible for the majority of the historical cumulative emissions, and so they were given quantified commitments to reduce emissions in the Kyoto Protocol.³

There are several technologies being used to separate CO₂ from a flue gas of fossil fuel fired power plants, such as chemical absorption, physical absorption, cryogenic methods,

membrane separation and biological fixation. Of these technologies, chemical absorption process is generally considered as the most effective technology. Monoethanolamine (MEA), diethanolamine (DEA), and MDEA are widely used in the chemical absorption process. In addition, sterically hindered amines such as AMP has been studied, with a particular attention to its absorption capacity, absorption rate, and degradation resistance advantages over conventional amines.^{4–7}

To utilize the advantages of each amine, blended amines have been suggested. For example, a blend of primary (MEA) and tertiary amine (MDEA) could combine a high absorption rate of MEA and a high equilibrium capacity of MDEA.^{8,9} In addition, AMP can be an attractive alternative due to its advantages as mentioned above. A number of research papers related to the absorption of CO₂ into aqueous AMP solutions and blended amine (AMP/MEA, AMP/DEA, AMP/sulfolane) solutions containing AMP have been reported.^{10–17}

In this study, the rates of absorption of CO₂ in the aqueous solutions of AMP and blended amines (AMP/HMDA, AMP/MDEA, AMP/piperazine) were measured using a stirred-cell reactor at 303, 313, 323, and 343 K. Kinetics and rate constants were determined by measuring their absorption rate for CO₂.

Theoretical background

Absorption reaction mechanism

Reaction of CO₂ with the amino group of AMP could result in three reactions: the formation of carbamate, the formation of bicarbonate, and the reversion of carbamate to bicarbonate or formation of the carbonate ion.¹⁸

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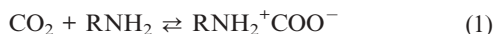
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Carbamate formation:



Bicarbonate formation:



Simultaneously, the additive piperazine and MDEA may react with CO_2 in the liquid film to form an intermediate, as follows:



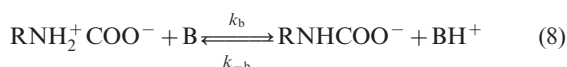
Piperazine and MDEA act as an effective activator in AMP solution, respectively. Its main contribution to absorption of CO_2 is the fact that CO_2 can be transferred through the intermediate to AMP.¹⁹



Also, HMDA, having two amine groups, could act as an effective activator in AMP solution through reaction (3) and reaction (5).

Determination of the reaction rate constant

It is generally accepted that the zwitterion mechanism governs the formation of carbamate for primary and secondary amines. The first step in the reaction of CO_2 with AMP is the formation of an intermediate zwitterion:¹⁴



Based on the zwitterion mechanism and the assumption of quasi-steady-state for the concentration of the zwitterion, the expression for the CO_2 reaction rate is as follows:

$$r_{\text{CO}_2} = \frac{k_2[\text{CO}_2][\text{RNH}_2]}{1 + k_{-1}/\sum k_b[\text{B}]} \text{ kmol m}^{-3} \text{ s}^{-1} \quad (9)$$

When the term $k_{-1}/\sum k_b[\text{B}] \ll 1$, the analysis is simplified to second-order kinetics, and the following equation can be used:

$$r_{\text{CO}_2} = k_2[\text{CO}_2][\text{RNH}_2] \text{ kmol m}^{-3} \text{ s}^{-1} \quad (10)$$

The influence on absorption kinetics of all chemical reactions between dissolved CO_2 and reactants in solution is usually expressed by an "enhancement factor" E over physical absorption:

$$N_A = Ek_L C_A^* \quad (11)$$

E is a function of the Hatta number (Ha) and the instantaneous reaction enhancement factor (E_i) is defined as follows.

$$Ha = \left(\frac{2}{m+1} D_A k_{mn} (C_A^*)^{m-1} C_B^n \right)^{1/2} / k_L \quad (12)$$

$$E_i = \left(\frac{D_A}{D_B} \right)^{1/2} + \left(\frac{D_B}{D_A} \right)^{1/2} \frac{C_B}{ZC_A^*} \quad (13)$$

The experimental conditions were selected to ensure that the absorption of CO_2 in amine solutions was in a region of fast pseudo- mn -order reaction in the range of Ha between 3 and E_i . If the value of Ha is in this range, E becomes equal to Ha , and the following specific absorption rate is obtained.¹⁸

$$N_A = \left(\frac{p_A}{H_A} \right)^{(m+1)/2} \left(\frac{2}{m+1} D_A k_{mn} C_B^n \right)^{1/2} \quad (14)$$

The slope of the straight line fitting the data of $\ln N_A$ versus $\ln p_A$ will give the order of m with respect to the dissolved gas concentration C_A . The order of n with respect to the amine concentration can also be found in an analogous manner by plotting $\ln(N_A/p_A^{(m+1)/2})/(D_A^{1/2}/H_A^{(m+1)/2})$ versus $\ln C_B$. For a fast chemical reaction between the dissolved gas and a reactant, the specific absorption rate is following:

$$N_A = C_A^* \sqrt{D_A k_{ov} C_B} \quad (15)$$

For fast pseudo- mn -order reaction conditions, when the equilibrium pressure of CO_2 contributed by the CO_2 in solutions is small compared to the absorption pressure and where the gas-phase resistance is negligible, the absorption rate is given by eqn (16).^{14,18} After integrating eqn (17), a reaction rate constant (k_2) can be achieved by eqn (18).

$$-\frac{V_g}{RT} \left(\frac{dP_{\text{CO}_2}}{dt} \right) = A_S \sqrt{D_{\text{CO}_2} k_{ov} C_B} \left(\frac{P_{\text{CO}_2}}{H_{\text{CO}_2}} \right) \quad (16)$$

$$-\left(\frac{dn}{dt} \right) = A_S \sqrt{D_{\text{CO}_2} k_{ov} C_B C_A^*} \quad (17)$$

$$\left(\frac{N_A H_A}{\sqrt{D_A P_A}} \right)^2 = k_2 C_B \quad (18)$$

Experimental

An experimental apparatus was constructed to explore the absorption of CO_2 into amine solutions as shown in Fig. 1. CO_2 gas was preheated in a water bath and went through a temperature-controlled and stirred cell reactor. The flow rate of the injected CO_2 gas was controlled by mass flow controller. The stirred cell reactor has an internal diameter of 12.5 cm, a height of 15 cm, and four 5 mm wide glass plates adhered to inner walls of the reactor as a baffle. After the temperature of the reactor became constant, 850 ml of each amine solution was injected into the reactor and well mixed with CO_2 at a stirrer speed of 150 rpm by using a two-blade impeller (60 mm $\times$ 15 mm) immersed in the amine solution. AMP (Acros Organics) was used as a main amine solution, and HMDA (Junsei Chemical), MDEA (Tokyo Kasei Kogyo), and piperazine (Acros Organics) were used as additives. Purities

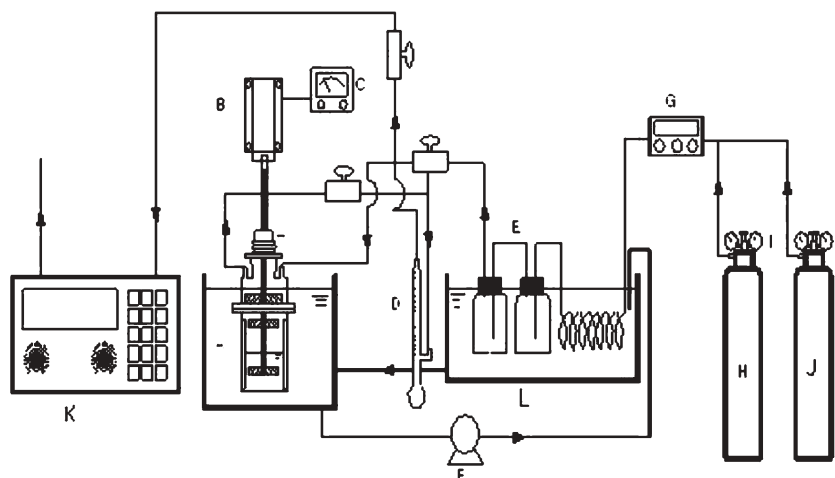


Fig. 1 Schematic of an experimental apparatus: A. stirred-cell reactor, B. motor, C. controller, D. soap bubble meter, E. saturation, F. circulation, G. mass flow controller, H. CO₂ cylinder, I. gas regulator, J. N₂ cylinder, K. CO₂ analyzer, L. water bath.

of all absorbents were 99%. Also, high purity CO₂ and N₂ (99.99%) gases were used. The concentrations of absorbents are presented in Table 1.

The stirred cell reactor operated with a smooth and horizontal gas–liquid interface. An interfacial area between gas and liquid was determined as 122.7 cm². The flow rate of the effluent CO₂ gas was measured by a bubble meter. Hence, the amount of CO₂ absorbed into each amine with time was determined by the difference between the inlet and outlet flow rate of CO₂.

Table 1 Unit conversion of each absorbent

Absorbents (wt%)	Conversion/kmol m ⁻³			
	AMP	HMDA	MDEA	Piperazine
1		0.09	0.08	0.12
3		0.26	0.25	0.35
5		0.43	0.42	0.59
30	3.40			

Results and discussion

The CO₂–AMP reaction studied to check the validity of the method was found to be first order with respect to CO₂ and AMP. Literature information confirms this reaction order.^{10,12}

The value of 731 m³ kmol⁻¹ s⁻¹ for the reaction rate constant (*k*₂) at 313 K of the CO₂–AMP reaction obtained in this work was in good agreement with the rate constant values of 369 m³ kmol⁻¹ s⁻¹ and 740 m³ kmol⁻¹ s⁻¹ at 303 K and 313 K, respectively, found by Messaoudi *et al.*¹³

Specific absorption rates (*N_A*, kmol m⁻² s⁻¹) were obtained for the concentrations of each additive (1, 3, and 5 wt%) blended with 30 wt% AMP at several temperatures (303, 313, 323, and 343 K). Their results are summarized in Table 2.

The specific absorption rate of AMP increased by adding every additive. Of the additives used in these tests, HMDA showed the best performance in increasing the specific absorption rate of AMP.

Using the results, the order with respect to the concentration of additives into AMP was determined from eqn (18) by

Table 2 Specific absorption rates of CO₂ into aqueous solutions with additives and temperatures

Temperature absorbents (wt%)	<i>N_A</i> of CO ₂ /kmol m ⁻² s ⁻¹ × 10 ⁵			
	303 K	313 K	323 K	343 K
AMP(30)	3.03	3.75	4.25	4.92
AMP(30)/HMDA(1)	3.15	3.91	4.54	5.31
AMP(30)/HMDA(3)	3.27	4.08	4.81	5.77
AMP(30)/HMDA(5)	3.39	4.25	5.05	6.30
AMP(30)/MDEA(1)	3.08	3.86	4.45	5.13
AMP(30)/MDEA(3)	3.15	3.95	4.60	5.45
AMP(30)/MDEA(5)	3.27	4.07	4.68	5.74
AMP(30)/piperazine(1)	3.09	3.90	4.44	5.17
AMP(30)/piperazine(3)	3.21	4.03	4.63	5.57
AMP(30)/piperazine(5)	3.34	4.18	4.89	6.02

plotting (*N_AH_A/D_A^{0.5}/P_A*)² with the concentration of each additive. The values of *D_A* and *H_A* were obtained from the literature.²⁰ These plots shown in Fig. 2, 3, and 4 show straight lines (correlation coefficient >0.95) with a slope of 1.

Reaction rate constants (*k*₂) for each additive were obtained by plotting (*N_AH_A/D_A^{0.5}/P_A*)² with the concentration of each

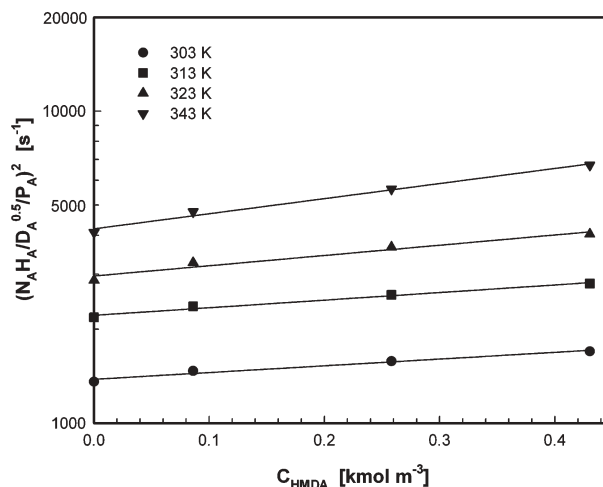


Fig. 2 Determination of a reaction order with respect to the concentration of HMDA at different temperatures.

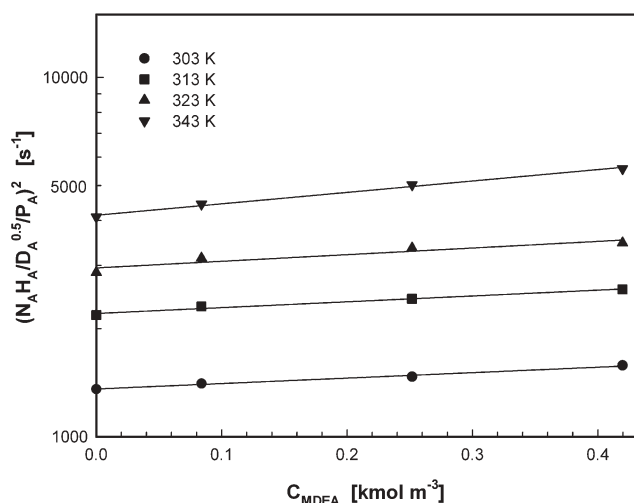


Fig. 3 Determination of a reaction order with respect to the concentration of MDEA at different temperatures.

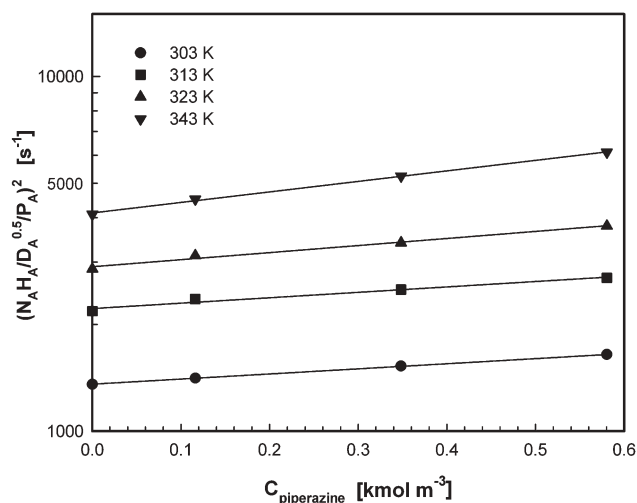


Fig. 4 Determination of a reaction order with respect to the concentration of piperazine at different temperatures.

additive at four different temperatures of 303, 313, 323, and 343 K as shown in Fig. 5. The calculated reaction rate constants (k_2) showed 1393, 882, and 859 $\text{m}^3 \text{kmol}^{-1} \text{s}^{-1}$ at 313 K for the additives of HMDA, MDEA, and piperazine blended with 30 wt% AMP respectively. These values are about 91%, 21%, and 18% higher than that of 731 $\text{m}^3 \text{kmol}^{-1} \text{s}^{-1}$ for AMP without an additive. This indicates that each additive acts as an effective activator in AMP solution due to its own absorption mechanism as mentioned reaction (3)–(6). It clearly shows that the absorption rate of CO_2 into AMP can be increased by the use of additives such as HMDA, MDEA, and piperazine, and the use of HMDA as an additive could mostly increase the absorption rate of AMP among three additives used in these tests.

Fig. 6 shows the correlation between the reaction rate constant and temperature by using the data presented in Table 3.

The values of activation energy obtained from the Arrhenius plots were 45, 41, and 42 kJ mol^{-1} for HMDA, MDEA, and piperazine blended with 30 wt% AMP respectively. The values

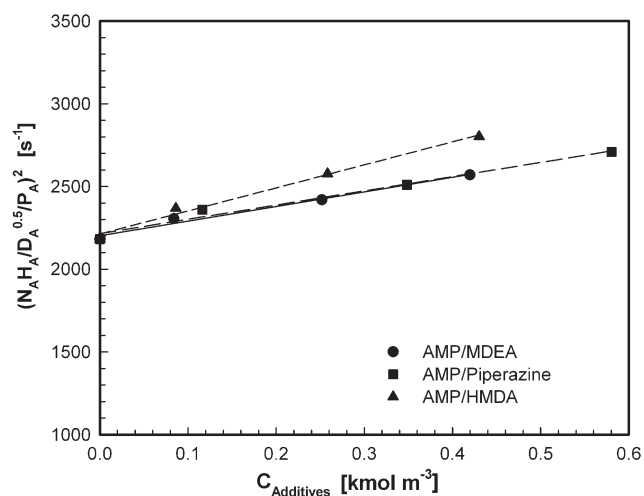


Fig. 5 Effect of additives concentration on $(N_A H_A / D_A^{0.5} P_A)^2$ at 313 K.

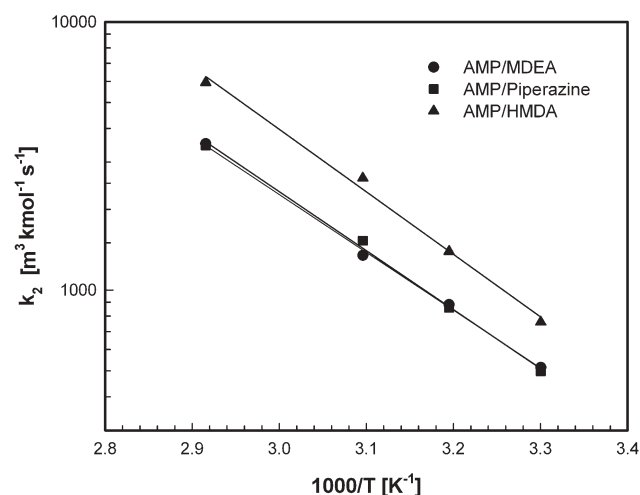


Fig. 6 Arrhenius plots for determining reaction rate constants.

Table 3 Reaction rate constants for each additive at different temperatures

Temperature/K	$k_2/\text{m}^3 \text{kmol}^{-1} \text{s}^{-1}$		
	AMP/HMDA	AMP/MDEA	AMP/Piperazine
303	760	515	498
313	1393	882	859
323	2615	1347	1527
343	5938	3515	3456

of activation energy of 41–45 kJ mol^{-1} closely matches with the values of 41.7 kJ mol^{-1} and 43 kJ mol^{-1} reported by Alper¹⁰ and Saha *et al.*¹²

Conclusions

The addition of HMDA, MDEA and piperazine into AMP increases their reaction rate constants by 91%, 21%, and 18% as compared to AMP without an additive. Of three blended amines used in these tests, a blend of HMDA and AMP can show the highest reaction rate for CO_2 removal, and its

reaction rate constant was given by $k_H = 3.84 \times 10^{10} \exp(-5361/T)$.

Abbreviations

A_s	interfacial area of gas in contact with liquid/m ²
C_A^*	dissolved gas concentration in equilibrium at the gas-liquid interface(= p_A/H_A)/kmol m ⁻³
C_B	total amine concentration/kmol m ⁻³
D_A	diffusion coefficient of gas in liquid/m ² s ⁻¹
D_B	diffusion coefficient of reactants in liquid/m ² s ⁻¹
E	enhancement factor
Ha	Hatta number
H_A	Henry's law constant/kPa m ³ kmol ⁻¹
k_{-1}	reverse first-order reaction rate constant/s ⁻¹
k_2	second-order reaction rate constant/m ³ kmol ⁻¹ s ⁻¹
k_b	second-order reaction rate constant for base B/m ³ kmol ⁻¹ s ⁻¹
k_L	liquid-phase mass transfer coefficient of CO ₂ in amine/m s ⁻¹
k_{ov}	overall pseudo-first-order reaction rate constant/s ⁻¹
N_A	specific absorption rate/kmol m ⁻² s ⁻¹
P_A	CO ₂ partial pressure/kPa
R	gas constant/J mol ⁻¹ K ⁻¹
T	temperature/K
V_g	gas volume/m ³

Acknowledgements

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Multi-functional zwitterionic compounds as new membrane materials for separating olefin–paraffin mixtures†

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Various types of multi-functional zwitterionic compounds containing both ester and sulfonate groups were prepared and their silver nitrate salts were tested as carriers for facilitated olefin transport membranes in the separation of ethylene–ethane and propylene–propane mixtures. Ester group-containing multi-functional zwitterionic silver compounds exhibited much higher performances in comparison with methyl group-containing zwitterionic compounds. A FT-IR study showed that ester-containing zwitterionic compounds interact with silver ions through both sulfonate and ester functional groups.

Introduction

Olefin–paraffin separation, one of the most important processes in the petrochemical industry, is being carried out using a highly energy-intensive low temperature distillation. Accordingly, there have been many reports on alternative processes to replace the current low temperature process.^{1–7} Among a number of alternative separation processes, silver-based facilitated transport through a perfluorosulfonated ionomer membrane such as Nafion has been considered as the most promising alternative due to the high stability and excellent performance of the ionomer membrane in separating olefins from paraffin mixtures. Unfortunately, however, ionomer membranes require costly and complicated preparation steps, which limit the commercial application of these membranes.^{8–12}

Recently, we have shown that ionic liquid-based zwitterionic compounds with a covalently bound sulfonate group could be used in place of Nafion in the separation of C₂–C₅ olefin–paraffin mixtures.^{13,14} Continuing our line of our study to develop cost effective and high performance membrane materials based on ionic liquids, we report here on the synthesis and characterization of a series of multi-functional zwitterionic compounds containing both ester and sulfonate groups, and their utilization in the facilitated transport membranes for the separation of ethylene–ethane and propylene–propane mixtures.

Experimental

Method and materials

All manipulations were carried out under an argon atmosphere unless otherwise stated. Solvents were distilled over appropriate

drying agents prior to use. Imidazole (99%), 2-methylimidazole (99%), 1-(2-hydroxyethyl) pyrrolidine (97%), 4-(2-hydroxyethyl) morpholine (99%), methylchloroacetate (98%), acetyl chloride (98%), sodium hydride (dry, 99%), 1,3-propanesultone (99+%), and AgNO₃ were purchased from Aldrich Chemical Co. and used as received. Zwitterionic compounds, **1a–c** and **2a–c** were prepared according to the literature procedures.^{15–17} Ethylene, ethane, propylene, propane, 1-butene, isobutylene, and 1,3-butadiene were obtained from Sinyang Gas Co. Gas chromatographic analyses of feed mixtures and permeates were made on a Gaw-Mac gas chromatograph equipped with a TCD and Unibead 2S 60/80 column.

Synthesis of 1-(methoxy carbonyl methyl) imidazolium-3-(propyl sulfonate), **2a**

A solution of imidazole (6.8 g, 100 mmol) in 100 mL DMF was added dropwise at room temperature into a 250 mL flask containing sodium hydride (2.6 g, 110 mmol) in 50 mL of anhydrous DMF. The mixture was then heated to 60 °C and reacted for 1 h at that temperature. After the reaction, excess NaH was filtered to give a yellowish solution. To this solution, methyl chloroacetate (10.8 g, 100 mmol) was added slowly at room temperature over a period of 30 min. After 3 h, the sodium chloride precipitates were removed by filtration and the resulting solution containing methyl imidazole-1-yl-acetate was reacted with 1,3-propanesultone (12.8 g, 105 mmol) overnight at 80 °C. After the reaction, DMF was removed under vacuum and the solids were collected, washed with acetone (100 mL), then dried under vacuum to give **2a** (18.8 g, 71%). Elemental analysis calcd (%) for C₉H₁₄N₂O₅S: C, 41.2; H, 5.4; N, 10.7. Found: C, 41.6; H, 5.2; N, 11.0. ¹H NMR (300 MHz, D₂O, 25 °C): δ (ppm) = 9.22 (s, 1H, CHN), 7.87 (d, 1H, CHN), 7.77 (d, 1H, CHN), 5.06 (s, 2H, CH₂N), 4.30 (t, 2H, CH₂), 3.70 (s, 3H, OCH₃), 2.81 (t, 2H, SCH₂), 2.22 (m, 2H, CH₂).

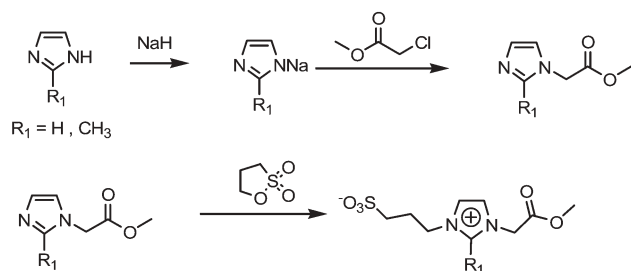
Synthesis of N-(2-acetoxyethyl) pyrrolidinium-N-(propyl sulfonate), **2b**

The title compound was prepared in three steps: To a solution of 1-(2-hydroxyethyl) pyrrolidine (11.5 g, 100 mmol) in 150 mL

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Scheme 1 Synthetic scheme of 1-(methoxy carbonyl methyl) imidazolium-3-(propyl sulfonate).

acetone, acetyl chloride (9.4 g, 120 mmol) was added dropwise at 0 °C and reacted overnight with a vigorous stirring. Then the hygroscopic white precipitated chloride salt was collected, washed several times with acetone and neutralized with 1 equivalent of sodium hydroxide in 100 mL acetonitrile in the presence of MgSO_4 . After filtering off the solids, the solution of 2-(1-pyrrolidinyl)ethyl acetate in acetonitrile was reacted with 1,3-propanesultone (13.5 g, 110 mmol) overnight at reflux to give white precipitates. The precipitates were recovered, washed with acetonitrile several times, dried under vacuum, and stored in a globe-box for further use. The isolated yield for the whole process was about 58%. Elemental analysis calcd (%) for $\text{C}_{11}\text{H}_{21}\text{NO}_5\text{S}$: C, 47.3; H, 7.6; N, 5.0. Found: C, 48.1; H, 7.4; N, 5.3. ^1H NMR (300 MHz, D_2O , 25 °C): δ (ppm) = 4.52 (t, 2H, OCH_2), 3.75 (t, 2H, NCH_2), 3.51 (t, 4H, CH_2NCH_2), 3.45 (m, 2H, CH_2), 2.98 (t, 2H, NCH_2), 2.28–2.19 (m, 6H, SCH_2 , CH_2CH_2), 2.15 (s, 3H, COCH_3).

N-(2-acetoxyethyl)morpholinium-*N*-(propyl sulfonate), **2c** was prepared in a manner analogous to that used for preparing **2b**.

FT-IR experiments. The samples for FT-IR experiments were prepared by coating an aqueous solution of 10 wt% **2b** and AgNO_3 (molar ratio of **2b**/ AgNO_3 = 1 : 1) onto a 25 × 3 mm KRS-5 or CaF_2 window. The coated window was vacuum-dried for 2 h at room temperature. The coated and uncoated windows were placed in a specially designed gas cell and then the cell was heated to 80 °C for 1 h under vacuum to remove remaining water.^{18–20} FT-IR spectra were recorded on a Mattson Infinity spectrophotometer.

Performance of membranes. Composite membranes were prepared by casting an aqueous solution containing a zwitterionic compound (2.0 mmol) and AgNO_3 (2.0 mmol) in 0.5 mL H_2O onto a polyester microporous membrane support (0.1 μm , 47 mm, Whatman Industries Inc.) using a coater knife. The coated membrane was dried in an oven at

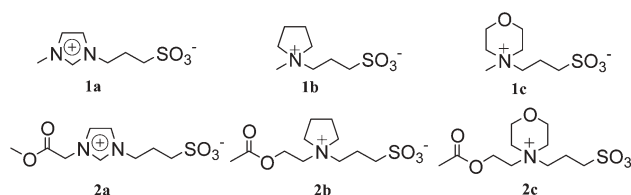


Fig. 1 Structures of zwitterionic compounds.

room temperature for 12 h under a stream of nitrogen, and then further dried in a vacuum oven at 40 °C for 24 h.

Separation measurements were performed with membranes placed in a stainless steel separation module with an olefin–paraffin (50 : 50) mixture gas as described elsewhere.²¹ The flow rates of feed mixtures were controlled using mass flow controllers. The total feed pressure of mixed gas was set at 20 psig by a back pressure regulator. The permeated gases were analyzed using a Gaw-Mac gas chromatograph equipped with a TCD and Unibead 2S 60/80 column.

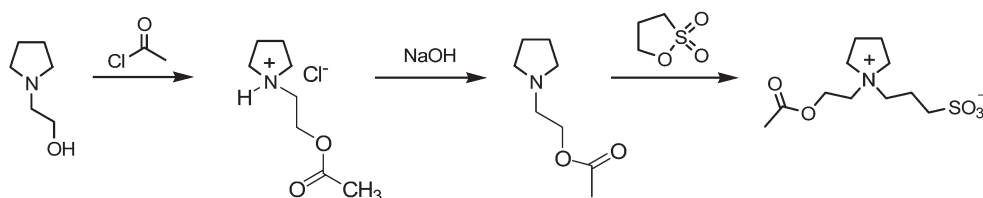
Results and discussion

The basis of the facilitated olefin transport is the reversible complexation of olefins with silver ions.^{22,23} It is well known that the reversible interaction of an olefin with a silver salt (Ag-X) and the consequent facilitated olefin transport through the membrane increase with the increase of Ag-X distance, in other words, with increasing dissociation of AgX to Ag^+ and X^- .^{24,25} The silver salt with a longer Ag-X distance such as AgBF_4 should provide more room for the olefin to complex with silver ions. In the polymer–silver salt membranes, the Ag-X distance, or the dissociation of AgX can be increased to a certain extent by the interaction of silver ion with oxygen atoms in the polymer back bone.^{24,26} Likewise, in the ionomer membranes, it is expected that the presence of an oxygen-containing functional group in the zwitterionic compound could facilitate the dissociation of silver salt.

For this reason, we have prepared various types of multifunctional zwitterionic compounds with an ester group as shown in Schemes 1 and 2. All the zwitterionic compounds used in this study are presented in Fig. 1.

To confirm the multiple interactions of silver ions with zwitterionic compounds bearing ester and sulfopropyl groups, we have conducted a FT-IR spectroscopic investigation of the interaction of AgNO_3 with **2b**.

As shown in Fig. 2, the peak associated with the free carbonyl group of **2b** at 1742.5 cm^{-1} shifted to lower frequencies at 1740.1 and 1739.1 cm^{-1} , upon interaction with 1.0 and 2.0 equivalents of AgNO_3 , respectively. Likewise, the



Scheme 2 Synthetic scheme of *N*-(2-acetoxyethyl) pyrrolidinium-*N*-(propyl sulfonate).

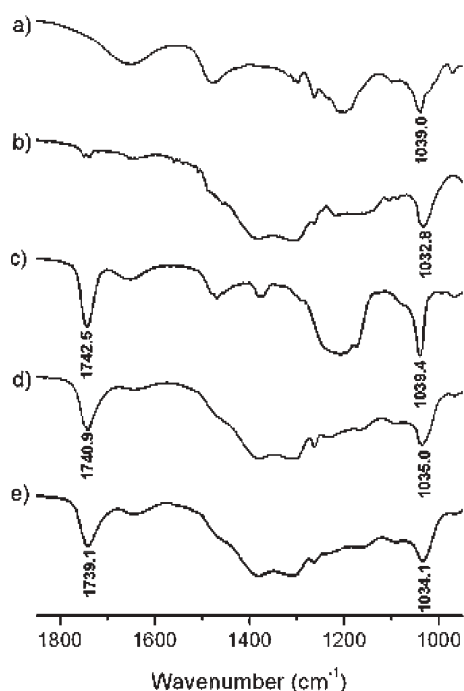


Fig. 2 FT-IR spectra showing the interaction of zwitterionic compounds with AgNO_3 : (a) **1b**, (b) **1b** + AgNO_3 ($\text{AgNO}_3/\mathbf{1b} = 1$), (c) **2b**, (d) **2b** + AgNO_3 ($\text{AgNO}_3/\mathbf{2b} = 1$), (e) **2b** + AgNO_3 ($\text{AgNO}_3/\mathbf{2b} = 2$).

stretching frequency assigned to the S=O double bond of the sulfonate functional group moved to a lower frequency from 1039.4 to 1035.0 and 1034.1 cm^{-1} with the increasing concentration of AgNO_3 .

It is worth mentioning here that the peak corresponding to S=O group of **2b** bearing an ester group shifted to a smaller extent from 1039.4 to 1035.0 cm^{-1} in comparison with that of the S=O group of **1b** with a methyl group from 1039.0 to 1032.8 cm^{-1} upon interaction with an equimolar amount of AgNO_3 . This result is a clear indication that silver ions interact not only with sulfonate groups but also with ester groups. Such an additional interaction could facilitate the dissociation of AgNO_3 to Ag^+ and NO_3^- as well as stabilizing sulfonate-bound silver ions.

The interactions of olefin with silver ions bound to a sulfopropyl group were also investigated with a film prepared from **2b** and AgBF_4 . To more clearly see the coordination of olefin by avoiding the peak overlaps caused by the NO_3^- group, AgBF_4 was used in place of AgNO_3 . Fig. 3a and 3b shows the interaction of AgBF_4 with **2b**. The peak associated with the carbonyl group shifted to a much lower frequency than that observed in the interaction between AgNO_3 with **2b**. This result can be rationalized by the larger dissociation constant of AgBF_4 compared with that of AgNO_3 . When the film, AgBF_4 -**2b** was exposed with 20 psi of propylene followed by N_2 purge, the peak corresponding to coordinated propylene appeared at 1587 cm^{-1} (Fig. 3c). The coordinated propylene peak was easily replaced by the peaks at 1556 and 1587 cm^{-1} upon contact with 1,3-butadiene followed by N_2 purge (see Fig. 3d). The presence of the two peaks for coordinated 1,3-butadiene suggests that there are two different bonding modes in the coordination of 1,3-butadiene to silver ions: η^2 - and η^4 - modes.

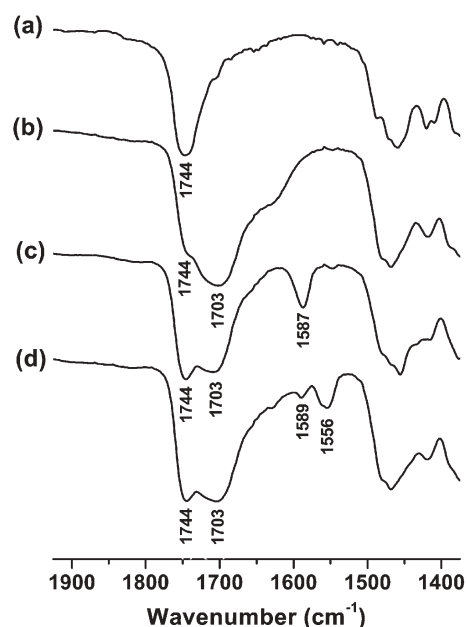


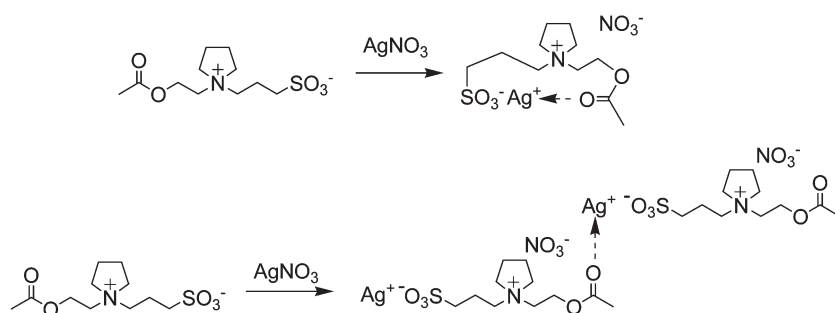
Fig. 3 FT-IR spectra showing the interaction of AgBF_4 with **2b** and olefin: (a) **2b**, (b) **2b** + AgBF_4 ($\text{AgNO}_3/\mathbf{2b} = 1$), (c) (b) + propylene + N_2 purge, (d) (c) + 1,3-butadiene + N_2 purge.

To see the effect of the multi-interactions and reversible olefin coordination on the facilitated olefin transport, zwitterionic compounds bearing an ester group, **2a–2c** were employed as membrane materials for the separation of ethylene–ethane and propylene–propane mixtures.

The composite membranes were prepared by casting an aqueous solution of a zwitterionic compound and a silver salt (AgNO_3) on top of porous polyester supports. Only defect-free membranes were used for the separation measurements. It is assumed that the membranes are defect-free when the gas (N_2) permeance is too low to be measured using a bubble flow meter, approximately lower than 0.1 GPU. In the beginning, one out of seven membranes was found to have a defect, possibly due to the presence of small dusts or insoluble impurities present in the casting solution. However, such a membrane defect could be prevented by filtering a casting solution using a syringe filter.

The performances of membranes containing a zwitterionic compound with an ester group **2a–2c** were investigated and compared with those of membranes containing a zwitterionic compound with a methyl group, **1a–1c**. Fig. 2–3 show the changes of selectivity of ethylene over ethane and propylene over propane with time at room temperature. The composite membranes containing **2a–2c** exhibited much higher selectivities compared with those containing corresponding methyl-substituted zwitterionic compounds, **1a–1c**. These results indicate that the performance of membranes is strongly influenced by the presence of an ester group. The higher selectivity for **2a–2c** is likely due to the additional interaction of silver ions bound to a sulfopropyl group with an ester group inter- or intra-molecularly, thereby facilitating the dissociation of AgNO_3 as shown in Scheme 3.

In the separation of propylene–propane mixtures, the performance of the membranes based on **1a–1c** was significantly



Scheme 3 Additional interaction of a silver ion bound to a sulfopropyl group with an ester group.

affected by the types of cations of zwitterionic compounds, but the membranes containing **2a–2c** showed similar performance irrespective of the types of zwitterionic compounds. In contrast, such a cation effect was less pronounced in the separation of ethylene–ethane mixtures. As can be seen in Fig. 4–5, the selectivities of ethylene over ethane were higher than those of propylene over propane. The reason for this is not clear at the moment, but it is most likely due to the difference in binding ability between ethylene and propylene. The methyl group on the propylene could limit the access

of propylene to the silver ion bonded to zwitterionic compounds.

Measurements of flux values of permeated gases were made approximately after 0.5 h of separation using a bubble flow meter. However, as can be seen in Fig. 6–7, steady states were attained after 2.5 and 5 h for **2a–2c** and **1a–1c**, respectively. As in the case of selectivity, the membranes containing a zwitterionic compound bearing an ester group, **2a–2c** exhibited higher fluxes than those bearing a methyl group, **1a–1c**. It

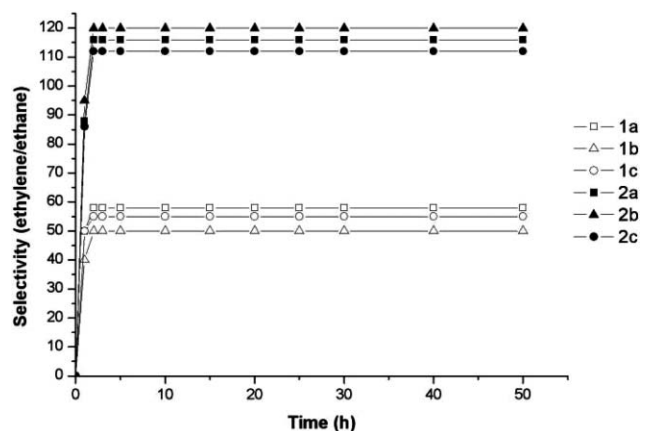


Fig. 4 Change of selectivity of ethylene over ethane with time for various membranes containing zwitterionic silver complexes.

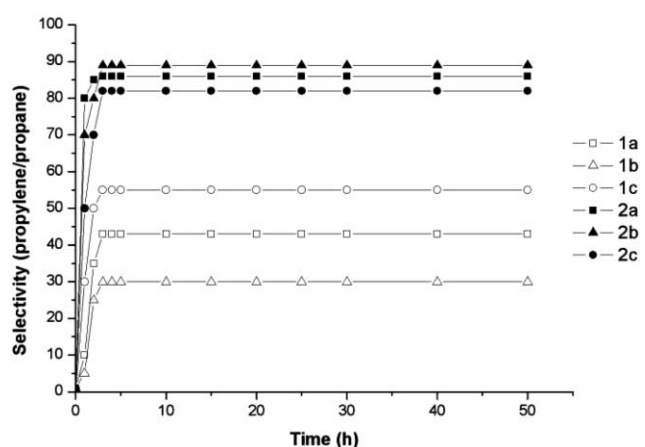


Fig. 5 Change of selectivity of propylene over propane with time for various membranes containing zwitterionic silver complexes.

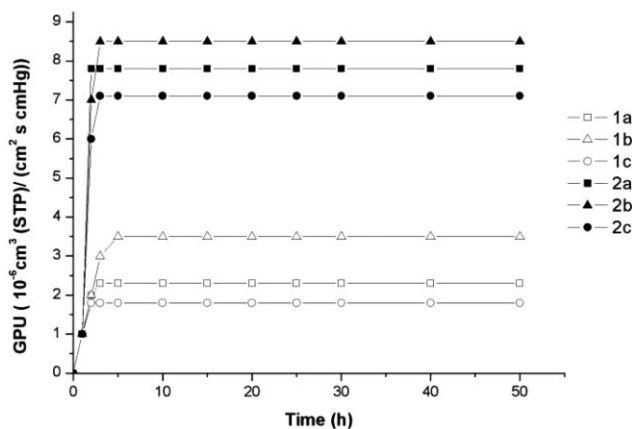


Fig. 6 Change of flux of permeated ethylene–ethane mixtures with time for various membranes containing zwitterionic silver complexes.

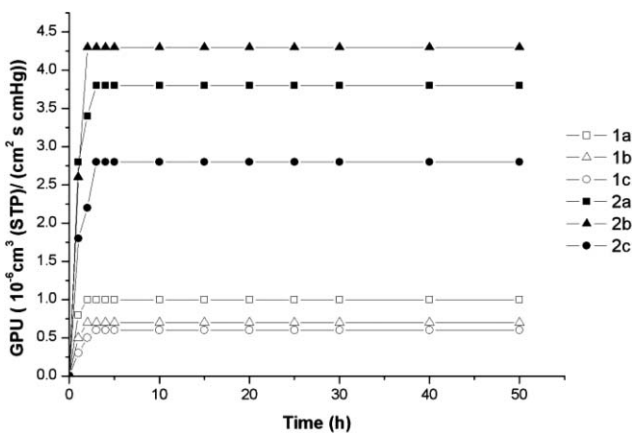


Fig. 7 Change of flux of permeated propylene–propane mixtures with time for various membranes containing zwitterionic silver complexes.

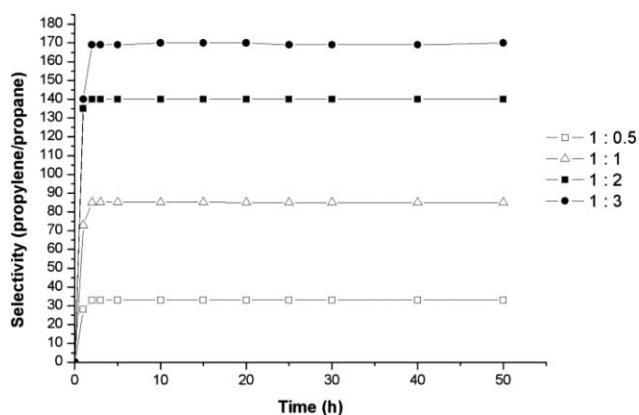


Fig. 8 Effect of molar ratio of $\text{AgNO}_3/2\mathbf{a}$ on the selectivity of propylene over propane through a membrane containing $2\mathbf{a}$.

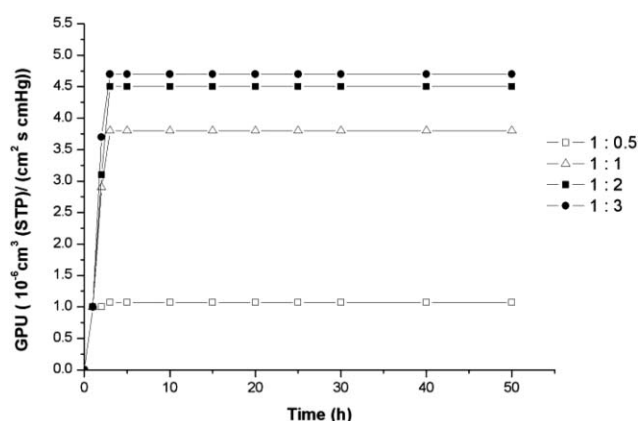


Fig. 9 Effect of molar ratio of $\text{AgNO}_3/2\mathbf{a}$ on the flux of permeated propylene–propane mixtures through a membrane containing $2\mathbf{a}$.

should be pointed out that the performances of membranes based on $2\mathbf{a}$ – $2\mathbf{c}$ are comparable to that of costly Nafion-based membranes in terms of selectivity and flux.^{12,27}

The effect of AgNO_3 concentration on the separation of propylene–propane mixtures was investigated. As shown in Fig. 8 and 9, the selectivity of propylene over propane and the flux increased rapidly with increasing molar ratio of $\text{AgNO}_3/2\mathbf{a}$ up to 2, but thereafter increased slowly. It is likely that, at higher molar ratio above 2, the formation of ion pairs and or aggregates seems to be facilitated, thereby limiting the utilization of silver ions to complex with propylene.^{24,28}

The performances of membranes for separating ethylene–ethane and propylene–propane mixtures were maintained throughout the experiments, demonstrating the stability of zwitterionic silver complexes toward the reduction of silver ions. Such a high stability of the membranes consisting of zwitterionic compounds, $2\mathbf{a}$ – $2\mathbf{c}$ and AgNO_3 can be ascribed to the multi-interaction of silver ions with sulfonate and ester groups of zwitterionic compounds.

It should be pointed out here that the ionomer membranes containing zwitterionic silver complexes as carriers are much easier to prepare and are more cost effective compared with the conventional fluorinated ionomer membranes. More importantly, the membranes containing zwitterionic silver

complexes are highly effective for separating olefins from paraffin mixtures.

Conclusions

Multi-functional zwitterionic compounds with an ester group were successfully introduced as new membrane materials to replace perfluorinated ionomer membranes such as Nafion, which are costly and difficult to prepare. Furthermore, the performances of membranes based on zwitterionic compounds with an ester group in separating olefin–paraffin mixtures were considerably higher than those containing corresponding methyl-substituted zwitterionic compounds, possibly due to the additional interaction of silver ion with an ester group.

It is expected that our results will provide valuable information to those interested in developing new types of ionic liquids and their applications in facilitated transport membranes for olefin–paraffin separation.

Acknowledgements

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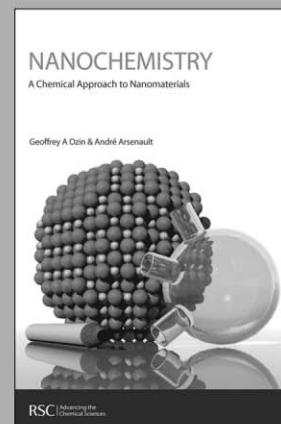
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Chemical kinetics of carbon dioxide with glycidyl methacrylate using immobilized tributylamine supported on poly(styrene-co-vinylbenzyl chloride) as a catalyst†

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A soluble copolymer-supported catalyst containing pendant tributylammonium chloride was synthesized by the radical copolymerization of *p*-chloromethylated styrene followed by the addition reaction of the resulting copolymer with tributylamine. The absorption rate of carbon dioxide was measured from the absorption experiment into glycidyl methacrylate (GMA) solutions containing the catalyst in a semi-batch stirred tank with a plane gas–liquid interface at 0.1013 MPa. The reaction rate constants of the reaction between carbon dioxide and GMA were obtained by the analysis of the mass transfer mechanism accompanied by chemical reactions based on the film theory.

Solvents such as toluene, *N*-methyl-2-pyrrolidinone, and dimethyl sulfoxide influenced the reaction rate constants. Furthermore, this catalyst was compared to the monomeric tetrabutyl-ammonium chloride under the same reaction conditions.

Introduction

The chemical fixation of carbon dioxide has received much attention in view of environmental problems. An attractive strategy to deal with this situation is converting CO₂ into valuable substances.¹ The reaction of carbon dioxide with oxiranes leading to 5-membered cyclic carbonates is well known.¹ These cyclic carbonates can be used as polar aprotic solvents, electrolytes for batteries and sources for reactive polymers.²

The synthesis of cyclic carbonates by the reaction of CO₂ with oxirane has been performed using Lewis acids, transition metal complexes, and organometallic compounds as catalysts at high pressure such as 10–50 atm.^{3,4} Some articles reported the synthesis of 5-membered cyclic carbonates under mild conditions at atmospheric pressure in the presence of metal halides or quaternary onium salts.^{5–7}

Quaternary onium salts are bound to polymer resins⁶ such as styrene–divinyl benzene related resins, which is used as an ion-exchange resin support.⁸ The polymer-supported catalysts can be easily separated from reaction mixtures and can be reused.

The reported papers about oxirane–CO₂ reactions^{3–7} have focused only on the study of the reaction mechanism, the overall reaction kinetics, and the effect of the catalyst on the conversion. However, the diffusion⁹ of solutes in the gas–liquid heterogeneous system accompanied by chemical reactions may affect the analysis of the reaction kinetics such as the oxirane–CO₂ reaction.

In our previous work,^{10–12} we studied the kinetics in the reaction between CO₂ and glycidyl methacrylate (GMA) using 18-crown-6, Aliquat 336, and tetrabutylammonium bromide as a catalyst in series. We presented the reaction rate constants as a combined form using the pseudo-first-order reaction method based on the reaction mechanism⁴ with two steps. In this study, the same reaction was performed using two kinds of catalysts such as monomeric tetrabutylammonium chloride (TBAC) and immobilized tributylammonium chloride. We prepared the immobilized tributylammonium chloride catalyst (poly-cat) using the soluble copolymer of styrene and vinylbenzyl chloride, and determined the reaction rate constants using the measured absorption rate of CO₂ and the mass transfer mechanism of CO₂ accompanied by chemical reactions. Effect of solvents such as toluene, *N*-methyl-2-pyrrolidinone (NMP), and dimethyl sulfoxide (DMSO) on the catalytic activities was observed.

To focus our work on green chemistry,¹³ we selected carbon dioxide as an appropriate starting material by fixation with GMA. We used a polymer-supported catalyst as a preferred catalyst for reduction of the energy requirement for the synthesis of 5-membered cyclic carbonate by lowering the reaction pressure from 50 atm to 1 atm. Also, the reaction kinetics were selected for maximum incorporation of the reactants into the final product by controlling the conversion of CO₂ using the reaction rate constants.

Theory

The overall reaction⁷ between CO₂ (A) and GMA (B) using poly-cat (QX) at atmospheric pressure to form (2-oxo-1,3-di oxolan-4-yl) methacrylate (DOMA, C) is proposed as follows:



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The overall reaction in eqn (1) with the rate-determining step of the attack of the anion part of the catalyst to GMA,⁷ is assumed to consist of two steps⁴ as follows:

(i) A reversible reaction between B and QX to form an intermediate complex (C_1), (ii) an irreversible reaction between A and C_1 to form QX and five-membered cyclic carbonate(C)



The reaction rate (r_A) of CO_2 , under the condition of steady-state approximation, in the formation of C_1 is presented as follows:

$$r_A = \frac{C_B Q_o}{\frac{1}{k_1} + \frac{k_2}{k_1 k_3 C_A} + \frac{C_B}{k_3 C_A}} \quad (4)$$

where Q_o is total concentration of catalyst.

If the value of k_1 is very large, eqn (4) is arranged to

$$r_{Af} = \frac{C_A C_B Q_o}{\frac{1}{K_1 k_3} + \frac{C_B}{k_3}} \quad (5)$$

where K_1 is the reaction equilibrium constant defined as k_1/k_2 . Species B is a nonvolatile solute, which is dissolved into the liquid phase prior to its introduction into the gas absorber. It is assumed that gas phase resistance to absorption is negligible by using pure species A, and thus, the concentration of species A at the gas–liquid interface corresponds to equilibrium with the partial pressure of species A in the bulk gas phase.

Under the assumptions mentioned above, the mass balances of species A and B, using the film theory accompanied by a chemical reaction and the boundary conditions, are given as follows:

$$D_A \frac{d^2 C_A}{dz^2} = r_{Af} \quad (6)$$

$$D_B \frac{d^2 C_B}{dz^2} = r_{Af} \quad (7)$$

$$z=0; \quad C_A = C_{Ai}; \quad \frac{dC_B}{dz} = 0 \quad (8)$$

$$z = z_L; \quad C_A = C_{AL}; \quad C_B = C_{Bo} \quad (9)$$

where C_{Ai} and C_{AL} are concentrations of CO_2 at the interface of gas–liquid and in the bulk liquid phase, respectively.

If the diffusion rate of A is not smaller than the reaction rate and the amount of the dissolved A that reacts in the diffusion film adjacent to the phase boundary compared to that which reaches the bulk liquid phase in the unreacted state is negligible, the concentration of A in the bulk liquid phase is a finite quantity (C_{AL}). C_{AL} can be obtained from the following equation:⁹

$$k_L a_V (C_{Ai} - C_{AL}) = \frac{C_{AL} C_{Bo} Q_o}{\frac{1}{K_1 k_3} + \frac{C_{Bo}}{k_3}} \quad (10)$$

The enhancement factor of CO_2 (β), defined as the ratio of the flux of CO_2 with chemical reaction to that without chemical reaction, is shown as follows:

$$\beta = - \left. \frac{da}{dx} \right|_{x=0} \quad (11)$$

where $a = C_A/C_{Ai}$, $x = z/z_L$

Eqn (6) and (7) is not solved if the reaction rate constants, such as k_1 , k_2 , and k_3 , are not known. The pseudo-first-order reaction method⁹ is used in the following situation to obtain the reaction rate constants.

If the concentration of B is constant as C_{Bo} , the reaction between CO_2 and GMA is assumed to be pseudo-first-order with respect to the concentration of CO_2 , and r_{Af} of eqn (5) is given by

$$r_{Af} = k_o C_A \quad (12)$$

where k_o is pseudo-first-order reaction rate constant.

The k_o expressed as $C_{Bo} Q_o / [1/(K_1 k_3) + C_{Bo}/k_3]$ rearranges to

$$\frac{Q_o C_{Bo}}{k_o} = \frac{1}{K_1 k_3} + \frac{C_{Bo}}{k_3} \quad (13)$$

The mass balance of species A with the film theory accompanied by a pseudo-first-order reaction is given by

$$D_A \frac{d^2 C_A}{dz^2} = k_o C_A \quad (14)$$

From the exact solution of eqn (14), β is presented as follows:

$$\beta = \frac{Ha}{\tanh Ha} \quad (15)$$

where Ha is the Hatta number, $\sqrt{k_o D_A} / k_L$

Experimental

Chemicals

All chemicals were of reagent grade and were used without further purification. Purity of both CO_2 and N_2 was more than 99.9%. GMA, styrene (ST), vinylbenzyl chloride (VBC), and 2,2'-azobisisobutyronitrile (AIBN) were supplied by Aldrich chemical company, USA

Absorption procedure

The flow rate of outlet gas was measured using a mass flow meter (Brook Instrument, USA) at GMA concentrations in the range of 0.5–3 $kmol\ m^{-3}$ and a poly-cat of 0.05 $kmol\ m^{-3}$ at a temperature in the range of 80–90 °C in a semi-batch stirred tank (0.075 m inside diameter, 0.13 m height) with a plane gas–liquid interface. C_{AL} is obtained from the difference of flow rate of gas at the inlet and outlet of the absorber at a given absorption time.¹⁴ Flow rate of CO_2 at the inlet was maintained at 50 $cm^3\ min^{-1}$. The experimental procedure used to obtain the absorption rate duplicated in detail the reported approach.¹² The experimental procedure used to obtain the absorption rate closely matched the reported approach.

Table 1 Physical properties of the CO₂/GMA system

Temp./°C	Solvent	μ/cp	$C_{\text{Ai}}/\text{kmol m}^{-3}$	$D_{\text{A}} \times 10^9/\text{m}^2 \text{s}^{-1}$	$D_{\text{B}} \times 10^9/\text{m}^2 \text{s}^{-1}$	$k_{\text{Lo}} \times 10^5/\text{m s}^{-1}$
80	Toluene	0.322	0.0783	9.379	3.665	1.268
	NMP	0.848	0.0711	3.694	1.444	1.204
	DMSO	0.857	0.0612	3.245	1.268	2.595
85	Toluene	0.307	0.0727	9.977	3.898	1.472
	NMP	0.797	0.0679	3.986	1.558	2.285
	DMSO	0.808	0.0576	3.490	1.364	2.864
90	Toluene	0.294	0.0698	10.563	4.128	1.946
	NMP	0.750	0.0629	4.295	1.678	1.998
	DMSO	0.764	0.0544	3.743	1.463	3.110

Preparation of catalyst

The copolymer of ST and VBC was synthesized by the radical copolymerization of VBC (31.3 mol%) with ST (68.7 mol%) using AIBN as an initiator in toluene (100 cm³) at 60 °C for 5 h, and then at 80 °C for 2 h under nitrogen gas, followed by precipitation into methanol and two reprecipitations from tetrahydrofuran (THF) solution into methanol. The VBC unit in the synthesized copolymer was measured by ¹H-NMR and its value was 41 mol%. The copolymer was reacted with tributylamine in dimethylformamide (DMF) at 80 °C for 48 h. The resulting polymer was purified by reprecipitating twice from methanol solution into diethyl ether, and dried at 50 °C under vacuum to obtain the catalyst. The attached amount of N⁺ in the catalyst was measured by elemental analysis and its value was 1.46 mmol g⁻¹ catalyst and the VBC unit with N⁺ in the catalyst was calculated and its value was 26 mol%. The preparation procedure to obtain the soluble polymer-supported catalyst containing pendant tributylammonium chloride residue was reported elsewhere.¹⁵

Physical properties of CO₂ and GMA

Solubility (C_{Ai}) of CO₂ in organic solvents such as toluene, NMP, and DMSO at 0.1013 MPa was obtained by measuring the pressure difference of CO₂ before and after equilibrium between gas and liquid phases, similar to the procedure reported elsewhere.¹⁶ Diffusivity (D_{A} , D_{B}) of CO₂ and GMA in solvent was estimated from the Wilke–Chang equation.¹⁷ Viscosity (μ) of solvent was measured with a Cannon–Fenske viscometer. The viscosity of solvent, solubility, mass transfer coefficient, and diffusivities of CO₂ and GMA in each solvent are given in Table 1.

Analysis of the five-membered cyclic carbonate

The presence of DOMA, which was produced from the reaction between CO₂ and GMA using TBAC and poly-cat, respectively, was confirmed to be the same by instrumental analysis, such as FT-IR (cyclic carbonate C=O peak at 1800 cm⁻¹) and ¹³C-NMR (cyclic carbonate C=O at 160 ppm) spectra.

Results and discussion

The ratio of the absorption rate with reaction to that without reaction in a continuous absorber and the ratio of the liquid-side mass transfer coefficient (k_{L}) of gas with reaction to that without reaction¹⁸ in a semi-batch absorber are used to obtain

the experimental β due to the chemical reaction in gas absorption. In this study, the latter was used and k_{L} was obtained as follows:

The procedure employed to determine k_{L} is based on measuring the amount of gas absorbed, according to:

$$\frac{dC_{\text{AL}}}{dt} = k_{\text{L}} a_{\text{V}} (C_{\text{Ai}} - C_{\text{AL}}) \quad (16)$$

where a_{V} is the specific contact area at the gas–liquid interface, and its value was 14.287 m² m⁻³.

Integrating eqn (16), the graphical representation of $\ln[C_{\text{Ai}}/(C_{\text{Ai}} - C_{\text{AL}})]$ vs. time is obtained from the following equation.

$$\ln[C_{\text{Ai}}/(C_{\text{Ai}} - C_{\text{AL}})] = k_{\text{L}} a_{\text{V}} t \quad (17)$$

Fig. 1 shows typical plots of measured flow rates of gas at outlet against the absorption time in DMSO solution of GMA containing poly-cat and TBAC respectively, at the impeller speed of 50 rev min⁻¹ and 85 °C. As shown in Fig. 1, the measured flow rate increases with increasing absorption time, and decreases with increasing GMA concentration. Also, the flow rate using poly-cat is larger than that using TBAC.

Fig. 2 shows typical plots of $\ln[C_{\text{Ai}}/(C_{\text{Ai}} - C_{\text{AL}})]$ vs. time under the same experimental conditions as those listed in

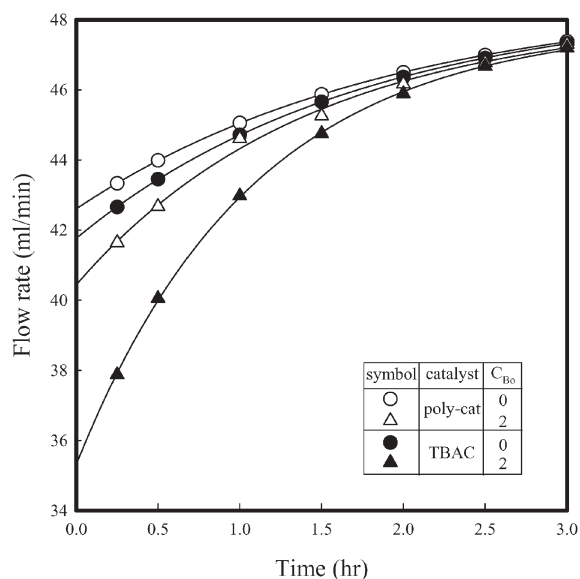


Fig. 1 Flow rate of gas at outlet vs. time in DMSO solution with Q_0 of 0.05 kmol m⁻³ at 80 °C.

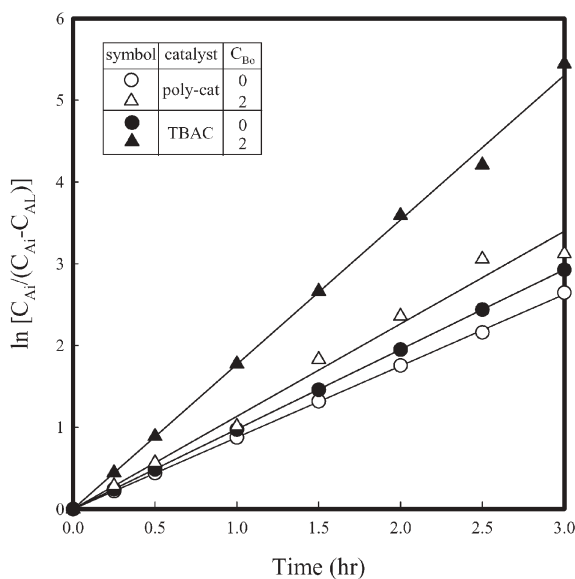


Fig. 2 $\ln [C_{Ai} / (C_{Ai} - C_{AL})]$ vs. time under the same conditions listed in Fig. 1.

Fig. 1. The plots in Fig. 2 show straight lines through the origin, from the slope of which k_L was obtained. The mass transfer coefficients without a chemical reaction (k_{Lo}) are listed in Table 1. The experimental β was obtained from the ratio of k_L to k_{Lo} , and then k_o was obtained from eqn (15).

Fig. 3 shows plots of $Q_o C_{Bo} / k_o$ against C_{Bo} for various solvents; these plots satisfy straight lines. The values of k_3 and K_1 were obtained from the slope and intercept of these straight lines. The values of k_3 and K_1 in toluene, NMP and DMSO at 85 °C were $0.387 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$, $0.138 \text{ m}^3 \text{ kmol}^{-1}$, $1.376 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$, $0.236 \text{ m}^3 \text{ kmol}^{-1}$, $2.057 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$ and $0.3774 \text{ m}^3 \text{ kmol}^{-1}$, respectively.

Using the obtained values of k_3 and K_1 at the given C_{Bo} , Q_o and D_A , eqn (6) and (7) were solved by a finite element method

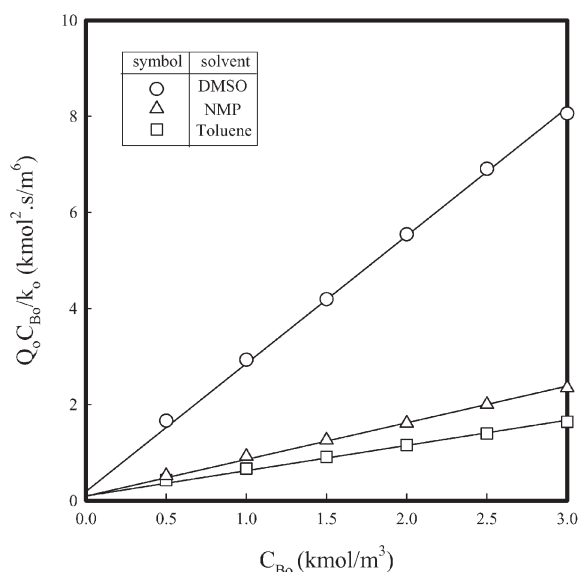


Fig. 3 $Q_o C_{Bo} / k_o$ vs. C_{Bo} for various solvents with a poly-cat of 0.05 kmol m^{-3} at 80 °C.

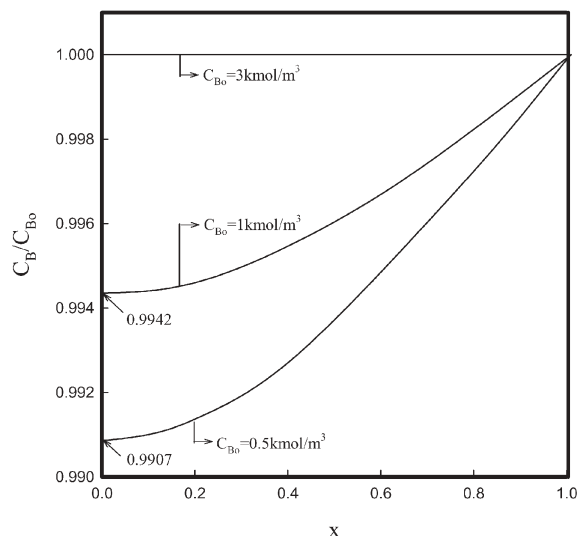


Fig. 4 Dimensionless concentration profile of GMA under the same conditions listed in Fig. 1.

to give the profiles of C_A and C_B . The typical profiles of C_B for various C_{Bo} under the same conditions as those listed in Fig. 1 are shown in Fig. 4. As shown in Fig. 4, the values of C_B / C_{Bo} at the gas–liquid interface were larger than 0.99, from which the reaction between CO_2 and GMA could be assumed to be a pseudo-first-order reaction with respect to the concentration of CO_2 .

The calculated β values were obtained from eqn (11) using the concentration profile of CO_2 . The experimental and calculated values of β were plotted against C_{Bo} as open symbols and solid lines in Fig. 5, respectively. As shown in Fig. 5, the values of β increase with increasing GMA concentration and increased in the order toluene, NMP, DMSO.

The rate constants of an organic reaction in a solvent generally reflect the solvent effect. Various empirical measurements

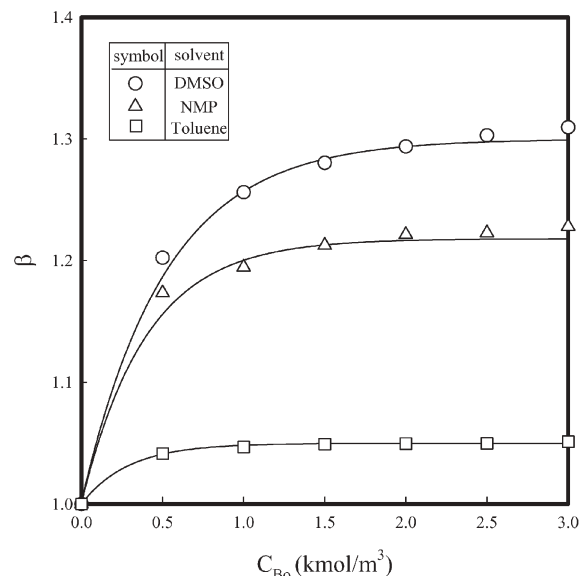


Fig. 5 β vs. C_{Bo} for various solvents with a poly-cat of 0.05 kmol m^{-3} at 85 °C.

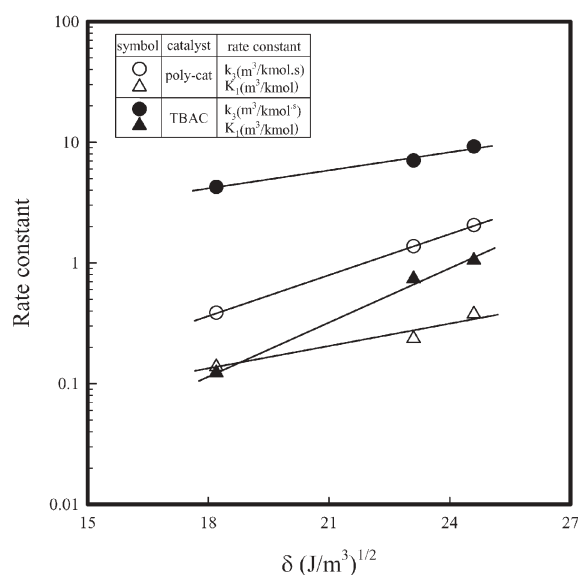


Fig. 6 Relationship between reaction rate constant and solubility parameter of solvent at 85 °C.

about the solvent effect have been proposed to correlate with the reaction rate constant.¹⁹ Some of them have a linear relationship with the solubility parameter (δ) of solvent. Then, using the data of k_3 , K_1 and δ^{20} of toluene, NMP and DMSO of 18.2, 23.1, and 24.6 (J m^{-3})^{0.5}, respectively, the logarithms of k_3 and K_1 were plotted against δ . Fig. 6 demonstrates this relationship; the plots satisfy the linear relationship between the reaction rate constant and δ . The solvent polarity is increased with increasing δ . It may be assumed that increased instability and solvation of C_1 arising from the increased solvent polarity enhance the dissociation reaction of C_1 and the reaction between C_1 and CO_2 , such as SN_1 (nucleophilic substitution) by solvation,²¹ respectively; thus, the values of K_1 and k_3 increase upon increasing δ , as shown in Fig. 6. This result coincides with that of Nishikubo *et al.*⁶ They found that they had increased greater yields of cyclic carbonate with toluene, NMP and DMSO respectively in the addition reaction of 2-phenoxy methyloxirane with CO_2 using a soluble polymer-supported catalyst with quaternary onium salt. They explained the increase of the product by aprotic polarity. They found that the yield of cyclic carbonate increased in the order: toluene, NMP and DMSO, in the addition reaction of 2-phenoxy methyloxirane with CO_2 using a soluble polymer-supported catalyst with quaternary onium salt, and explained the increase of the product with aprotic polarity.

To observe the effect that the reaction temperature has on the reaction rate constants, k_3 and K_1 , absorption rates of CO_2 were measured while the reaction temperature was changed over the range of 80–90 °C in a particular solvent, *e.g.*, DMSO. Fig. 7 shows plots of the reaction rate constants against $1/T$ in a semi-logarithm scale; the plots satisfy straight lines. The activation energy of reaction in eqn (3) was obtained from the slope of the line for k_3 ; its value is 46.73 kcal mol⁻¹. These reaction rate constants will be used to control the reaction yield of CO_2 for maximum incorporation of the reactants into the final product.

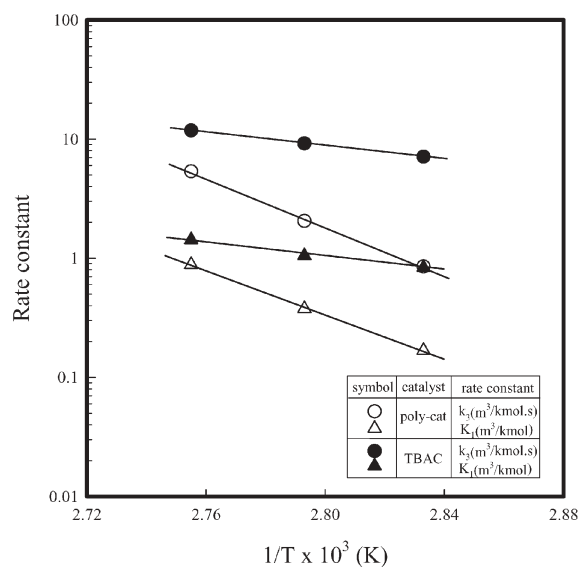


Fig. 7 Dependence of reaction temperature on reaction rate constant in DMSO solution.

To compare the catalytic activity of poly-cat with that of the corresponding monomeric quaternary onium salt, the reaction rate constants, k_3 and K_1 for TBAC were obtained using the same procedure as that for poly-cat. The reaction rates are plotted *vs.* δ of the solvent and *vs.* $1/T$ in Fig. 6 and 7, respectively. As shown in Fig. 6 and 7, the values of the reaction rate constants, k_3 and K_1 , for TBAC are larger than those for poly-cat and the activation energy of reaction (3) for TBAC is 13.55 kcal mol⁻¹. It is generally known that immobilized quaternary salt catalysts have lower catalytic activity than homogeneous ones.⁶ However, the distinct comparison of the reactivity of homogeneous and immobilized quaternary salt catalysts is not easy since the structure of cation and counter anion of the catalyst greatly affects the catalytic performance. The activity of soluble polymer-supported catalysts is normally affected by the kinds of alkyl groups found on the pendant quaternary onium salt residue and by the degree of introduction of the pendant quaternary onium salt residues in the polymer chain due to both the lipophilic interaction between the pendant onium salt residue and the steric hindrance of the catalyst.

Conclusions

Two elementary reactions consisting of first, a reversible reaction of GMA and the catalyst to form an intermediate and second, an irreversible reaction of the intermediate with carbon dioxide, were considered to evaluate the reaction kinetics of the overall reaction between CO_2 and GMA using an immobilized tributylammonium chloride catalyst. A pseudo-first-order reaction method was used to obtain the elementary reaction rate constants using absorption data for CO_2 at 0.1013 MPa. The catalytic activity of poly-cat was compared with that of the corresponding monomeric catalyst, and the solubility parameters of solvents used in this study influenced the reaction rate constants.

Nomenclature

C_i	concentration of component, i/kmol m ⁻³
k_1	forward reaction rate constant in reaction (2)/m ³ kmol ⁻¹ s ⁻¹
k_2	backward reaction rate constant in reaction (2)/s ⁻¹
k_3	reaction rate constant in reaction (3)/m ³ kmol ⁻¹ s ⁻¹
z	distance/m
z_L	film thickness/m

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Effect of pore size on the performance of mesoporous zirconia-supported cobalt Fischer–Tropsch catalysts†‡

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Mesoporous zirconia with different pore sizes have been prepared and investigated as supports of cobalt catalysts for Fischer–Tropsch synthesis (FTS). It was found that the F–T catalytic performances were closely correlated to the pore sizes of the mesoporous zirconia. The average crystalline sizes of Co_3O_4 grew with increasing the pore size. Furthermore, their reduction degrees were enhanced, in that the Co–ZrO₂ interaction decreased with the increase of pore size. The results from the catalyst testing showed that the FTS catalytic activity, C_5^+ selectivity, C_{18}^+ selectivity and the selectivity to C_{12} – C_{18} paraffins were enhanced, whereas C_1 selectivity decreased with increasing pore size. Based on the systemic study on the effects of the pore sizes of mesoporous zirconia on FTS, it was shown that the Co/PMZ-12 catalyst supported on the large pore size mesoporous zirconia exhibited the largest cobalt oxide particle size, the highest reducibility, and thus showed the highest FTS catalytic activity, with especially good selectivity to C_{12} – C_{18} paraffins as the main component of the clean diesel oil fraction. The result was attributed to the combination of two factors. One was the improvement of the reducibility of the cobalt catalyst, the control of re-adsorption of the α -alkene and chain growth derived from the large pore size and narrow pore size distribution of the mesoporous support. The other was that the cobalt catalyst supported on zirconia displayed a high FTS catalytic activity and C_5^+ selectivity.

Introduction

The increasing exhaustion of petroleum resources makes oil refining industries difficult to meet the enhancing demand in clean transportation fuel. The Fischer–Tropsch synthesis (FTS) is one of the most promising alternative routes for producing ultra-clean fuels from non-crude-oil feedstocks.¹ Supported cobalt is the preferred catalyst for the Fischer–Tropsch synthesis of long chain paraffins.² The texture and surface properties of the support have a significant influence on the dispersion, reducibility and catalytic performance of cobalt catalysts.³

Among the textural properties, the pore size of the support is one of the key factors, which affects the size of the cobalt oxide particles,⁴ the mass transfer of reactants and products,⁵ the re-adsorption of the α -alkene, and the chemisorption ratio of H_2 and CO on the surface active sites;⁶ consequently, these influence the performance of cobalt catalyst in the F–T synthesis. The support with a smaller pore size results in a higher dispersion of the cobalt catalyst but limits the diffusion of syngas and products, thus yielding light hydrocarbons. In

contrast, the support with a larger pore size improves the reducibility, favors the diffusion of syngas and products, and thus produces heavy hydrocarbons.⁷ However, Ernst *et al.*⁸ studied the F–T activity and selectivity of Co/SiO₂ prepared by a sol–gel technique in acid and base media. It was found that the activity for FTS increased with the specific surface area, and the selectivity for higher molecular weight hydrocarbon was favored in the case of a catalyst with a pore diameter of support less than 4 nm. From a survey of the literature, it can be seen that the effect of the porosity of support on the F–T reaction and hydrocarbon selectivities remains controversial.

Mesoporous silicas have attracted widespread attention in F–T synthesis because of their high surface area, which is beneficial to increase the cobalt dispersion, and of the large pore size and narrow pore size distribution, which can well control the cobalt particle size, improve the diffusion of reactants and products in the mesoporous channel, and improve the distributions of hydrocarbon products from the F–T synthesis.^{9–14} For example, the cobalt catalyst supported on mesoporous aluminosilicate with a pore size of 3.4 nm exhibits a selectivity for the C_{10} – C_{20} fraction as high as 38.5%.¹³ Therefore, mesoporous materials are appropriate model supports for studies on the effect of porosity on the F–T activity and hydrocarbon selectivities. However, mesoporous silicas possess surface silanol (Si–OH) groups that can interact with cobalt oxides, and thus, are inclined to form the irreducible cobalt silicate species.¹⁵ Consequently, seeking other mesoporous supports is necessary to improve the reducibility and the F–T reaction performance of cobalt catalysts.

On the other hand, as a promoter or a support of cobalt-based catalysts, zirconia enhances the activity and C_5^+

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‡ Electronic supplementary information (ESI) available: N_2 adsorption/desorption isotherms, pore size distributions and textural properties of mesoporous zirconia-supported cobalt catalysts. See DOI: 10.1039/b614266d

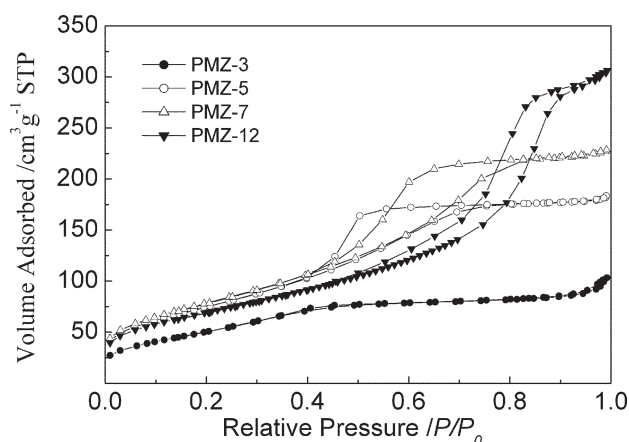


Fig. 1 N₂ adsorption/desorption isotherms of mesoporous zirconia.

selectivity for FTS reaction. This is due to the formation of the highly reducible cobalt oxide species derived from the mild Co–ZrO₂ interaction.^{5,16–18} It may be expected that mesoporous zirconia, possessing the characteristics of zirconia and mesoporous materials, will be a promising support for the cobalt catalyst. No work has been reported on mesoporous zirconia as supports for cobalt catalysts for FTS. In the present work, mesoporous zirconia with different pore sizes have been prepared according to our work reported previously¹⁹ and a systemic study has focussed on the effects of the pore size of the mesoporous zirconia on the F–T synthesis.

Results and discussion

Textural properties

The nitrogen adsorption/desorption isotherms and the pore size distributions of the samples PMZ-3, PMZ-5, PMZ-7, and PMZ-12 are shown in Fig. 1 and Fig. 2, respectively. The type IV isotherms with H1 hysteresis loops for these samples were observed, indicating the existence of the mesopore structure. Additionally, the synthesis parameters and the textural properties of the samples are listed in Table 1 and Table 2, respectively. Obviously, the pore properties depend upon the synthesis parameters, including the pH of the synthesis system and the molar ratio of diglycol : Zr added in the initial system.

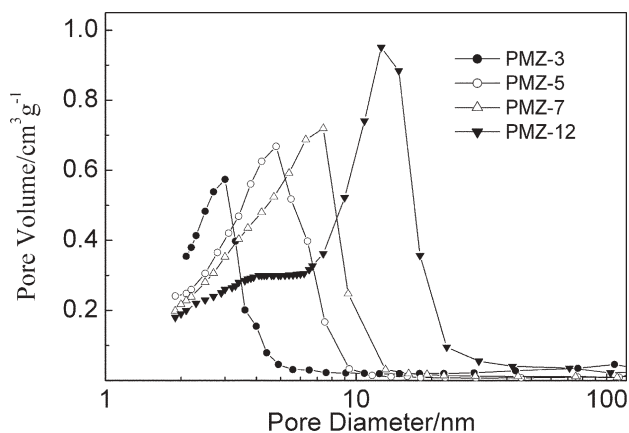


Fig. 2 BJH pore size distribution curves of mesoporous zirconia.

Table 1 Synthesis parameters of mesoporous zirconia with different pore sizes

Sample	Pore size/nm	HNO ₃ /ml	Diglycol/ml	pH
PMZ-3	2.9	6	0	3.0
PMZ-5	4.8	4	30	4.5
PMZ-7	7.4	6	30	3.0
PMZ-12	12.6	8	30	2.5

Under the same pH of 3, the addition of diglycol at the molar ratio of diglycol : Zr from 0 to 2 led to the enhancement of the pore sizes from 2.9 to 7.4 nm. The observation was believed to be that the stabilizer (diglycol) could effectively slow the hydrolysis/condensation rates of the zirconium source,^{20,21} and thus restrain the strong tendency to precipitate and to avail the self-assembly process. On the other hand, at the constant molar ratio of diglycol : Zr = 2, the pore sizes of the resultant materials decreased from 12.6 to 4.8 nm with an increase of pH from 2.5 to 4.5. The lower pH can favor the hydrolysis,²² hinder the condensation,²³ and favor the formation of large mesoporosity; in contrast, the higher pH can promote the condensation,²⁴ and avail the formation of small mesoporosity. The variation of pore size with the synthesis parameters was in good agreement with the result in our previous report.¹⁹ The nitrogen adsorption/desorption isotherms and the pore size distributions of the catalysts Co/PMZ-3, Co/PMZ-5, Co/PMZ-7, and Co/PMZ-12 are similar to their corresponding supports (see ESI, Fig. S1 and Fig. S2†).

The N₂ adsorption/desorption isotherms and pore size distribution and textural properties of the used Co/PMZ-12 are shown in the ESI† (Fig. S3 and Table S1). It can be seen that mesoporous zirconia-supported cobalt catalysts possess good thermal stability after the F–T reaction.

Phase structure

The XRD patterns of the samples Co/PMZ-3, Co/PMZ-5, Co/PMZ-7, and Co/PMZ-12 are presented in Fig. 3. All four samples show wide diffraction peaks located at 31°, characteristic of the tetragonal zirconia phase. Moreover, these corresponding diffraction peaks with the same intensities were observed, implying that the supports with the similar crystallite phase were used in the four samples. In addition, the diffraction peak situated at 36.7°, attributed to Co₃O₄ particles, could be observed in the XRD patterns of the four samples, and the intensities of the diffraction peak of the four samples were

Table 2 Physico-chemical properties of mesoporous zirconia and corresponding cobalt catalysts

Sample	BET surface area/m ² g ^{−1}	Pore volume/cm ³ g ^{−1}	Pore size/nm	Co ₃ O ₄ size by XRD/nm	Reducibility by TPR at <673 K (%)
PMZ-3	186	0.16	2.9	—	—
Co/PMZ-3	141	0.11	2.5	3.8	59.5
PMZ-5	274	0.28	4.8	—	—
Co/PMZ-5	199	0.20	4.3	8.2	66.7
PMZ-7	287	0.35	7.4	—	—
Co/PMZ-7	214	0.24	6.3	9.0	73.3
PMZ-12	253	0.47	12.6	—	—
Co/PMZ-12	201	0.29	11.0	14.1	93.8

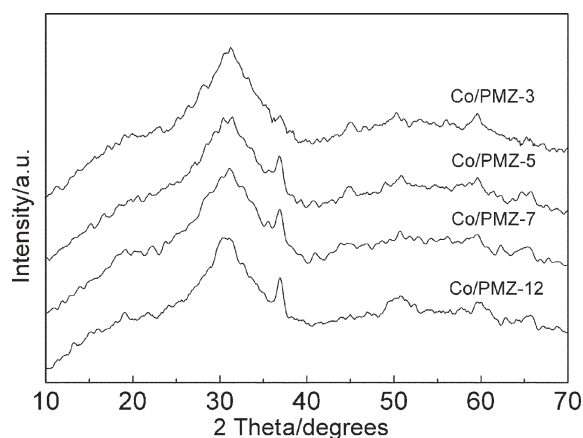


Fig. 3 XRD patterns of mesoporous zirconia-supported cobalt catalysts.

enhanced with increasing pore size of the corresponding supports. According to the XRD half-width of the diffraction peak, the average Co_3O_4 crystalline sizes for Co/PMZ-3, Co/PMZ-5, Co/PMZ-7, and Co/PMZ-12 deduced from the Scherrer equation were 3.8, 8.2, 9.0 and 14.1 nm (see Table 2), respectively. It is well known that the average crystalline size of Co_3O_4 increased with increasing pore size.^{4,12} It was clear that the result was in good agreement with that in the literature.^{4,12}

Reduction behavior

Fig. 4 shows the temperature programmed reduction (TPR) profiles of the samples Co/PMZ-3, Co/PMZ-5, Co/PMZ-7, and Co/PMZ-12. Three peaks were observed in each TPR profile, where the three peaks were in sequence identified with the reduction of Co_3O_4 to CoO (peak α),^{3,25} then CoO to Co (peak β),⁵ and of cobalt species derived from a mild Co–ZrO₂ interaction to metallic Co (peak γ).¹⁷ However, the intensities of the corresponding peaks in the four catalysts were distinctly different. Besides a slight difference for the peak α , the intensity of the peak β enhanced with increasing the pore size of mesoporous zirconia support, whereas that of the peak γ varied inversely compared with the former, indicating that the

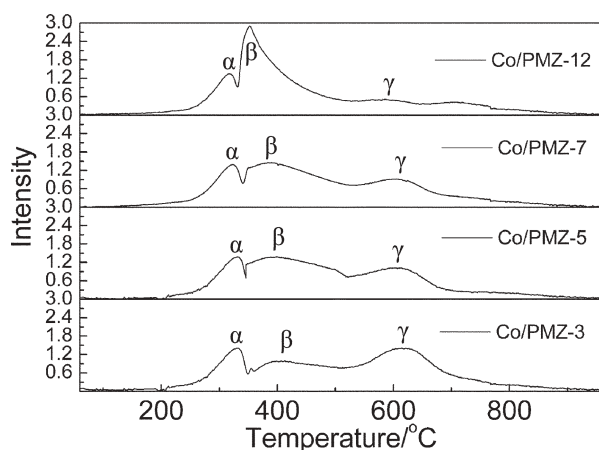


Fig. 4 H_2 -TPR profiles of mesoporous zirconia-supported cobalt catalysts.

Co–ZrO₂ interaction decreased with the increase of pore size. The reduction degrees of the samples Co/PMZ-3, Co/PMZ-5, Co/PMZ-7, and Co/PMZ-12 were 59.5, 66.7, 73.3 and 93.8% (as listed in Table 2), respectively, which were closely related to the cobalt–support interaction. The Co/PMZ-3 showed the poorest reducibility due to the strongest Co–ZrO₂ interaction, originating from the smallest cobalt oxide particle supported on this mesoporous zirconia with the smallest pore size. The Co/PMZ-5 displayed a slightly higher reducibility due to the relatively weaker Co–ZrO₂ interaction as compared with Co/PMZ-3. Then the higher reducibility of the sample Co/PMZ-7 resulted from the weaker Co–ZrO₂ interaction on the catalyst with a larger pore size in comparison with the sample Co/PMZ-5. Co/PMZ-12 exhibited the highest reducibility due to its largest pore size and average crystalline size of Co_3O_4 , implying the weakest Co–ZrO₂ interaction for the catalyst.^{5,13} It could be concluded that their reduction degrees were enhanced with the increase of pore size of the mesoporous zirconia supports due to that the Co–ZrO₂ interaction decreased with increasing pore size.

DRIFT spectra of CO and CO/H₂ adsorption

The DRIFT absorption bands of CO adsorbed onto reduced Co/PMZ-3 and Co/PMZ-5 appeared at 2072 and 1948 cm^{-1} . For Co/PMZ-7, the adsorption bands appeared at 2064 and 1938 cm^{-1} . CO adsorption bands of Co/PMZ-12 at 2064, 1948 and 1812 cm^{-1} were observed (see Fig. 5). The bands above 2000 cm^{-1} were assigned to the linear-type CO species, and those <2000 cm^{-1} were attributed to the bridged-type species.^{3,25} It was clear that the absorption intensities of the bridged-type CO species were enhanced with the increase of the pore sizes of mesoporous zirconia-supported cobalt catalysts. Fig. 6 shows the DRIFT spectra of CO + H₂ at 230 °C over catalysts with different pore sizes. The band at 2050 cm^{-1} corresponded to the linear-type CO on Co. Additionally, the bands at 2924, 2852 and 1463 cm^{-1} were assigned to symmetric, antisymmetric C–H vibrations and C–H bending of $-\text{CH}_2-$ groups, respectively, while the shoulder at 2954 cm^{-1} was typical of symmetric C–H stretches of $-\text{CH}_3$ groups.^{26,27} It can be seen that the intensities of the C–H bands of $-\text{CH}_2-$ groups were enhanced with the increase

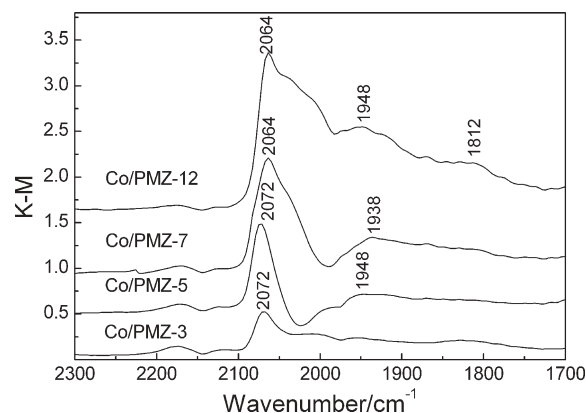


Fig. 5 DRIFT spectra of CO adsorbed on mesoporous zirconia-supported cobalt catalysts.

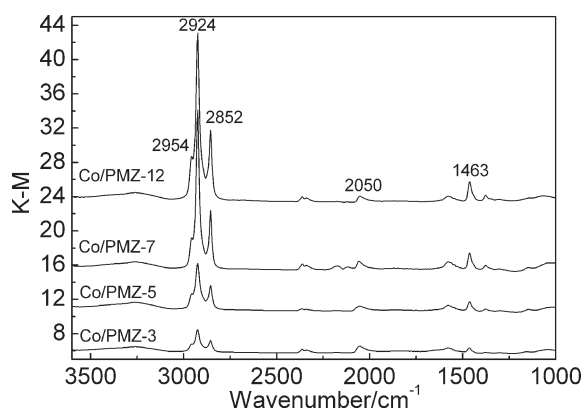


Fig. 6 DRIFT spectra of CO + H₂ adsorbed on mesoporous zirconia-supported cobalt catalysts.

of pore size, implying that the chain growth was favored for catalysts with larger pore size because the methylene groups were believed to be the basic species for chain propagation.^{26,28}

F–T reaction performances

The F–T reaction performances of the catalysts are listed in Table 3. Under the same reaction temperature of 230 °C, the FTS catalytic activity, C₅⁺ selectivity, C₁₈⁺ selectivity, and the selectivity for C₁₂–C₁₈ paraffins were enhanced, whereas C₁ selectivity (methane selectivity) decreased with increasing pore size of the mesoporous zirconia supports. It should be noted that the cobalt catalyst supported on the mesoporous zirconia with the pore size of 12.6 nm (Co/PMZ-12) showed not only the highest FTS catalytic activity but also the highest selectivity for the C₁₂–C₁₈ fraction, as high as 32%. It has been accepted that the support with a smaller pore size results in a higher dispersion of cobalt catalyst, but this limits the diffusion of syngas and products, thus yielding light hydrocarbons; in contrast, the support with a larger pore size improves the reducibility, favors the diffusion of syngas and products, and thus produces heavy hydrocarbons.^{4,7,12} Many authors pointed out that the bridged-type CO species favored the dissociation of CO and chain growth of –CH₂– groups.^{3,25,29,30} In combination with above characterization results, including XRD, TPR and DRIFT, it is well understood that the F–T reaction performances of the catalysts vary as a function of pore size. Furthermore, the large pore size and narrow pore size distribution of the mesoporous molecular sieve supports permit better control of the cobalt particle size and the distribution of hydrocarbon products from the F–T synthesis compared with the conventional supports,^{12,13} due to

Table 3 Fischer–Tropsch reaction performance of mesoporous zirconia-supported cobalt catalysts^a

Sample	CO conv. (%)	C ₁ (%)	C ₅ ⁺ (%)	C ₁₈ ⁺ (%)	C ₁₂ –C ₁₈ (%)
Co/PMZ-3	13.58	44.91	36.36	1.03	9.56
Co/PMZ-5	42.41	24.40	46.46	1.95	14.01
Co/PMZ-7	81.03	12.15	69.86	12.87	20.31
Co/PMZ-12	86.12	10.61	86.69	19.23	32.32

^a Reaction conditions: *T* = 230 °C, *P* = 2 MPa, GHSV = 1000 h^{–1}, H₂ : CO = 2 : 1.

the control of the re-adsorption of the α-alkene and chain growth.³¹ Also, the cobalt-based catalyst supported on zirconia is characterized by a mild Co–ZrO₂ interaction, thus leading to the high reducibility of cobalt oxide species and further the high activity and C₅⁺ selectivity for the F–T reaction.^{5,17} The complex interplay among the factors might result in the high FTS catalytic activity and the high selectivity for C₁₂–C₁₈ paraffins as the main component of the clean diesel oil fraction for Co/PMZ-12 with a large pore size mesoporous zirconia as support.

Experimental

Catalyst preparation

The synthesis of mesoporous zirconia was carried out in the same manner as our work reported previously.¹⁹ In a typical synthesis, one solution A, comprising 15.8 g of P123 (EO₂₀PO₇₀EO₂₀, Aldrich), 400 ml of ethanol (anhydrous, SCR), 86 ml of distilled water, of 6, 4, 6 or 8 ml of nitric acid (HNO₃, 68 wt.%, SCR), adjusting pH value of the final reaction system to 3.0, 4.5, 3.0 and 2.5, respectively, was prepared during stirring at room temperature. The solution B, comprised of 400 ml of ethanol, 0 or 30 ml of diglycol [O(CH₂CH₂OH)₂, 99%, ACROS ORGANICS], 70 ml of zirconium(IV) n-propoxide [Zr(OC₃H₇)₄, 23–28% free alcohol, STREM CHEMICALS], was prepared with stirring at room temperature. Then the solution B was slowly added to solution A. The final reaction system was stirred at room temperature for 1 h. Finally, the resulting sol was gelled at 313 K in a closed container for 24 h, followed by refluxing in aqueous ammonia (pH 10) for 48 h. The obtained products were filtered, and then dried at 373 K. The overall molar composition of the final mixture was 1 Zr : 0 or 2 diglycol : 0.017 P123 : 30 H₂O : 90 ethanol. The as-synthesized samples were then calcined at 873 K for 4 h to remove the template. The resulting mesoporous zirconia were designated as PMZ-3, PMZ-5, PMZ-7 and PMZ-12, respectively according to the pore sizes of the materials (shown in Table 1). The cobalt catalysts (Co 10 wt%), denoted as Co/PMZ-3, Co/PMZ-5, Co/PMZ-7 and Co/PMZ-12, were prepared by incipient wetness impregnation using an aqueous solution containing the desired amount of cobalt nitrate. The catalyst precursors were dried at 393 K for 12 h, and then calcined from room temperature to 673 K at the ramp rate of 2 K min^{–1} and kept at 673 K for 4 h in air.

Catalyst characterization

N₂ adsorption/desorption isotherms of the samples were measured at 77 K on a Micromeritics Tristar 3000 sorptometer. Prior to the measurement, all samples were outgassed at 473 K and 10–6 mmHg overnight. The specific surface areas of the samples were calculated by the BET method. The pore size distributions were determined from the adsorption branch of the isotherms using the BJH method, and pore sizes were obtained from the peak positions of the distribution curves.

X-Ray diffraction (XRD) patterns of the samples were recorded on a Bruker B5005 diffractometer using Cu Kα radiation. The mean Co₃O₄ crystallite sizes were deduced from the XRD data using the Scherrer equation.

TPR was carried out in a U-tube quartz reactor at the ramp rate of 10 K min^{-1} in a 5% H_2/Ar (vol.) flow of 30 ml min^{-1} . The H_2 consumption was monitored by TCD using the reduction of CuO as the standard. The reduction percentage of the cobalt oxides at temperatures less than 873 K was calculated from the TPR profiles.

The CO and CO/H_2 diffuse reflectance FTIR (DRIFT) method was described previously.^{26,32} Spectra were recorded using a Bruker Equinox 55 FTIR spectrometer equipped with a Spectra-Tech Diffuse Reflectance Accessory and a high temperature *in-situ* cell with ZnSe windows. A KBr beam splitter was used with a TGS detector. The catalyst was reduced *in-situ* at 673 K for 4 h under atmospheric pressure by a stream of H_2 . After switching to Ar, the sample was cooled down to room temperature and the spectrum collected was used as a background, and then the temperature of the system was increased to the desired value (373 or 503 K). Subsequently, CO (99.999%) or H_2/CO (2 : 1) was introduced for 15 min. Afterwards, the system was cooled down to room temperature, purged with argon (99.99%), and the spectrum was collected at a resolution of 8 cm^{-1} and 400 scans. Each spectrum was obtained with subtraction of the background.

Catalyst testing

Catalysts were evaluated in a pressured fixed-bed reactor at 2 MPa, 1000 h^{-1} , 503 K and with a H_2/CO ratio of 2 after reduction at 673 K for 6 h. Wax was collected with a hot trap and the liquid products were collected in a cold trap. The gas effluents were analyzed on-line by using a Carbosieve-packed column with TCD. The gas hydrocarbons were analyzed on-line using a Porapak-Q column with FID. Oil and wax were analyzed off-line in OV-101 capillary columns. 5% N_2 was added to syngas as an internal standard. The carbon balance and mass balance were $100 \pm 5\%$.

Conclusions

For the cobalt catalysts supported on mesoporous zirconia with different pore sizes, the average crystalline sizes of Co_3O_4 grew with increasing pore size. Furthermore, their reduction degrees were enhanced with an increase of the pore sizes. The catalyst testing showed that the FTS catalytic activity, C_5^+ selectivity, and the selectivity for $\text{C}_{12}\text{--C}_{18}$ paraffins were enhanced, whereas C_1 selectivity decreased with increasing pore size. On the basis of systemic investigation about the influences of the pore sizes of mesoporous zirconia-supported cobalt catalysts on the catalytic performance in Fischer–Tropsch synthesis, it was shown that a novel cobalt catalyst (*i.e.* Co/PMZ-12) supported on the large pore size mesoporous zirconia has been successfully prepared due to its high activity and selectivity for $\text{C}_{12}\text{--C}_{18}$ paraffins as the main component of the diesel oil fraction. The result was attributed to the combination of two factors. One was the improvement of the reducibility of cobalt catalyst, the control of re-adsorption of the α -alkene and chain growth derived from the large pore size and narrow pore size distribution of the mesoporous support. The other was that the cobalt catalyst supported on zirconia displayed the highest FTS catalytic activity and C_5^+ selectivity.

Acknowledgements

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Synthetic natural gas from biomass by catalytic conversion in supercritical water†

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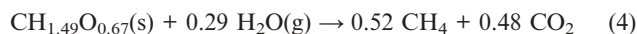
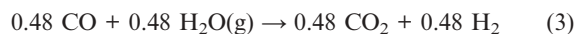
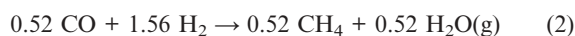
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Biomass can be effectively converted to synthetic natural gas (Bio-SNG) in water near or above its critical point (374 °C, 22.1 MPa). If an active and selective catalyst is used, no tars or char are formed. The onset of the gasification reaction was visualized in sealed quartz capillaries as high pressure batch reactors, by using an optical microscope. By pressure differential analysis of batch experiments, the onset temperature was found around 250 °C, which is much lower than conventional atmospheric gasification processes operating at 800–900 °C. The temporal evolution of the gaseous products in the batch experiments was consistent with a sequential gasification–methanation mechanism, where methane is formed from CO₂ and H₂. A Ru on carbon catalyst exhibiting excellent long-term stability was tested at 400–500 °C and space velocities up to 33 g_{HC} g_{cat}^{−1} h^{−1} in a continuous test rig at 30 MPa.

Introduction

Biomass may be converted to a variety of energy forms, including heat, electricity and mechanical work in the form of traction power. Most of the biomass used for energy purposes is combusted to produce electricity and/or heat. Biomass conversion to transportation fuels has been the subject of many studies.^{1–4} Among all options, biogenic synthetic natural gas (Bio-SNG) is an attractive alternative because its combustion produces much less atmospheric pollutants than fossil fuels and it can be distributed using the existing natural gas grid. The superior environmental performance of Bio-SNG was recently published in a comprehensive comparison of different biofuel options.⁵

Biomass may be converted to synthesis gas *via* conventional gas-phase gasification processes (*e.g.* endothermic steam gasification, reaction (1)), which may subsequently be converted to methane, CO₂, and hydrogen (reactions (2) and (3)):



The net overall reaction from wood to methane and CO₂ is slightly exothermic (reaction (4)). The major problem associated with the conventional gasification technology is the formation of tars and char.⁶ These substances may represent a significant portion of the heating value of the biomass and thus

lower the gasification efficiency, if not used thermally. Tars must be removed from the synthesis gas before entering other downstream equipment.⁷ In the 1970s, Modell⁸ observed that wood could be gasified in supercritical water without the formation of tars and char, but the yield of gaseous products was low.

Conversion of biomass near the critical point of water (374 °C, 22.1 MPa) or above it makes the energy-intensive need to dry the feedstock before thermal conversion obsolete. Fig. 1 depicts the changes of the specific enthalpy for heating water to different temperatures for pressures below and above the critical pressure. As the system pressure is increased above the critical pressure of 22.1 MPa, no distinct phase change occurs and the enthalpy change is less than that for evaporating and superheating the water to the same temperature at a subcritical pressure (*e.g.* 0.1 MPa). Due to this fact, overall net thermal process efficiencies, for wood-to-methane, as high as 70% can be expected.⁹

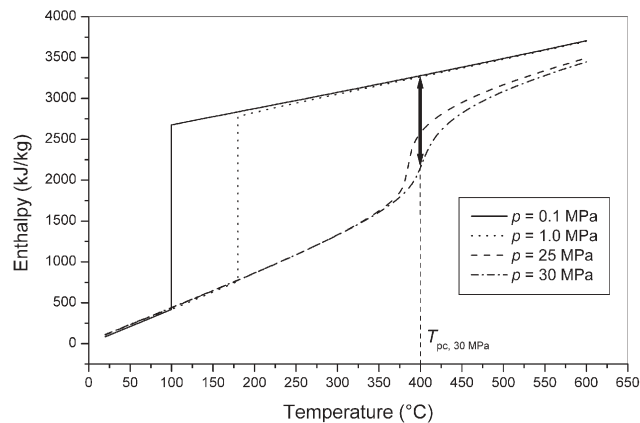


Fig. 1 Change of the specific enthalpy when heating pure water at different pressures. The dashed vertical line indicates the pseudo critical temperature for a pressure of 30 MPa.

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According to thermodynamics, methane is preferably formed at lower temperatures (below 600 °C), whereas at higher temperatures hydrogen is the main product, besides CO₂. The thermodynamic equilibrium concentration of methane at 400 °C and 30 MPa depends also on the feed concentration. It reaches maximum values of 50 vol% (dry gas) for feed concentrations exceeding *ca.* 20 wt%, corresponding to a maximum yield of 0.33 g CH₄ g⁻¹ wood (dry ash-free). At temperatures around 400 °C, a catalyst is needed to obtain useful gasification rates. The catalyst of choice must be active for gasifying a wide range of organic molecules, be selective towards methane formation, and be stable under hydrothermal conditions.

Research in our group has focused on catalyst screening^{10,11} and long-term catalyst testing under hydrothermal conditions.¹¹ Earlier work revealed the rapid deactivation of a very active skeletal nickel catalyst due to sintering of the nickel crystallites.¹² Here we report on recent results with a stable Ru on carbon (Ru/C) catalyst, as well as new results with skeletal nickel from the onset of gasification. Besides real wood slurry, a carefully selected mixture of five organic compounds was used as feed.

Experimental

Batch reactor

This reactor, with an internal volume of 24 mL, has been described in detail elsewhere.¹⁰ To study the temporal evolution of gaseous products, two high pressure needle valves were attached to the reactor. Small amounts of gas were collected in gas sampling bags and analyzed off-line using gas chromatography.

Quartz capillaries

Quartz tubes with an internal diameter of 1.4 mm (outer diameter of 6 mm) were cut to a length of *ca.* 145 mm, sealed at one end by melting the glass in a propane–oxygen flame, and then filled with the ground wood slurry and the catalyst (particle size *ca.* 30 µm). The loading was calculated such as to reach the desired pressure inside the capillary when the maximum temperature was reached. The other end of the capillary was closed by melting it in the flame while keeping the opposite end cold in liquid nitrogen to avoid evaporation of water. The capillaries were placed in an electrical heating block fitted with grooves a bit larger than the outer diameter of the capillaries. A protective shield made of quartz glass was placed directly on top of the heating block. Another shield made of macrolon was placed *ca.* 10 cm above the quartz shield. The gap in between the two shields was cooled with air to prevent any deformation of the macrolon. Pictures were taken using a Leica Wild M3Z stereo microscope and a digital camera connected to the microscope.

Continuous test rig

This rig used a fixed-bed reactor and has been described in detail elsewhere.¹²

Results and discussion

Onset of gasification using a nickel catalyst

Conventional biomass gasification by steam is carried out at atmospheric pressure and at temperatures of 800–900 °C. For the conversion of wet biomass in a pressurized aqueous environment, a reaction temperature as low as possible is desirable to reach high thermal efficiencies (compare Fig. 1). Reforming catalysts used at high temperatures (*e.g.* Ni/ α -Al₂O₃) were found not to be sufficiently active around the critical point of water. Their use resulted in the formation of a significant amount of tars and char. A catalyst that is usually used for hydrogenations in the liquid phase at temperatures below 300 °C is skeletal nickel. This catalyst was found to be very active and selective for the formation of methane from wood in pressurized water. We have used sealed quartz capillaries to visually document and determine the onset of gasification with skeletal nickel. Fig. 2 shows the formation of a gas bubble within the ground wood slurry, just above a grain of catalyst around 293 °C and *ca.* 8 MPa.

More quantitative data on the onset of the gasification was obtained from a differential pressure analysis. Two experiments were carried out at the same conditions in the batch reactor, but one experiment was performed without wood. To achieve a comparable thermal mass inside the reactor, quartz sand was added instead. The difference of the recorded time-dependent pressure data was plotted against the temperature inside the reactor in Fig. 3.

These experiments were conducted without gas sampling during the experiments. Up to 250 °C, only a slight positive difference in pressure between the reactive experiment and the non-reactive reference experiment was observed. Note that the total pressure increased during all experiments as the temperature increased, due to the vapor pressure of water and the formation of the gases when wood was present. At around 250 °C an increase in pressure differential was observed, with a maximum at around 370 °C, followed by a decrease up to 400 °C. Using the reaction scheme presented in eqn (1–4), a plausible explanation is as follows: below 250 °C the wood

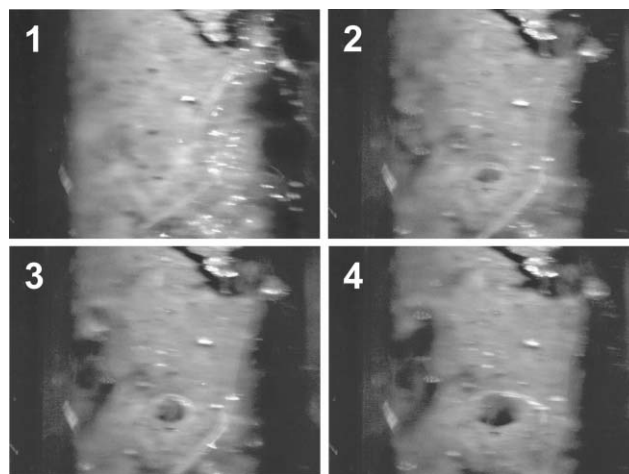


Fig. 2 Formation of a gas bubble from a wood slurry, above a grain of skeletal nickel, in pressurized hot water. Time elapsed between images 1 and 4 is *ca.* 1 min.

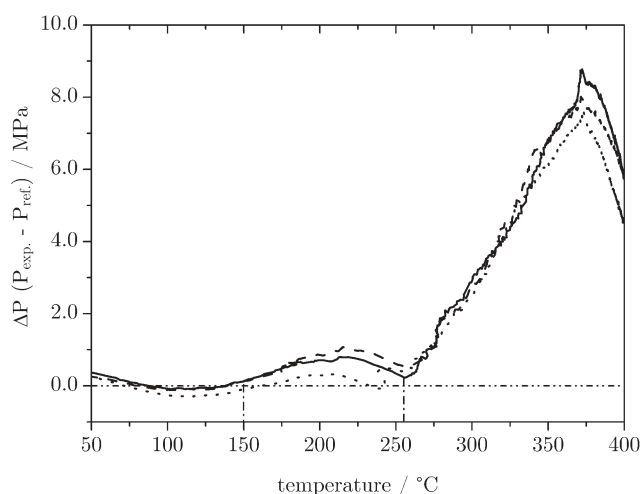


Fig. 3 Pressure difference for three similar experiments in a batch reactor: Exp = performed with wood, Ref = performed without wood, all other conditions identical. Catalyst: skeletal nickel.

macromolecules (cellulose, hemicelluloses, lignin) are hydrolyzed and decomposed into smaller aromatic (*e.g.* phenolics) and aliphatic molecules. Starting at around 250 °C, these molecules are gasified to CO, CO₂ and H₂, resulting in an increase in the number of moles. This is reflected by the increasing pressure differential. Around 370 °C the methanation of CO and CO₂ is fast, leading to a reduction in the number of moles, and thus to a decrease of the pressure differential. This analysis offers clear evidence for the onset of gasification around 250 °C and supports a consecutive gasification–methanation reaction sequence. As a result of extended activity tests and thermal process efficiency calculations, 400 °C and 30 MPa were found to represent a good compromise between high methane yields, high thermal process efficiencies and a good reactivity.

Evolution of gaseous products over time

For the purpose of studying the catalytic reactions during hydrothermal gasification of wood and other biomass types, a model mixture consisting of five organic compounds (ethanol, acetic acid, formic acid, phenol and anisole) was selected and gasified in the batch reactor. In a first experiment, a wood–water slurry (10 wt% wood) was filled into the reactor without a catalyst, heated up to 330 °C within 8 min and held at 330 °C for 4 min. At these conditions the wood was liquefied to a dark, viscous liquid, and only a small amount of CO₂ was formed. After cooling down the reactor, the catalyst was added to the liquefied wood, closed, pressurized with 1.8 MPa of argon and heated to 405 °C. The first gas sample was taken when the temperature had reached *ca.* 250 °C. The evolution of the gas composition as well as the temperatures at which the samples were taken are depicted in Fig. 4 (solid lines and filled symbols). The model mixture of five organic compounds representing the liquefied wood (synthetic liquefied wood or SLW) was gasified at the same conditions, but of course the liquefaction step was omitted (dashed lines and open symbols in Fig. 4). The general trend for both feeds is consistent. CO₂ is formed early during the gasification,

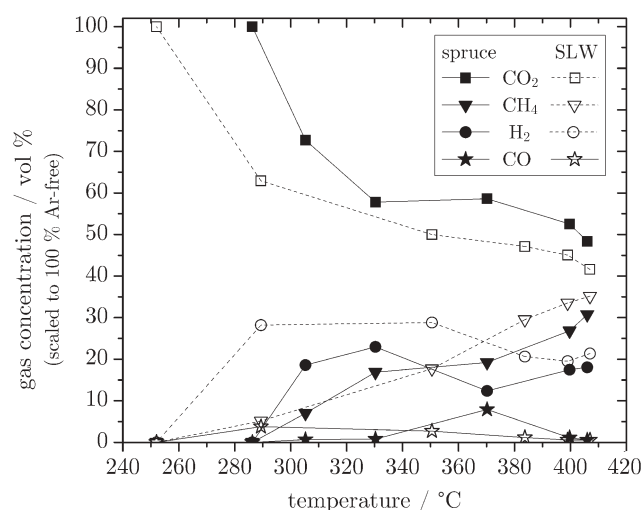


Fig. 4 Temporal evolution of the gasification products for spruce wood and a mixture of five organic compounds with the same C : H : O ratio (SLW). Catalyst: Ru/C.

probably by decarboxylation of low molecular weight carboxylic acids formed during the liquefaction step. Hydrogen evolution is already important around 290 °C for the model mixture, but less important for the real wood. The formation of methane is similar for both feedstocks. Its concentration increases as the concentration of CO₂ decreases. This indicates that methanation of CO₂ takes place as soon as there is hydrogen present.

For the real wood, almost equilibrium composition of the gas is achieved after a holding time of *ca.* 35 min at 405 °C (not shown). Repeated experiments revealed that the gas sampling had an effect on the gas composition, because the gas volumes removed were a significant part of the total volume of the reactor. Therefore, these data indicate trends only.

Long-term catalyst stability testing

Tests with the skeletal nickel catalyst were conducted in our continuous test rig first with ethanol and then with the previously selected mixture of five organic compounds. After a few hours on stream, both skeletal nickel and a ruthenium-stabilized variant deactivated due to sintering of the nickel crystallites.¹² Further screening work in our batch reactor using other skeletal type nickel catalysts and Ru/C catalysts resulted in the identification of an active and selective catalyst that exhibited no signs of deactivation after the batch test. A long-term test with this catalyst was performed using the synthetic liquefied wood mixture.

Details of the Ru/C catalyst are proprietary to the manufacturer. Guided by our previous results with skeletal nickel, an initial weight hourly space velocity (WHSV) of 2 g_{HC} g_{cat}⁻¹ h⁻¹ was selected. The feed concentration of the organics was 20 wt%, and the total pressure was 30 MPa. The nominal gasification and methanation temperature was selected as 400 °C. Throughout all gasification runs, the temperature profile in the undiluted catalytic bed was always within 10 K of the set point. The rig was operated at these conditions for *ca.* 120 h, yielding a constant gas composition,

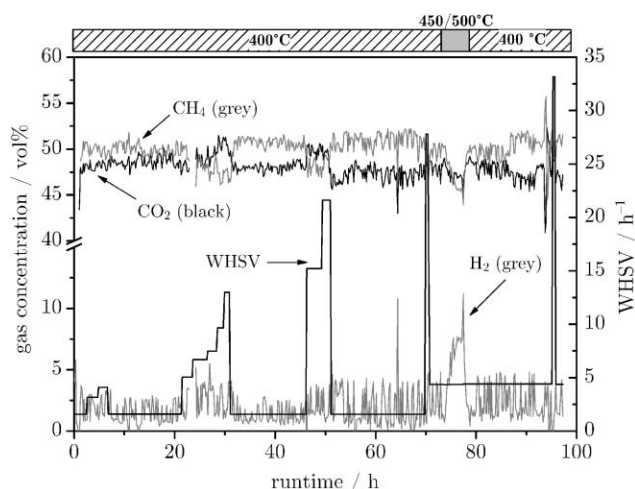


Fig. 5 Dry gas concentrations of CH₄, CO₂, and H₂ for a Ru/C catalyst in the continuous test rig. Stepped line: space velocity (WHSV as h⁻¹). A first run lasting 100 h at 400 °C and constant space velocity preceded the run shown in this figure.

and without any signs of catalyst deactivation. After the successful completion of this run, another run of 100 h was started without changing the catalyst in order to study the effect of varying the WHSV and the temperature. The gas composition *versus* time on-stream is shown in Fig. 5.

A mixture of *ca.* 50 vol% CH₄, 2–3 vol% H₂, and 47–48 vol% CO₂ was formed. CO was always below 0.1 vol%. This gas composition corresponded to the values predicted by thermodynamic equilibrium calculations. Changing the WHSV from 2 to 4 h⁻¹ did not change the gas composition. With a WHSV above *ca.* 7 h⁻¹ a slight decrease of the methane concentration was observed, but even at a WHSV of 22 h⁻¹ the methane concentration was still 47–48 vol%.

Increasing the temperature to 500 °C produced a gas consisting of 45–46% CH₄, 7–8% H₂, and 47% CO₂, again in accordance with the calculated equilibrium values for 500 °C. Switching back to 400 °C at a WHSV of 4 h⁻¹ produced the same gas composition as before. At all these operating conditions, the carbon conversion, measured as TOC, was >99.9%. In order to obtain a gas composition corresponding to incomplete conversion, the WHSV was increased drastically to 28 and 33 h⁻¹ at 400 °C. At these high space velocities the water flow rate could not be increased to the same proportion as the organic flow rate, therefore the concentration of the organics was 30 wt% and 35 wt%, respectively. Only at these two operating conditions did the carbon conversion decrease to 99.2% and 98.5%, respectively. Interestingly, the gas composition remained almost unaffected. However, this may be an effect of the higher concentration counterbalancing the shorter residence time. Detailed analyses of the fresh and spent catalyst using HRTEM (high-resolution transmission electron microscopy) revealed a modest Ru particle growth after the 220 h of continuous testing.¹¹

Conclusions

Woody biomass was gasified and converted to methane, CO₂, and small amounts of hydrogen in supercritical water around 400 °C and 30 MPa. This temperature was much lower than conventional atmospheric gasification processes. No tars and no char were formed. Hydrogen and CO₂ were both products of the early stages of the gasification reactions. They reacted to form methane (methanation of CO₂). CO was detected only in trace amounts in all catalytic experiments. Ru on carbon was identified as a hydrothermally stable catalyst for the production of methane.

This process is a good example for the application of green chemistry and green engineering, using a green feedstock (biomass), a green solvent and co-reactant (water), exhibiting a high thermal efficiency, and producing a fuel with a low environmental impact (Bio-SNG).

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Performance of NiMoS/Al₂O₃ prepared by sonochemical and chemical vapor deposition methods in the hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene†

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Different types of NiMoS/Al₂O₃ catalysts were prepared by a combination of sonochemical synthesis and chemical vapor deposition (CVD) methods. The performance of the prepared catalysts in the hydrodesulfurization (HDS) of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) was compared with that of catalysts prepared using the impregnation method. Ni that was selectively added to the MoS₂ surface by CVD promoted the HDS activity to a greater extent than Ni added by impregnation, particularly for the direct-desulfurization (DDS) route of the reaction. This was attributed to the former method allowing an intimate interaction between the added Ni and the MoS₂ surface, as confirmed by the XPS analysis of the catalysts. NiMoS/Al₂O₃ prepared by a combination of two methods, sonochemical and CVD, showed improvement in activity over the catalyst prepared by impregnation. Moreover, the hydrogenation (HYD) activity of the former catalyst was significantly higher than that of the latter due to the dominant effect of sonochemical synthesis on the activity. The improvement in activity was greater for the HDS of 4,6-DMDBT than for the HDS of DBT.

Introduction

Lowering of the sulfur contents in fuel has become an increasingly important global issue due to the recently imposed stringent environmental regulations.¹ In particular, refractory sulfur compounds such as dibenzothiophene (DBT) and alkyl-substituted DBTs need to be removed from diesel fuel in order to meet the environmental requirements.²

One of the strategies for improving the activity of catalysts for the hydrodesulfurization (HDS) of the refractory compounds is to increase the metal content while still maintaining a high dispersion of the catalytically active species on the support. Sonochemical synthesis was proposed for this purpose.³ It was shown that MoS₂ catalysts prepared by this method had an approximately five-fold higher HDS activity than that of the catalysts prepared using the conventional impregnation method over a wide range of MoS₂ loadings.³

Another strategy for improving the activity is to introduce a promoter, *e.g.*, Co or Ni, to the catalysts, such that the added promoter interacts closely with the MoS₂ surface. Chemical vapor deposition (CVD) was used for this purpose.^{4–6} For example, a catalyst prepared by the decomposition of Co(CO)₃(NO) on MoS₂/Al₂O₃ was twice as active on the HDS of thiophene as one prepared by impregnation. One

study developed active catalysts by combining the above two methods, which showed that the Co-promoted MoS₂ catalysts prepared by the combined methods were two to three times more active in the HDS of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) than those prepared by impregnation.⁵

In this study, the above methods, sonochemical synthesis and CVD, were extended to the case of Ni-promoted MoS₂ catalysts, and the performance of prepared catalysts in the HDS of two model sulfur compounds, DBT and 4,6-DMDBT, was compared with that of the catalysts prepared by impregnation. The prepared catalysts were characterized by infrared and X-ray photoelectron spectroscopy (XPS).

Experimental

Catalyst preparation

A procedure for preparing MoS₂/Al₂O₃ by a sonochemical method, designated as Mo(s), is described elsewhere.³ In a typical procedure, a slurry of Mo(CO)₆, S₈ and γ -Al₂O₃ (CONDEA, 206 m² g^{−1}, 0.49 cm³ g^{−1}) suspended in a mixed solvent of *n*-hexadecane and mesitylene was irradiated with high intensity ultrasound (20 kHz) in an Ar atmosphere at 333 K for 1.5 h. The resulting powder was washed several times with *n*-hexane before being dried in a vacuum at 473 K for 2 h. Another sample of MoO₃/Al₂O₃ was prepared by impregnating alumina with an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O, followed by drying in air at 383 K for 12 h and subsequent calcination in air at 723 K for 4 h. The oxide catalyst was sulfided in a gas stream containing a 12.9% H₂S/H₂ mixture at 673 K for 2 h, and was designated as Mo(i).

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In the Ni CVD process, both Ni precursor generation and deposition were conducted under atmospheric pressure. At first, Ni dispersed on activated carbon (Ni/C, 0.8 g, NiO 30 wt%) was reduced in H₂ at 773 K for 2 h. After reduction, the sample was cooled down to room temperature in an N₂ stream, and then slowly heated to 308 K (0.5 K min⁻¹) in a CO flow of 10 cc min⁻¹. Ni(CO)₄ was produced by the reaction of metallic Ni with CO at 308 K.⁷ When temperature reached 308 K, a valve was switched to introduce the Ni precursor, Ni(CO)₄, into a reactor containing the Mo(s) or Mo(i) catalyst in flowing CO. Ni(CO)₄ was decomposed on Mo(s) or Mo(i) at room temperature for 5 min. The Ni-modified catalyst was then treated in flowing N₂ at 373 K for 0.5 h in order to completely decompose the surface Ni species to Ni. Another set of catalysts was obtained by adding Ni, either by CVD or by impregnation, to the MoO₃/Al₂O₃ prepared by the impregnation method. The metal content of the catalysts was analyzed by inductively coupled plasma and atomic emission spectrometry (ICP-AES). Prior to the HDS tests, the catalysts were sulfided in a pentadecane solution, containing 18% dimethyldisulfide (DMDS), at 573 K under an H₂ pressure of 40 bar for 4 h. The sample catalysts were designated as Ni(c)Mo(s), Ni(c)Mo(i) and Ni(i)Mo(i), according to their preparation methods.

Reaction

The catalysts were tested for the HDS of DBT and 4,6-DMDBT in an autoclave at 593 K under an H₂ pressure of 4.0 MPa, using 0.03 g of the reactant in 30 cm³ of solvent. Pentadecane and dodecane were used as solvents for the DBT and 4,6-DMDBT, respectively. A larger amount of the catalyst, 0.1 g, was used for 4,6-DMDBT than for DBT 0.05 g to compensate for the low HDS rates of the former reactant. After reaction for pre-determined periods, *i.e.*, 30 min for DBT HDS and 60 min for 4,6-DMDBT HDS, the reaction mixture was sampled through a 1/8 inch-diameter tube, and analyzed using a gas chromatograph equipped with a silicone capillary and a flame ionized detector.

Characterization

The decomposition of Ni(CO)₄ in the CVD reactor was detected indirectly by observing the Fourier transform infrared (FTIR) spectrum of the exit stream from the reactor. XPS of the sulfided catalysts were obtained using an AXIS (KRATOS) equipped with a magnesium anode. The spectra were recorded at a chamber pressure lower than 10⁻⁸ mbar, and the binding energies of the samples were estimated using the C 1s line at 284.6 eV as a reference. NO uptakes were measured by a pulse injection method using a catalyst analyzer (BET-CAT, BEL JAPAN, Inc.) The catalyst sample was pretreated with Ar at 200 °C for 1.5 h and then cooled to room temperature. 5% NO/Ar gas was injected in pulses to a reactor containing the catalyst at room temperature. After the saturation of the sample surface with NO, physisorbed NO was removed in an Ar stream at 393 K for 1 h. Then, the second adsorption experiment was conducted in the same manner as for the first adsorption. The amounts of chemisorbed NO were estimated from differences in the

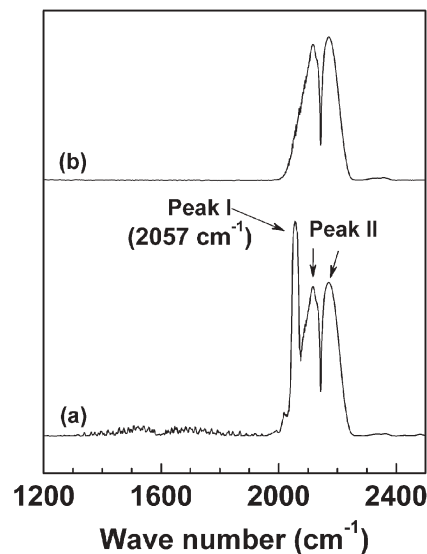


Fig. 1 IR spectra of the exit streams from a CVD reactor containing either (a) Al₂O₃ or (b) MoS₂/Al₂O₃.⁷

adsorbed amounts between the first and second adsorption experiments.

Results

Selective deposition of Ni on MoS₂

Fig. 1 shows FTIR spectra of the exit stream of a CVD reactor containing either alumina (Fig. 1a) or MoS₂/Al₂O₃ (Fig. 1b).⁸ A sharp peak observed at 2057 cm⁻¹ was assigned to gaseous Ni(CO)₄ and the two peaks at 2100–2200 cm⁻¹ to CO, which was used as a carrier gas of the stream. A single Ni(CO)₄ peak was observed in the exit stream when the reactor contained alumina, which suggests that Ni(CO)₄ remains intact or is only partially decomposed on alumina. On the other hand, the stream from the reactor containing MoS₂/Al₂O₃ showed no Ni(CO)₄ peak, indicating that Ni(CO)₄ had been completely decomposed by contact with MoS₂/Al₂O₃. Accordingly, the FTIR results suggest that Ni(CO)₄ is selectively decomposed on MoS₂ under the conditions examined in this study.

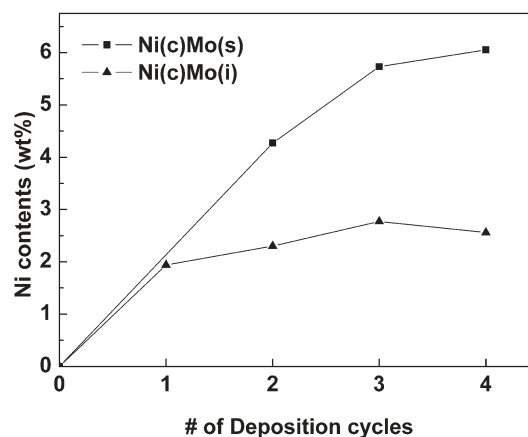


Fig. 2 Changes in the amounts of Ni deposited on MoS₂/Al₂O₃ with CVD cycles.

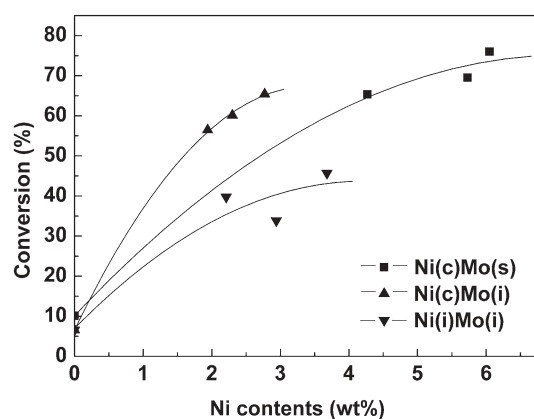


Fig. 3 The HDS of DBT versus the Ni content of NiMoS/Al₂O₃ prepared by different methods.

Fig. 2 shows changes in the amounts of deposited Ni on two types of MoS₂/Al₂O₃ catalysts, Mo(i) and Mo(s), with the number of CVD cycles. The amounts of Ni deposited on the two catalysts were nearly the same after the first cycle, which suggests that the mechanism of Ni deposition is identical. In Ni(c)Mo(i), the amounts of deposited Ni approached saturation after the second cycle. On the other hand, the Ni content of Ni(c)Mo(s) increased almost in proportion to the number of initial CVD cycles up to the third cycle. As a result, the Ni contents in the two catalysts were significantly different after the fourth cycle, by approximately 2.5-fold. The deviation in the Ni contents between the two catalysts is due to different amounts of MoS₂ exposed to the surface. It was previously reported that the dispersion of MoS₂ was significantly increased when MoS₂/Al₂O₃ was prepared using a sonochemical method instead of impregnation.³ This trend was confirmed by measuring the amounts of NO adsorbed to Mo(i) and Mo(s). The measured amounts of Ni deposited on Al₂O₃ were less than 0.1–0.2 wt%, which is in accordance with the IR results that indicated the selective deposition of Ni on MoS₂.

HDS of DBT and 4,6-DMDBT

Fig. 3 and 4 show the conversions of DBT and 4,6-DMDBT, respectively, which were obtained using the catalysts with different Ni contents. Table 1 shows the amounts of products obtained in the reactions using the catalysts that showed the

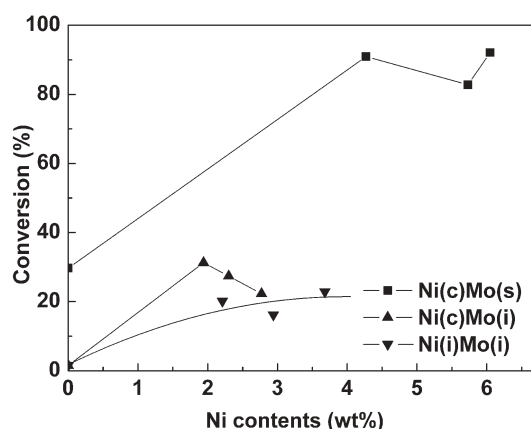


Fig. 4 The HDS of 4,6-DMDBT versus the Ni content of NiMoS/Al₂O₃ prepared by different methods.

maximum activity for individual reactions. All catalysts, except for one sample (see footnote 'f' in Table 1), showed a S/Mo atomic ratio close to 2.0, when it was assumed that Ni in the catalysts combines with S to form NiS. The catalyst activity increased with increasing Ni content, which demonstrates the role of added Ni as a promoter. In DBT HDS (Fig. 3), Ni(c)Mo(s) showed the highest activity, with a conversion higher than 75% at a Ni content of approximately 6 wt%. Ni(c)Mo(i) showed a more rapid increase in conversion with increasing Ni content than Ni(c)Mo(s). However, the Ni content of Ni(c)Mo(i) was limited to lower than 3 wt%, as indicated by Fig. 2. Therefore, the maximum conversion obtained using Ni(c)Mo(i) was lower than that obtained using Ni(c)Mo(s). Ni(i)Mo(i) showed the lowest activity of the three catalysts.

The performance of the catalysts, which were selected from among those showing the maximum activity for individual reactions in Fig. 3, can be correlated with the distribution of products listed in Table 1. In the case of Ni(c)Mo(i), the amounts of biphenyl (BP) and cyclohexylbenzene (CHB) increased by 53.8% and 6.5%, respectively, compared with those obtained using Ni(i)Mo(i). Accordingly, the origin of the increased conversions of Ni(c)Mo(i) is the enhanced production of BP. On the other hand, Ni(c)Mo(s) produces approximately 4.2 times more CHB than Ni(i)Mo(i), while BP is produced in smaller amounts than in the case of

Table 1 Product distribution in the HDS of DBT and 4,6-DMDBT

Catalysts ^a	Reaction	Conversion (%) (relative values)	Products distribution (10 ⁻⁵ mol) (relative values)		
			BP DMBP	CHB MCHT	DCH DMDCH
Ni(i)Mo(i) ^b	DBT HDS	45.7 (1.00)	5.76 (1.00)	1.68 (1.00)	0
Ni(c)Mo(i) ^c		65.4 (1.44)	8.86 (1.54)	1.79 (1.07)	0
Ni(c)Mo(s) ^d		76.0 (1.66)	4.83 (0.84)	7.06 (4.20)	0.2
Ni(i)Mo(i) ^e	4,6-DMDBT HDS	20.2 (1.00)	0.66 (1.00)	1.85 (1.00)	0.33 (1.00)
Ni(c)Mo(i) ^f		31.3 (1.55)	1.15 (1.74)	2.82 (1.52)	0.44 (1.33)
Ni(c)Mo(s) ^d		92.1 (4.56)	2.41 (3.65)	6.35 (3.43)	4.21 (12.8)

^a Catalysts were selected among those showing the maximum activity for individual reactions in Fig. 3 and 4. ^b Ni 3.68 wt%, Mo 11 wt%. ^c Ni 2.77 wt%, Mo 11 wt% and S 8.66 wt%, S/Mo atomic ratio (assuming S/Ni = 1) = 1.94. ^d Ni 6.05 wt%, Mo 30 wt% and S 22.8 wt%, S/Mo atomic ratio (assuming S/Ni = 1) = 1.94. ^e Ni 2.21 wt%, Mo 11 wt% and S 7.87 wt%, S/Mo atomic ratio (assuming S/Ni = 1) = 1.81. ^f Ni 1.94 wt%, Mo 11 wt% and S 7.04 wt%, S/Mo atomic ratio (assuming S/Ni = 1) = 1.63.

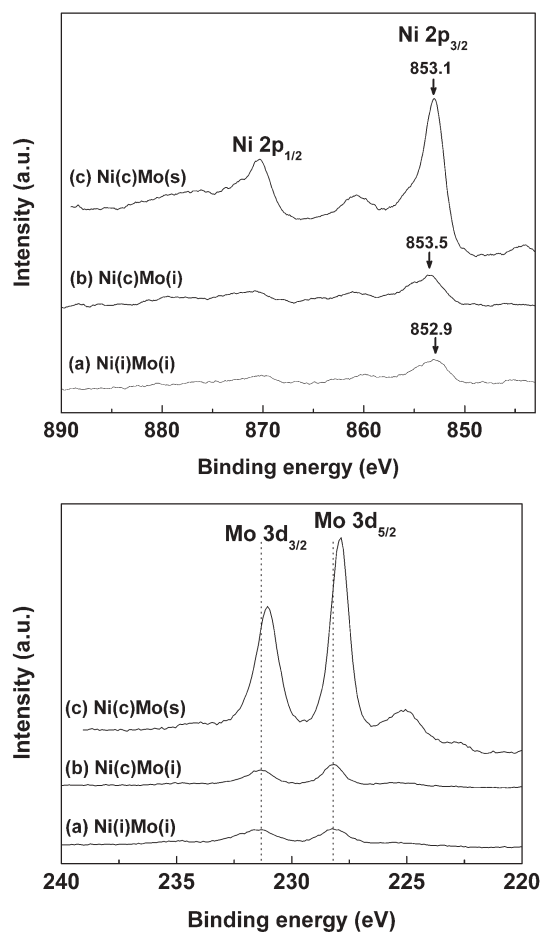


Fig. 5 XPS of Ni 2p and Mo 3d for NiMoS/Al₂O₃ prepared by different methods.

Ni(i)Mo(i). Consequently, the conversion of Ni(c)Mo(s) was increased largely due to the enhanced production of CHB.

The results of 4,6-DMDBT HDS obtained using the different catalysts (Fig. 4) show a trend similar to the one observed for the DBT HDS. That is, the conversion by the catalysts increased in the order Ni(i)Mo(i) < Ni(c)Mo(i) < Ni(c)Mo(s). However, it should be noted that the difference in the observed conversions between Ni(c)Mo(s) and Ni(i)Mo(i) was much greater for 4,6-DMDBT HDS (4.6 fold) than for DBT HDS (1.7 fold). As shown in Table 1, the amounts of dimethylbiphenyl (DMBP) and methylcyclohexyltoluene (MCHT) were promoted to similar extent when either Ni(c)Mo(i) or Ni(c)Mo(s) was used instead of Ni(i)Mo(i), which is unlike the case of DBT HDS. An exception is the production of dimethyldicyclohexyl (DMDCH), which is significantly enhanced (12.8 fold) in the case of Ni(c)Mo(s).

Discussion

Nature of Ni added by CVD

Fig. 5 shows the XPS of Ni 2p and Mo 3d for three sample catalysts. In Table 2, the amounts of surface Ni and Mo estimated from the XPS results are compared with their bulk amounts measured by ICP-AES. The XPS results (Fig. 5) show that the binding energy of Ni increased when Ni was added to MoS₂/Al₂O₃ by CVD instead of impregnation. That is, the position of the Ni 2p_{3/2} peak was shifted from 852.9 eV for Ni(i)Mo(i) to 853.5 eV and 853.1 eV for Ni(c)Mo(i) and Ni(c)Mo(s), respectively. It was previously reported that the binding energy of Ni increased when Ni formed mixed sulfide species with Mo, the so-called Ni–Mo–S phase, and when these species were in a highly dispersed state.^{9,10} The shift in the binding energy by 0.6 eV for Ni(c)Mo(i) indicates that Ni added by CVD interacts more efficiently with the MoS₂ than when added by impregnation, which means that a larger amount of Ni–Mo–S species are produced in the former case. This is supported by the results of catalyst surface analyses (Table 2), which show that the ratio in the amounts of surface Ni to those of the total added Ni was higher for Ni(c)Mo(i) than for Ni(i)Mo(i). Hence, the Ni species are dispersed to a greater extent in Ni(c)Mo(i) than in Ni(i)Mo(i).

Ni(c)Mo(s) showed an increase in the binding energy of Ni by 0.2 eV, which is smaller than that observed for Ni(c)Mo(i). This result suggests that the interactions between the Ni and Mo species are weaker in Ni(c)Mo(s) than in Ni(c)Mo(i), which can be explained as follows. Unlike Mo(i), which was calcined at 723 K and sulfided at 673 K after preparation by an impregnation method, Mo(s) contains the MoS₂ species, which are obtained as highly dispersed particles in a sonochemical process carried out at 333 K, and are therefore vulnerable to sintering. Ni(c)Mo(s) was obtained by the final sulfidation of the deposited Ni species at 573 K, in which step the MoS₂ species are expected to be sintered to a certain extent. The sintering of MoS₂ particles will weaken the interactions between the Ni and MoS₂ species, eventually leading to a smaller shift in the binding energy of Ni in Ni(c)Mo(s) than in Ni(c)Mo(i). This scenario is supported by the findings in our previous study on Co(c)Mo(s), which showed that the MoS₂ species prepared by the sonochemical method were sintered when the catalyst was sulfided at 573 K after adding Co by CVD.⁵ Regardless of the reason for the difference in the binding energy shifts, it can be concluded that Ni interacts more efficiently with MoS₂ when it is added by CVD instead of impregnation.

Role of Ni added by CVD

Fig. 3 and 4 clearly show that the HDS activity of Ni(c)Mo(i) is higher than that of Ni(i)Mo(i). This trend originated from

Table 2 Comparison of surface Ni compositions in NiMoS/Al₂O₃ prepared by different methods

Catalysts	Surface Ni (wt%): A	Bulk Ni (wt%): B	A/B	Surface Mo (wt%): C	Bulk Mo (wt%):	A/C
Ni(i)Mo(i)	1.44	2.21	0.65	7.59	11	0.19
Ni(c)Mo(i)	2.98	2.68	0.74	10.03	11	0.20
Ni(c)Mo(s)	4.68	6.05	0.77	36.85	30	0.13

the improved interactions between Ni added by CVD and the MoS₂ surface, as indicated by the XPS results (Fig. 5). Ni(c)Mo(s) shows a higher activity than Ni(c)Mo(i), which is particularly significant in the case of 4,6-DMDBT HDS. The activity of Ni(c)Mo(s) was enhanced largely by the high dispersion of MoS₂ species in Mo(s), which provides the high surface area of MoS₂ and therefore allows MoS₂ to interact with relatively large amounts of added Ni, *ca.* 6 wt%. An advantage of CVD over impregnation as a method for adding Ni to Mo(s) is that the former method minimizes the sintering of the highly dispersed MoS₂ species in the catalyst sulfidation step. The Ni species of Ni(c)Mo(s), which were added by CVD, were finally sulfided at 573 K, while the Ni species of Ni(i)Mo(s), which were added by impregnation in the form of Ni(NO₃)₂, were decomposed in air at 723 K prior to the final sulfidation at 573 K. As a result, the MoS₂ species of Ni(c)Mo(s) were only slightly sintered during the final treatment steps compared with those of Ni(i)Mo(s).

The HDS of DBT compounds proceeds through two major pathways: the direct hydrogenolysis of the C–S bond (DDS), which produces BP and DMBP, and the hydrogenation of the aromatic ring(s) followed by desulfurization (HYD), which produces CHB, dicyclohexyl (DCH), MCHT and DMDCH. Fig. 6 shows the ratios in the amounts of products, obtained by either HYD or DDS, for the different catalysts and reactants. The data were calculated based on Table 1. The HYD/DDS product ratios were lower for Ni(c)Mo(i) than for Ni(i)Mo(i) in both the case of DBT and 4,6-DMDBT HDS, which indicates that the DDS pathway is promoted to a greater extent when Ni is added by CVD instead of impregnation. This is in accordance with the XPS findings, which showed that the interaction between Ni and Mo led to the formation of the Ni–Mo–S species, which are known as more preferable active sites for DDS than for HYD,^{11,12} was stronger in Ni(c)Mo(i) than in Ni(i)Mo(i). On the other hand, the HYD/DDS product ratios were higher for Ni(c)Mo(s) than for Ni(i)Mo(i) because the highly dispersed MoS₂ species, which were obtained by sonochemical synthesis, significantly promoted the HYD pathway.³ In this case, the contribution of Ni(c) to the promotion of DDS is dominated by the contribution of Mo(s)

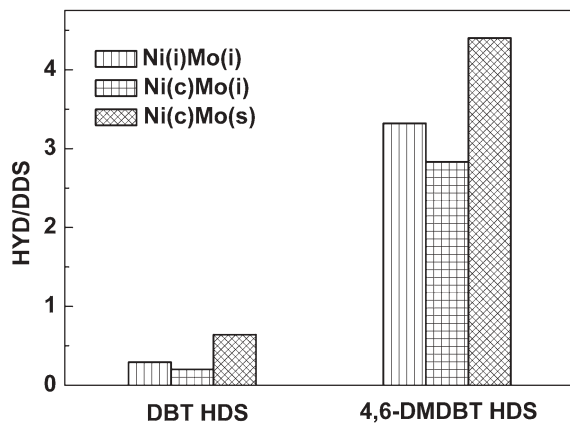


Fig. 6 Hydrogenation selectivity in DBT HDS and 4,6-DMDBT HDS of NiMoS/Al₂O₃ prepared by different methods: (a) (CHB+DCH)/BP; (b) (MCHT+DMDCH)/DMBP.

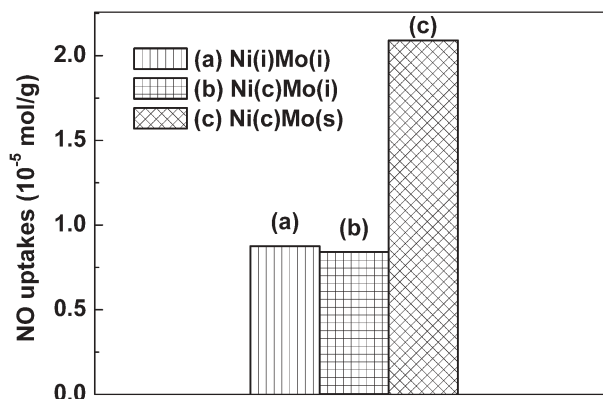


Fig. 7 NO uptakes by NiMoS/Al₂O₃ prepared by different methods: (a) Ni 3.1 wt% and Mo 11 wt%; (b) Ni 2.6 wt% and Mo 11 wt%; (c) Ni 4.3 wt% and Mo 30 wt%.

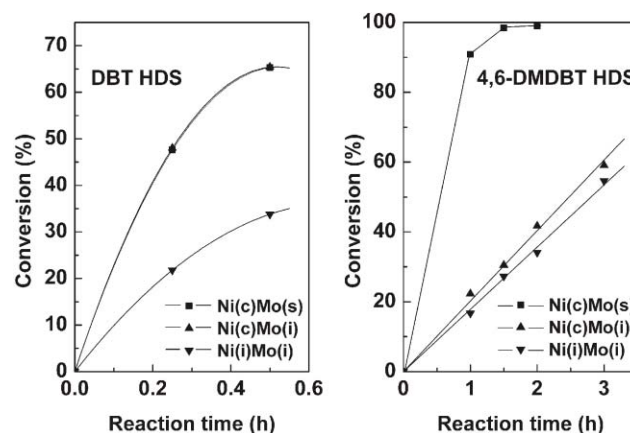


Fig. 8 The HDS of DBT and 4,6-DMDBT *versus* reaction time using NiMoS/Al₂O₃ prepared by different methods: (a) Ni 3.1 wt% and Mo 11 wt%; (b) Ni 2.6 wt% and Mo 11 wt%; (c) Ni 4.3 wt% and Mo 30 wt%.

to HYD, in a manner similar to that observed with Co(c)Mo(s).^{5,6} In fact, the trends observed in this study with Ni(c)Mo(i) and Ni(c)Mo(s) are the same as those observed with Co(c)Mo(i) and Co(c)Mo(s), except that the former catalysts have a higher HYD activity than the latter due to the promotional effect of Ni.^{11–13}

NO is used as a probe molecule to measure the HDS active sites of the catalyst.¹⁴ Fig. 7 shows the NO chemisorption data for Ni(i)Mo(i), Ni(c)Mo(i) and Ni(c)Mo(s). Conversions in the HDS of DBT and 4,6-DMDBT *versus* reaction time obtained

Table 3 Intrinsic activity of NiMoS/Al₂O₃ prepared by different methods

Catalysts	Intrinsic activity ^a /s ⁻¹	
	DBT HDS	4,6-DMDBT HDS
Ni(i)Mo(i)	9.0×10^{-2}	8.0×10^{-3}
Ni(c)Mo(i)	20.7×10^{-2}	9.4×10^{-3}
Ni(c)Mo(s)	8.2×10^{-2}	17.0×10^{-3}

^a Intrinsic activity = [(initial reaction rate (h⁻¹) × initial sulfur contents (mol)]/[catalyst (g) × NO uptakes (mol g⁻¹) × 3600 (s h⁻¹)]

using NiMoS/Al₂O₃ prepared by different methods are plotted in Fig. 8, and the initial reaction rates were estimated from the results. Based on the amounts of NO chemisorption and the initial reaction rates, the intrinsic activity of each catalyst was calculated (Table 3). The amounts of NO adsorbed on Ni(c)Mo(s), prepared by sonochemical synthesis, were 2-fold larger than those adsorbed on the other two catalysts. These results were obtained because the Mo dispersion was different between Mo(i) and Mo(s).³ A remarkable point in the results is that similar amounts of NO were adsorbed on two Mo(i) catalysts, Ni(i)Mo(i) and Ni(c)Mo(i), which indicates that two catalysts have a similar number of active sites even though Ni(c)Mo(i) shows a higher activity than Ni(i)Mo(i). So the intrinsic activity for Ni(c)Mo(i) was higher than for Ni(i)Mo(i) (Table 3). This supports the hypothesis that the intimate interaction between Ni added by CVD and Mo is responsible for the increased activity of Ni(c)Mo(i).

In Table 3, Ni(c)Mo(s) shows the lowest activity for DBT HDS and the highest activity for 4,6-DMDBT HDS among the three sample catalysts. These results can be explained by the following. The HDS of DBT proceeds largely *via* the DDS route¹⁵ and the DDS rate increases with the surface Ni/Mo ratio, showing a maximum when the ratio is 0.4.¹⁶ Table 2 indicates that the surface Ni/Mo ratio is the smallest for Ni(c)Mo(s) among three catalysts, thus explaining the lowest activity of the catalyst. Unlike DBT HDS, the HDS of 4,6-DMDBT proceeds largely *via* the HYD route¹⁵ and the HYD rate is significantly increased when Mo is added by a sonochemical method, due to increased Mo dispersion, instead of impregnation.³ Mo(c)Mo(s) shows the highest activity for 4,6-DMDBT HDS because the enhancement in the HYD rates due to the sonochemical synthesis of Mo(s) outweighs the enhancement in the DDS due to the addition of Ni by CVD.

Conclusions

NiMoS/Al₂O₃ catalysts prepared by a combination of sonochemical synthesis and CVD methods, Ni(c)Mo(s), showed remarkably high activity for DBT and 4,6-DMDBT HDS

compared with the catalyst prepared by the conventional impregnation method. In particular, the sonochemical synthesis of MoS₂ promoted the HYD route of the HDS, and the introduction of Ni by CVD promoted the DDS route as a result of the improved interaction between Ni and MoS₂. Due to the higher activity of Ni(c)Mo(s) for HYD than DDS, 4,6-DMDBT HDS, which proceeds largely *via* the HYD route, was enhanced to a greater extent than DBT HDS.

Acknowledgements

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Steam reforming of methane on a Ru/Al₂O₃ catalyst promoted with Mn oxides for solar hydrogen production†‡

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A new type of solar heated reformers have been developed in recent years. In these reactors, called volumetric reformers, concentrated solar radiation directly illuminates the catalyst through a transparent window. This new type of solar reformer can operate at higher temperatures (1000–1100 °C), since the surface temperature limit of a regular metal tube reactor used in the industry is eliminated and a much higher heating rate is feasible. In the last few years the Weizmann Institute has gathered experience in developing high temperature steam reforming catalysts for its “DIAPR-Kippod” based volumetric reformer. The configuration of the absorber in this reformer is an array of ceramic pins. The thermal stability of the catalysts is crucial for the viability of such reactors. Ru/Al₂O₃ catalysts promoted with Mn oxides are studied. The effect of Mn on the dispersion and sintering of the Ru particles is investigated in the present work with the aid of TEM and EDS. It was found that addition of Mn oxides decreases in the rate of the sintering of the Ru particles. Catalytic elements for use in a volumetric reformer have been developed and tested. The Ru/Al₂O₃ catalyst promoted with Mn oxides was supported on ceramic pins (made of alumina) by wash coating. The long-term test confirmed the chemical and thermal stability of the catalyst even after operating for 500 hours at 1100 °C.

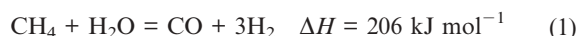
Introduction

The sun is an enormous source of energy; in a single year the amount of solar energy incident on the earth is about 15 000 times the world's energy demand. However, as the solar energy intensity is low, the challenge is to find an efficient way of converting the solar radiation into an energy form that can be readily utilized. One of the promising concepts is using the concentrated solar energy to upgrade fuels such as methane into energy rich synthesis gases. Synthesis gas (syngas), a key intermediate in the chemical industry, is a mixture of hydrogen, carbon monoxide and carbon dioxide, which can be used in a number of highly selective syntheses of a wide range of chemicals and fuels, and as a source of pure hydrogen and carbon monoxide. Syngas can also be burned in a conventional gas turbine to produce electricity.

The solar process for making syngas (solar reforming) is attractive where the sun is plentiful and where natural gas is available close by. The products can be piped in the existing pipeline and can be used as a fuel by customers far from the solar plant. The solar reforming process enriches the heat of combustion of the reactants by about 25%, contributed by the solar energy. Furthermore, biogas, landfill gas and contaminated natural gas (CH₄ with a high content of CO₂) can be

processed and upgraded, using the solar technology. With this feedstock, the reduction of CO₂ emission is significantly enhanced. This makes the solar reforming a promising candidate for the future hydrogen economy.

Solar reforming is a catalytic reaction between methane and steam (or carbon dioxide) which takes place in the solar reactor. Steam reforming of methane is a highly endothermic reaction accompanied mainly by the side reaction of the water–gas shift (WGS) which is slightly exothermic:



One of the challenges is avoiding the cracking of the methane resulting in carbon deposition:



An excess of steam is usually used to reduce the tendency for carbon formation. Steam can be replaced by CO₂. In this case, the resulting products have a H₂/CO ratio close to 1:



Reforming of methane with mixed CO₂ and steam could be used to decrease the danger of carbon depositions and adjust the H₂/CO ratio.

Many attempts have been made for using biogas, produced from anaerobic biomass digestion. Biogas is composed of approximately 50–65% CH₄, 35–50% CO₂, 1% H₂O and traces of NH₃ (80–100 ppm) and H₂S (1000–3000 ppm). Biogas can

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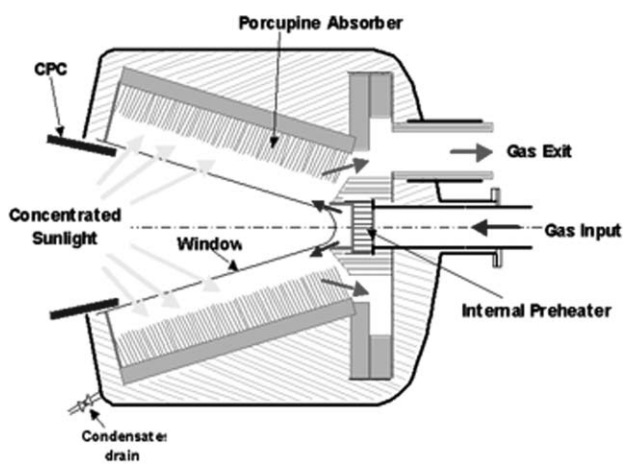


Fig. 1 Schematic view of a DIAPR solar reformer.

be used as potential feed in CH_4 reforming with CO_2 (after purification from H_2S and NH_3) for production of H_2 , which is considered to be a clean fuel. However, the reforming of biogas with CH_4/CO_2 ratio >1 would cause significant carbon deposition. Options to reduce carbon deposition include coupling the biogas conversion with steam reforming.

Numerous studies have been focused on developing solar-powered reactors with direct solar irradiation of the catalyst.^{1–8}

A directly irradiated annular pressurized receiver (DIAPR) with ceramic pins absorber⁹ was developed recently for operation at high temperatures and pressures.¹⁰ The test results for heating air at various irradiation conditions and flow rates are reported by Kribus *et al.*¹¹ Exit air temperatures of up to 1200°C and an operating pressure of 17–20 bar were obtained. The catalytic solar reformer based on the DIAPR conception is under construction. Fig. 1 shows schematically a DIAPR type reformer.¹²

An array of ceramic pins loaded with the catalyst (Fig. 2) is used for both the absorption of the solar radiation and performing the chemical reaction

This type of solar reactor can operate at high temperatures (1000 – 1100°C), since the limit of the surface temperature of a metal tube in regular industrial reformers is eliminated. The time of contact could be in the range of 0.01 – 1 s. The main challenge is the chemical and thermal stability of the catalysts at these high operating temperatures. The activity of the catalysts decreases at high temperatures due to thermal

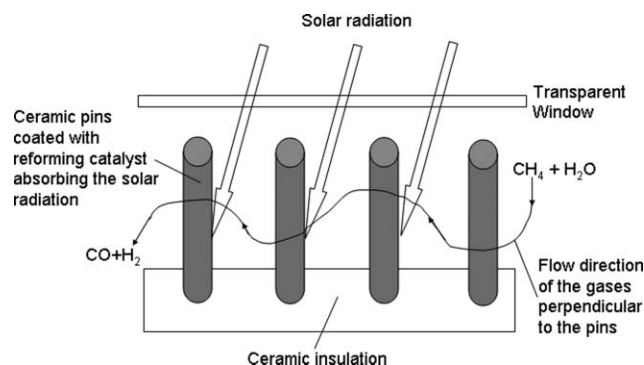


Fig. 2 Concept of a solar volumetric reformer.

sintering of the metallic particles and phase transformations in the support.¹³

Industrial steam reforming using Ni catalyst is performed at around 750°C , with steam to carbon molar ratio in the range of 2–5, to preserve stable catalyst activity. Coke formation is a major problem. It destroys the catalyst structure and hinders its activity. Lobo *et al.*¹⁴ found that the rate of carbon deposition can be suppressed considerably by using noble metals. A Rh catalyst was used by Worner and Tamme² for the reforming of methane with mixed steam and CO_2 .

The Ru catalysts are promising candidates for solar reformers.^{15,16} An additional advantage of the Ru catalyst is the possibility to work at lower steam to methane ratios without carbon deposition.¹⁷ It was found also that the thermal stability of the $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ catalysts can be improved by adding Ce oxide.¹⁸ Rare earth based promoters, alkaline-earth ions and Mn oxides have been described in the literature with respect to this objective.^{19–23}

In the present paper, a cost effective catalytic system for the DIAPR solar reformer was developed. The $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst promoted with Mn oxides was supported on ceramic pins by wash coating. The catalyst was characterized by XRD, TEM and BET. Results of the stability test are presented.

Experimental

Catalyst preparation

The alpha-alumina support for the Ru catalysts was prepared by calcinations of gamma-alumina spheres (La Roshe Chemicals, surface area of $230\text{ m}^2\text{ g}^{-1}$) at 1100°C for 5 hours. The support promoted with Mn oxides was prepared by impregnation of the alumina with Mn nitrate followed by drying at 110°C and calcination at 900°C . Finally Al_2O_3 and $\text{Al}_2\text{O}_3 + \text{MnO}_x$ supports were impregnated with Ru nitrosyl-nitrate solution.

Preparation of the catalytic elements

In the experiments, pins made of sintered alumina (99.7% Al_2O_3) were used. Standard sintered alumina (produced for kiln construction) fired at 1800°C has good mechanical properties. The disadvantage of the standard material for catalytic applications is its very low porosity of about 0.2%. The samples made of the porous alumina pins were supplied by Haldenwanger Company. The samples were fabricated by lowering the firing temperature. The samples are cylindrical rods (OD = 3.0 mm, length = 40 mm or 70 mm). Water adsorption was 11–12.5%, the surface area was 1 – $2\text{ m}^2\text{ g}^{-1}$, pore size was about 0.25 micron. The catalytic support (powder) was prepared by impregnation of the $\alpha\text{-Al}_2\text{O}_3$ with Mn nitrate solution, drying at 110°C and firing at 900°C for 10 hours. The porous pins were coated by the catalytic material on a layer of wash coating. The final thermal treatment was drying at room temperature for 24 hours and at 110°C for 10 hours, calcination at 600°C for 4 hours and firing at 900°C for 10 hours. The last stage was impregnation of the catalytic element with Ru nitrosyl nitrate solution. The weight of the wash coat was about 10–20% related to the weight of the pin. The amount of Ru was 5–10% related to the

weight of the wash coat. The weight of the catalytic element did not change after the stability test. Some samples were also prepared directly by impregnation of the porous pins with Ru nitrosyl nitrate solution. However, the samples prepared without wash coating were deactivated after testing at high temperature.

Catalyst characterization

TEM imaging was performed with a Philips CM-120 (with super-twin objective lenses and tungsten filament) microscope operating at 120 kV. Images were digitally recorded on a Gatan UltraScan 1000 CCD camera. EDS analysis was performed on a EDAX (Phoenix) system with a UTW Si(Li) detector and energy resolution of 137 eV at the Mn K α line. A 100 nm probe was used for collection of spectra and a recording time of 100 s. TEM specimens were prepared by scraping a small amount of powder from the catalyst sample and adding a drop of ethanol onto a carbon/collodion Cu 300 mesh grid.

The specific surface area was measured by nitrogen adsorption (using a CHEM BET 3000, by Quantachrome Comp.).

The structure of the Ru catalysts supported on alumina and promoted with Mn oxides was investigated by XRD using a Rigaku Rotaflex diffractometer equipped with a graphitic monochromator. The operating voltage and accelerating current were kept fixed at 50 kV and 150 mA, respectively.

The XRD pattern of the bare pin confirms the presence of highly crystalline α -Al₂O₃ as a dominant phase. The XRD pattern for the fresh basic alumina used for the preparation of coating material confirmed the presence of crystalline phase of α -Al₂O₃ and perfectly matched with PDF #10-0173 of the JCPDF files,²⁴ which also perfectly matched with the XRD pattern for the pin. The XRD pattern of the powder used for wash coating (alumina impregnated with manganese nitrate after drying and calcinations at 110 °C for 10 hours and then at 900 °C for 10 hours) confirmed the formation of mainly Mn₂O₃ and matched with PDF#24-0508.²⁴ Peaks for α -Al₂O₃, as depicted in the XRD pattern, matched with PDF#10-0173. The XRD pattern of the coating material scratched out from the catalytic element after 500 hours of activity test confirmed the formation of MnAl₂O₄ and Mn₃O₄, which matched with PDF#29-0880 and 24-073, together with α -Al₂O₃, which matched with PDF#10-0173. This XRD pattern clearly shows the formation of Mn aluminates and also reduction of Mn₂O₃ to Mn₃O₄ after 500 hours of the activity test at 1100 °C.²⁵

Experimental setup for activity testing

The experimental setup was constructed to perform the steam reforming of methane or biogas in the temperature range of 500–1100 °C. The catalyst was placed inside the tubular reactor, and its temperature was measured by a thermocouple. The reactor is fixed in a tubular electrical furnace made by Carbolite, model STF 15/50/450, with a maximum operation temperature of 1500 °C. The diameter of the furnace is 50 mm and the length of the isothermal zone is 450 mm. The ceramic reactor was made from alumina (D_{in} = 12 mm, L = 1300 mm). Mixtures of gases containing CH₄ and argon were fed into the reactor *via* mass flow controllers, and the steam generator used

also as a preheater. Water was introduced to the steam generator by means of a metering pump. The gas mixture passed *via* a water trap to a gas chromatograph. The products of the reforming (H₂, CO, CH₄ and CO₂) were separated using a column (1/8" $\times$ 8 m SS) packed with Paropak-Q. The activity of the catalysts for steam reforming of methane was measured in a flow reactor made of ceramics at a temperature range of 500–1100 °C and pressure of 1 bar. The weight of the sample was 0.125 g. The length of the pin was about 1 cm. The weight of the coating was 0.02 g. The amount of Ru was 0.001 g. Flow rates of methane and steam were 290 and 620 cm³ min⁻¹, respectively. For estimation of thermal stability the catalysts were treated at 1100 °C under argon flow for 20–500 hours.

Results and discussion

The Ru catalysts supported on alumina and promoted with Mn oxides and catalytic elements for using in the solar reactor were prepared, characterized and tested.

The Ru/(α -Al₂O₃ + MnO_x) catalysts

The Ru catalysts supported on alumina and promoted with Mn oxides were investigated by TEM and tested for steam reforming of methane and biogas. Transmission electron microscopy (TEM) and energy dispersive spectrometry (EDS) were used to study the dispersion of Ru supported on α -Al₂O₃ and α -Al₂O₃ + MnO_x (5wt% of Mn). Fig. 3 and 4 show the TEM images for the fresh 2%Ru/ α -Al₂O₃ and 2%Ru/(α -Al₂O₃ + MnO_x) catalysts.

Ru particles could be seen in Fig. 3 and 4 as small dark spots (considering the EDS results). The size of the Ru particles dispersed on alpha alumina is in the range 2–6 nm. The diameter of the Ru particles supported on the catalyst promoted with Mn oxides is about 1–3 nm. The XRD pattern

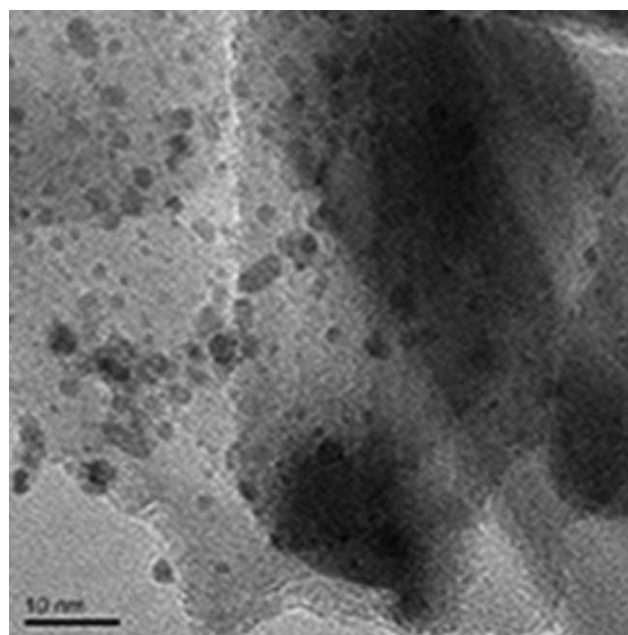


Fig. 3 The TEM image for fresh 2%Ru/ α -Al₂O₃ catalyst.

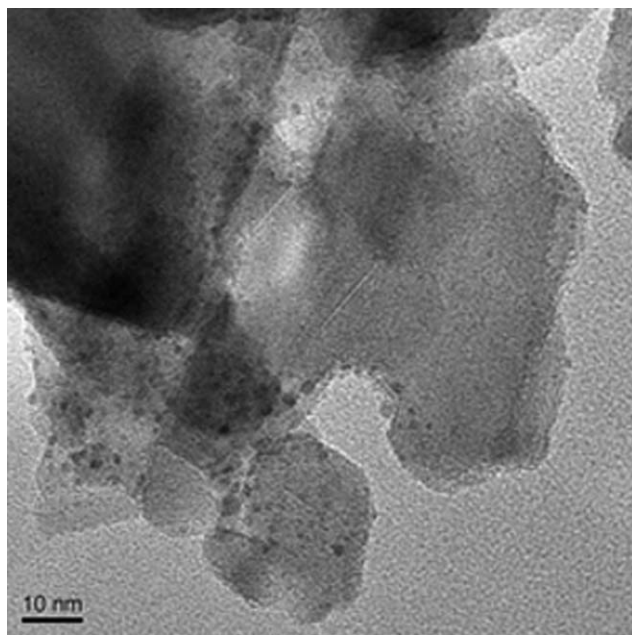


Fig. 4 The TEM image for fresh 2%Ru/(α -Al₂O₃ + MnO_x) catalyst.

for the promoted sample confirms the formation of Mn₂O₃. Therefore, addition of Mn₂O₃ causes an improvement of the dispersion of the supported Ru particles. The TEM images were also obtained for 2%Ru/ α -Al₂O₃ and 2%Ru/(α -Al₂O₃ + MnO_x) catalysts after reaction (steam reforming of methane at temperatures 500–1100 °C) under the same conditions (Fig. 5 and 6).

Comparison between Fig. 3–5 and 5–6 shows that sintering of the Ru particles is much more significant in non-promoted 2%Ru/Al₂O₃ catalyst. It can be concluded that addition of Mn oxides decreases the rate of sintering. The XRD pattern shows formation of the spinal phase MnAl₂O₄ and also reduction of Mn₂O₃ to Mn₃O₄ during the high temperature activity test. Apparently aluminates and Mn oxides are occupying the pores of the alumina and can impede the undesirable diffusion of the Ru particles.

The experiments on steam reforming were conducted at temperatures range of 500–1100 °C at a total pressure of one

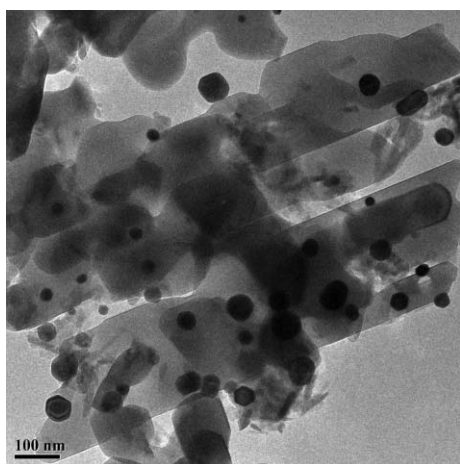


Fig. 5 The TEM image for 2%Ru/ α -Al₂O₃ catalyst after activity test.

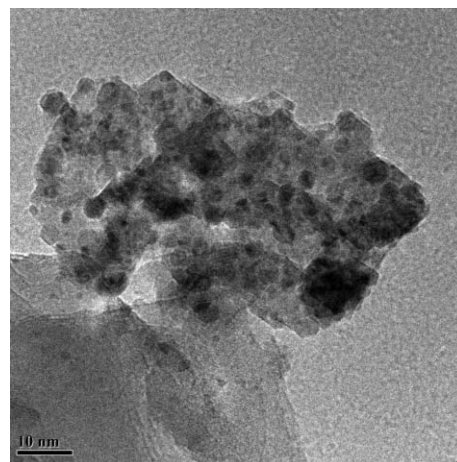


Fig. 6 The TEM image for 2%Ru/(α -Al₂O₃ + MnO_x) catalyst after activity test.

bar and steam to methane ratio of 2.5. The flow rate of methane was 290 cm³ min⁻¹ and the amount of the catalyst was 0.5 g. For estimation of the thermal stability of the catalyst, the samples were calcined at 1100 °C for 17 h. The activity tests were performed for the fresh samples and after calcinations at 1100 °C. Fig. 7 and 8 show the results for 2%Ru/(α -Al₂O₃ + MnO_x) and 2%Ru/ α -Al₂O₃ catalysts, respectively. It can be seen that catalyst promoted with Mn oxides is adequately stable after the high temperature test. Significant deactivation was observed in the case of 2%Ru/ α -Al₂O₃ catalyst. The same experiments were carried out on steam reforming of biogas. The gas mixture containing methane (65%) and CO₂ (35%) was used for simulation of biogas produced from anaerobic biomass digestion. Flow rate of the biogas, steam to carbon ratio and amount of catalyst were of 446 cm³ min⁻¹, 2.5 and 0.1 g, respectively.

Fig. 9 shows that the activity of the catalyst promoted with Mn oxides is practically the same even after calcination at 1100 °C for 129 hours.

The unpromoted 2%Ru/(α -Al₂O₃) catalyst was deactivated partly after calcination at 1100 °C for 17 hours (Fig. 10).

It can be concluded that addition of Mn oxides increases the thermal stability of the Ru catalysts supported on alumina.

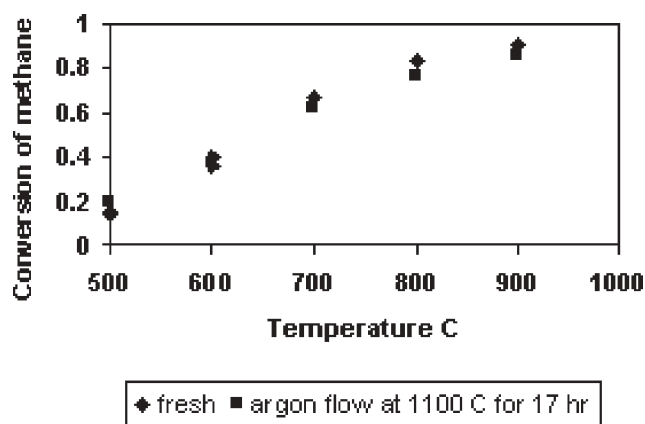


Fig. 7 Steam reforming of methane on 2%Ru/(α -Al₂O₃ + MnO_x) catalyst.

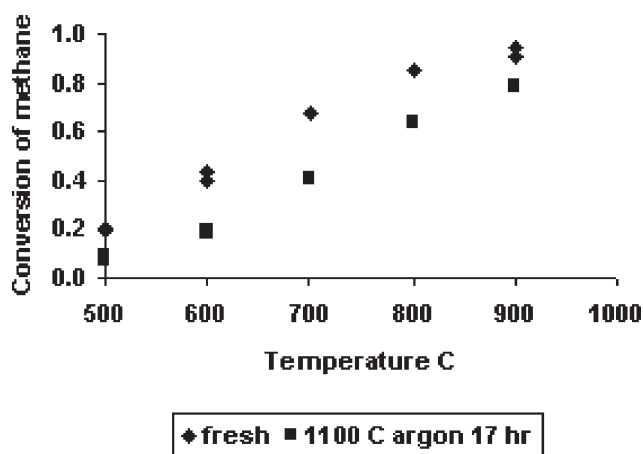


Fig. 8 Steam reforming of methane on 2%Ru/(α -Al₂O₃).

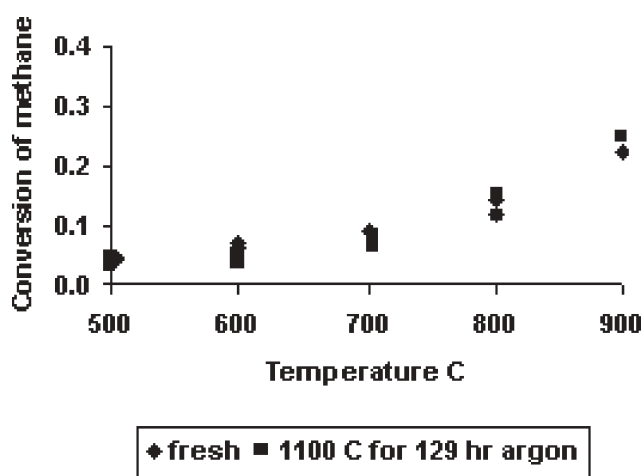


Fig. 9 Steam reforming of biogas on 2%Ru/(α -Al₂O₃ + MnO_x) catalyst.

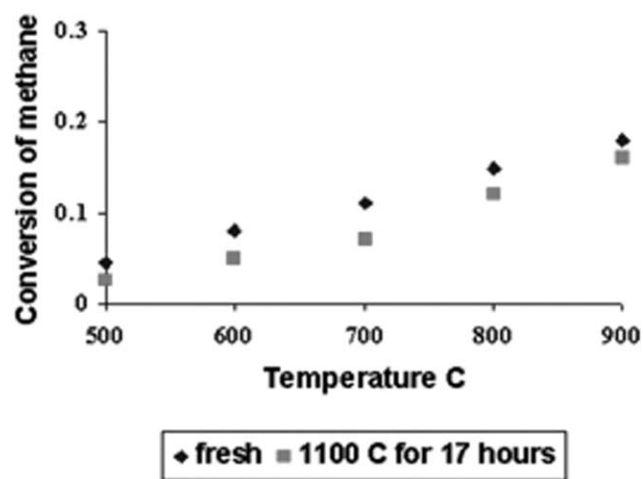


Fig. 10 Steam reforming of biogas on 2%Ru/(α -Al₂O₃) catalyst.

Activity test for catalytic elements for DIAPR reformer

The Ru/(α -Al₂O₃ + MnO_x) catalyst was supported on ceramic pins made of alumina. For the activity tests, small pieces of the

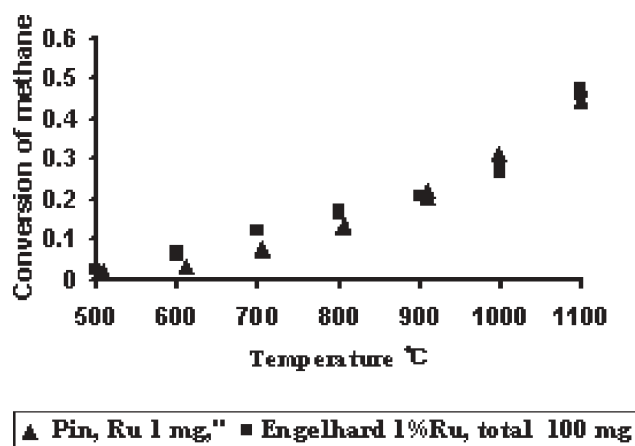


Fig. 11 Conversion of methane *versus* temperature for catalytic element for DIAPR reformer and commercial Engelhard catalyst.

pin were placed in the reactor (see details in the Experimental above). Fig. 11 shows a plot of the conversion of methane *versus* temperature for fresh catalysts.

Results for a commercial Engelhard catalyst (1% Ru supported on γ -alumina stars) are also presented for comparison. It can be seen that for the fresh catalysts, the activities are close. The experiments show that the activity of Engelhard catalyst decreased drastically after its calcination at 1100 °C for 17 hours because of phase transformation of the support.¹⁵

Thermal stability testing

The experiments on steam reforming of methane were conducted over a temperatures range of 500–1100 °C, at total pressure of one bar and steam to methane ratio of 2.5. The catalytic elements were placed inside the tube reactor made of alumina ($D = 12$ mm). The weight of the sample was 1 g, the weight of coating was 20% of that and the Ru was 7.5% related to the weight of coating. The flow rate of the methane was 290 cm³ min⁻¹.

For estimation of the thermal stability of the catalyst, the samples were calcined at 1100 °C for a certain period under argon flow. The activity tests were performed for the fresh samples and after calcinations at 1100 °C. The total time of calcination at high temperature was 506 h.

Fig. 12 shows the conversion as a function of temperature for the fresh sample as well as after 506 h at 1100 °C.

It is clear from Fig. 12 that the conversion of methane is ~92% for the fresh and remains stable after 506 hours of operation at 1100 °C. Also, at 900–1100 °C only negligible deactivation was observed even after 500 hours of operation at high temperature. Only small deactivation of the sample was observed at lower temperatures, *e.g.*, at 500–800 °C. Fig. 13 shows H₂/CO and H₂/(CO + CO₂) ratios as a function of time of operation at a temperature of 1100 °C. The values were measured at 1100 °C. It can be seen that the products distribution was also not changed during the stability test.

It is clear that the Ru/Al₂O₃ + MnO_x performs very well and shows stable performance even after 506 hours of operation at high temperature.

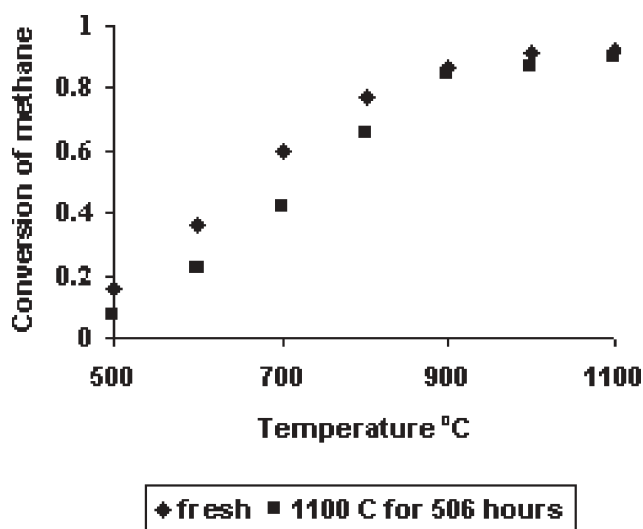


Fig. 12 Conversion of methane as a function of temperature at $P = 1$ bar for the fresh sample as well as after testing for 506 h at 1100 °C.

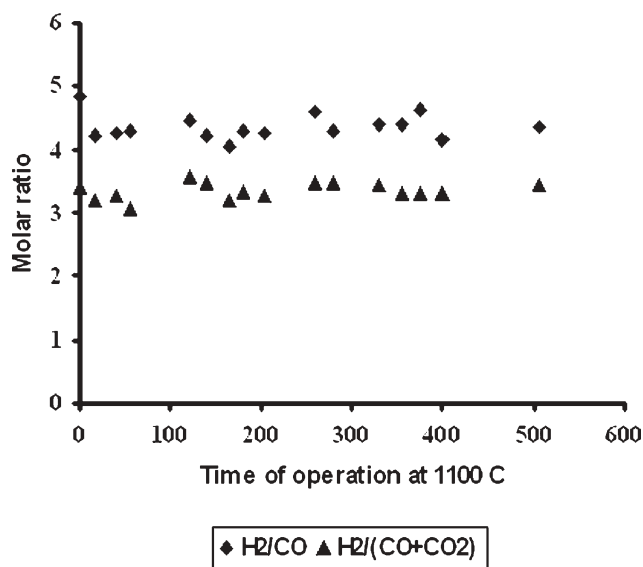


Fig. 13 H_2/CO and $H_2/(CO + CO_2)$ molar ratios versus time of operation at 1100 °C.

Conclusions

A catalytic system applicable for a directly illuminated solar reformer conception was constructed using an array of ceramic pins loaded with the catalyst. The Ru/Al_2O_3 catalyst promoted with Mn oxides was supported on the ceramic pins (made of alumina) by wash coating. Catalytic elements for use in a volumetric solar reformer have been developed. The Ru/Al_2O_3 catalysts promoted with Mn oxides show very good results. The effect of Mn on dispersion and sintering of the Ru

particles was investigated in the present work by TEM and EDS. It was found that addition of Mn oxides decreases the rate of the sintering of the Ru particles. The long-term test confirmed the chemical and thermal stability of the catalyst after operating for 500 hours at 1100 °C.

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Green approach to bulk and template-free synthesis of thermally stable reduced polyaniline nanofibers for capacitor applications†

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An extremely simple green approach is described that generates bulk quantities of nanofibers of the electronic polymer polyaniline in fully reduced state (leucoemeraldine form) in one step without using any reducing agent, surfactants, and/or large amounts of insoluble templates. Chemical oxidative polymerization of aniline with acetic acid instead of HCl (conventional synthesis) dramatically changes the morphology of the resulting doped polyaniline powder from nonfibrillar (particulate) to almost exclusively nanofibers of the reduced leucoemeraldine state in the diameter range 20 nm to 50 nm depending on the acetic acid concentration. These reduced leucoemeraldine polyaniline nanofibers undergo a spontaneous redox reaction with noble metal ions under mild aqueous conditions, resulting in deposition of various shapes, such as leaf, particulate, nanowires and cauliflower for Ag, Pd, Au, and Pt, respectively, on the surface of polyaniline nanofibers, affording a facile entry into this technologically important class of metal–polymer nanocomposites. These nanofibers also can act as seed templates to synthesize polyaniline nanofibers by conventional HCl doped synthesis where particulate morphology normally dominates. The ensuing polyaniline nanofibers have a broad final decomposition temperature which is at least 120 °C higher and have a very high dielectric constant ≈ 3500 at higher frequency when compared to reported reduced polyaniline and HCl based polyaniline.

Introduction

A straightforward single-step approach is described for the synthesis of bulk quantities of nanofibers of the electronic polymer fully reduced polyaniline (leucoemeraldine) without using any reducing agent, surfactants, and/or large amounts of insoluble templates. In contrast to the conventional HCl doped polyaniline which is in the nonfibrillar state (particulate), herein we describe the chemical oxidative polymerization of aniline with acetic acid which affords almost exclusively nanofibers of reduced leucoemeraldine state polyaniline in the diameter range 20 nm to 50 nm depending on acetic acid concentration. These reduced leucoemeraldine polyaniline nanofibers have a broad final decomposition temperature, which is at least 120 °C higher when compared to reported reduced polyaniline. The nanofibers undergo a spontaneous redox reaction with noble metal ions under mild aqueous conditions, resulting in deposition of Ag, Pd, Au, and Pt nanostructures in various shape forms, such as leaf, particulate, nanowires and cauliflower, respectively, thus affording a facile entry into this technologically important class of metal–polymer nanocomposites. These nanofibers can also act as seed template for the synthesis of polyaniline nanofibers by

conventional HCl media synthesis where particulate morphology normally dominates.

The conventional chemical oxidative polymerization approaches to 1D-nanostructured polyaniline include the use of the seeding concept,¹ insoluble solid templates, such as zeolites,² polycarbonate,³ anodized alumina,⁴ use of soft templates, for example, surfactants,⁵ micelles,⁶ liquid crystals,⁷ thiolated cyclodextrins,⁸ and polyacids,⁹ physical methods, *viz.* electrospinning,¹⁰ mechanical stretching,¹¹ and non-template approaches, such as interfacial polymerization.¹² However, these methods yield only emeraldine salt in the oxidized form with fiber diameters ranging from 30 to 150 nm. In order to get reduced leucoemeraldine polyaniline form it is necessary to use reducing agents, such as *N,N*-methylhydroxylamine, sodium tetrahydroborate, sodium dithionate, and hydrazine monohydrate.¹³ Herein, we describe a simple strategy for the bulk and template-free synthesis of reduced leucoemeraldine polyaniline nanofibers that range from as low as 20 nm to 50 nm at room temperature, without the use of any reducing agent.

Experimental

The leucoemeraldine polyaniline nanofibers were synthesized using acetic acid as follows. All chemicals, of analytical grade purity, were used as received. In a typical procedure for the preparation of polyaniline nanofibers, 4.6 mL of aniline monomer and 3.8 g of ammonium peroxydisulfate were dissolved in two separate beakers containing 200 mL of 1.0 M acetic acid. The prepared solutions were then poured rapidly into a 500 mL glass beaker and stirred with a magnetic stirrer (Corning Inc.) The product was filtered and washed

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with milli-Q water. Similarly separate experiments were conducted using 0.1 and 3 M acetic acid solutions. Scanning electron microscope (SEM) images were taken with a Philips EX 30 series environmental Field Emission SEM microscope. A small drop of the resulting dispersion was cast on a carbon tape/transmission electron microscope (TEM) copper grids for selected samples and dried in air for SEM imaging. Gold was coated prior to SEM imaging. The TEM measurement was done using a JEOL JSM 1200 II microscope. A small amount of powder was dispersed in acetonitrile and drop casted on a carbon coated copper grid (TEM grid) and dried at room temperature. TGA curves were obtained using a Perkin-Elmer Thermal Analyzer with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under air. The dielectric constant measurements were done using a HP impedance analyzer (Model No.4291 A) on pressed 1 cm pellets.

Results and discussion

The SEM and TEM images of the polyaniline powder obtained at room temperature using varying concentration of acetic acid show fibrillar morphology with fibers having an average diameter in the range 20–50 nm (Fig. 1 and Fig. 2). The use of lower concentrations of acetic acid, such as 0.1 M, afforded nanofibers with a diameter as low as 20 nm but in lower yields (see Fig. 2 for TEM images). At higher concentrations, *e.g.* in 1 M and 3 M acetic acid, higher yields of nanofibers were obtained, with diameters ranging from 30 nm to 50 nm. Further increase in acetic acid concentration started to generate particulate morphology. It is important to note that such a drastic quantitative change in the morphology of the bulk precipitate to nanofibers state with diameters ranging from as low as 20 nm to several hundred nanometers and lengths from a few microns to several hundred microns is significant. The control of diameter could be easily accomplished by changing the acetic acid concentration. The polyaniline nanofibers obtained were essentially identical to conventional nonfibrillar leucoemeraldine. For example, the

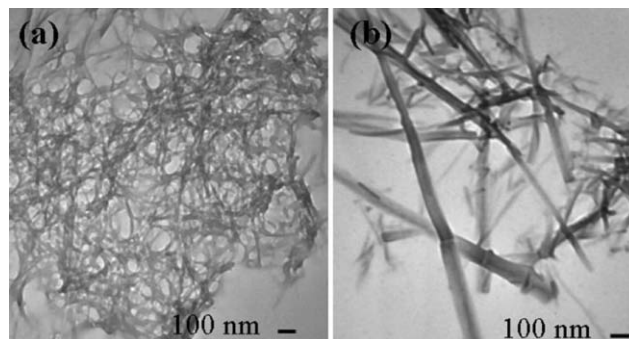


Fig. 2 TEM images of leucoemeraldine polyaniline nanofibers synthesized using (a) 0.1 M acetic acid and (b) 3 M acetic acid.

FT/IR and solution UV/Vis spectra (in *N*-methyl pyrrolidone, NMP) of the corresponding reduced forms are consistent with the polymer being in the leucoemeraldine oxidation state (see Fig. 3 and Fig. 4).¹³ The IR spectra exhibit a very weak peak at 1590 cm^{-1} and no absorption at 1160 cm^{-1} , typical of a quinonoid structure of reduced polyaniline. UV/Vis shows a sharp peak around 350 nm which is characteristic of reduced polyaniline. Although the reasons for the reduced oxidation state and fibrillar morphology of polyaniline are not clear, we believe it could be related to the ionic strength of the acid used and “dopant induced self assembly” in which functional organic dopants are used.¹⁴ This polymerization proceeds *via* an induction period followed by the rapid formation of a precipitate dictated by the acid strength, solubility of the monomer and conduction of ions. Consequently, polymerization would proceed favorably under low ionic strength to afford fibrillar morphology (see schematic diagram in the inset of Fig. 3). In the aniline polymerization reaction, an acidic solution enhances the head-to-tail coupling between aniline monomers and various methods have been used to synthesize polyaniline nanofibers.^{1–12} However, to the best of our knowledge, the present

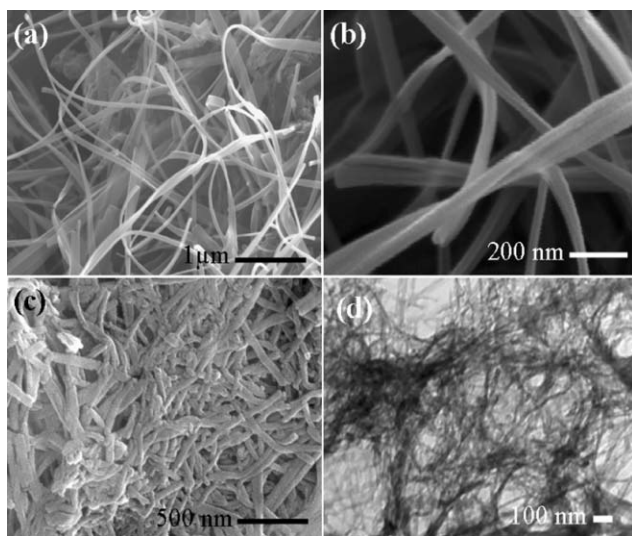


Fig. 1 SEM image of polyaniline synthesized using (a–b, low and high magnification) 3 M, (c) 1 M acetic acid, and TEM image of (d) 1 M acetic acid.

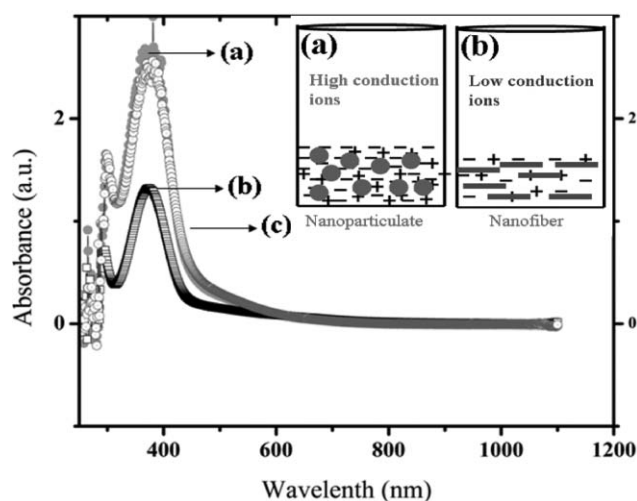


Fig. 3 UV spectra of (a) 0.1 M, (b) 1 M and (c) 3 M acetic acid media synthesized polyaniline nanofibers. Inset shows (a) conventional HCl synthesis with high-conduction ions and (b) acetic acid with relatively low-conduction ions.

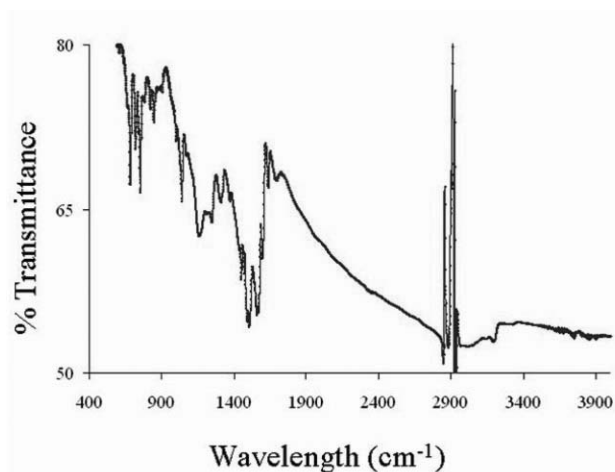


Fig. 4 IR spectra of polyaniline nanofibers synthesized using 1 M acetic acid.

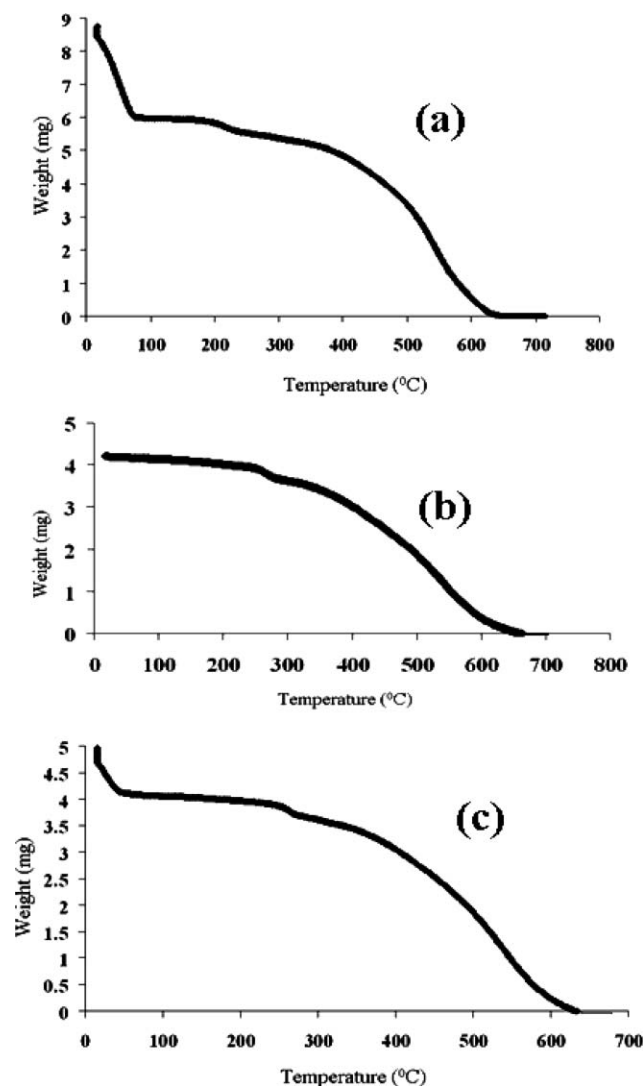


Fig. 5 Thermogravimetric analysis (TGA) of polyaniline nanofibers synthesized using (a) 0.1 M and (b) 1 M and (c) 3 M acetic acid.

study generated these polyaniline nanofibers in reduced oxidation state for the first time with diameters as low as 20 nm in the absence of any reducing agents and/or templates at room temperature.

These reduced leucoemeraldine polyaniline nanofibers have a broad decomposition temperature, with final decomposition being around 620–650 °C depending on the acetic acid concentration used for the preparation; this is at least 120 °C higher when compared to reported reduced polyaniline^{13a} (see Fig. 5 for TGA patterns).

These nanofibers can act as seed templates to synthesize polyaniline nanofibers by conventional HCl doped polyaniline wherein particulate morphology dominates (see Fig. 6 for SEM images). As synthesized, polyaniline nanofibers were colorless and spontaneously reduced noble metal ions to the corresponding metal nanostructures at room temperature without use of any capping or dispersing agents. For example, Ag formed leaf kinds of structures (see Fig. 7a) in the presence of polyaniline nanofibers under mild aqueous conditions at room temperature. Similarly, Au afforded self assembled nanowires (see Fig. 7c), Pd yielded nanoparticles with diameters less than 5 nm and Pt formed agglomerated flowery structures (see Fig. 8 for SEM and Fig. 9 for EDX results). The differences in shape are a result of the different reduction potential of noble metals, *e.g.* palladium (Pd, reduction potential 0.915 V *vs.* SCE), silver (Ag, 0.80 V *vs.* SCE), platinum (Pt 1.20 V *vs.* SCE) and gold (Au 1.50 V *vs.* SCE). Additionally, the shape and size formation of these noble nanostructures is also dependent on the reducing agent used and its reduction capability. The higher the reduction potential of the reducing agent the more chance of noble metal particle growth. In the present case, by controlling the oxidation state

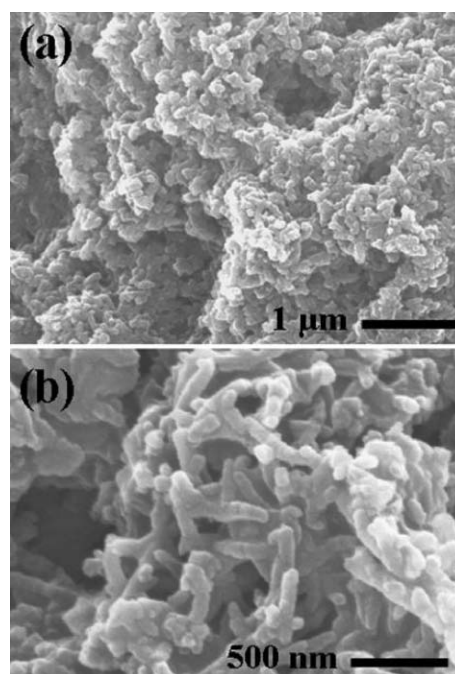


Fig. 6 SEM image of polyaniline synthesized using 1 M HCl as dopant (a) without and (b) with reduced polyaniline nanofiber seed.

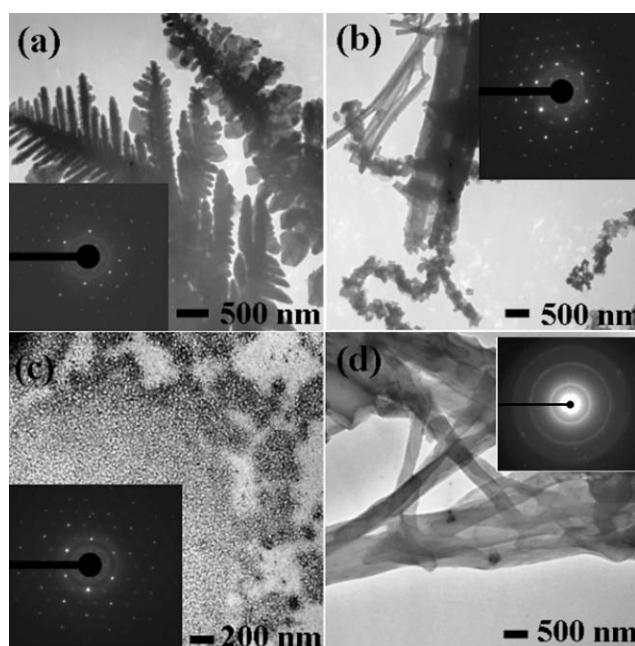


Fig. 7 TEM images of different shaped noble metal-polyaniline nanocomposites obtained using 1 M acetic acid synthesized polyaniline nanofibers: (a) Ag, (b) Pd, (c) Au and (d) Pt nanocomposites. Insets show corresponding electron diffraction patterns.

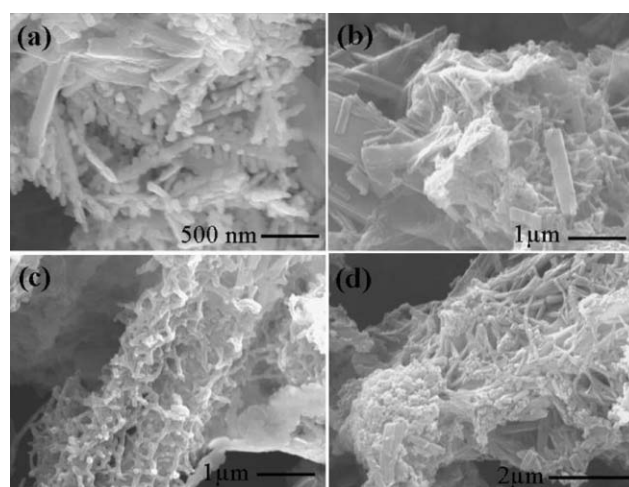


Fig. 8 SEM image of (a) Ag, (b) Pd, (c) Au and (d) Pt nanocomposites with polyaniline nanofibers on copper grid (TEM grid).

the polyaniline nanofibers it is possible to control the shape and size of the noble nanostructures. All these noble metal nanostructures crystallized in fcc symmetry.

Nanostructured forms of polyaniline, such as nanowires, nanofibers, and nanorods, have recently received much attention because of their high surface area for the detection

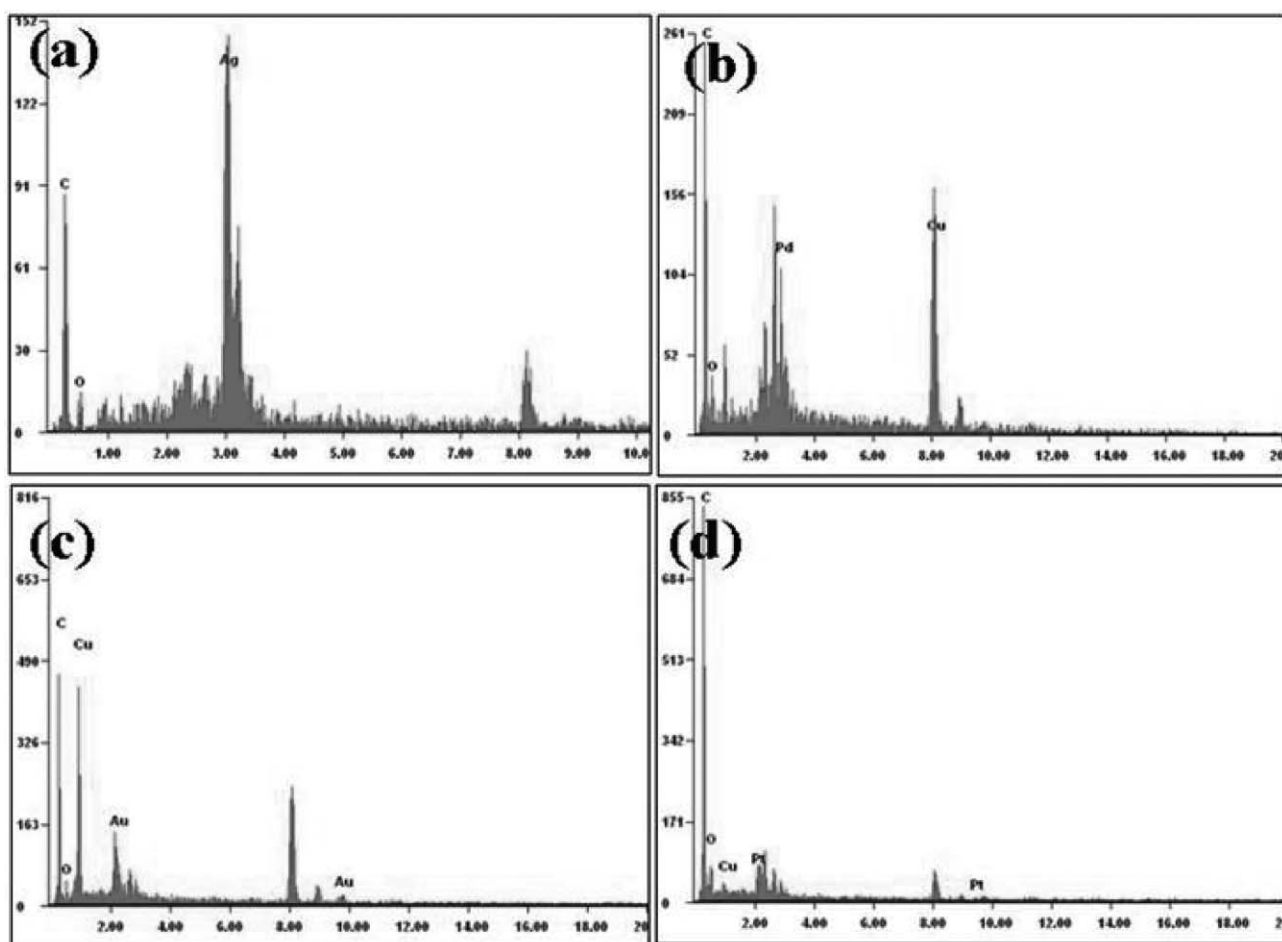


Fig. 9 Energy dispersive analysis (EDX) of (a) Ag, (b) Pd, (c) Au and (d) Pt nanocomposites with polyaniline nanofibers on copper grid (TEM grid).

of gases¹⁴ and, importantly, composites of Au-polyaniline nanofibers can be used as nonvolatile memory.¹⁵ This facile room temperature approach to synthesizing bulk quantities of reduced polyaniline nanofibers and noble metal nanocomposites may find useful applications in ever expanding science and technology endeavors.

Development of high dielectric constant polymer nanocomposites has been a major challenge of integral capacitor technology.^{16,17} High dielectric constant nanocomposites are being continuously explored by the electronics industries in response to the need for power-ground decoupling to secure the integrity of high-speed signals with reduced electromagnetic interference radiated noise.^{18,19} Ceramic nanocomposites with dielectric constant up to 150 are of great interest as embedded capacitor materials because they combine the processability of polymers with the high dielectric constant of ceramics.^{20,21} Some novel nanocomposites of epoxy and lead magnesium niobate-lead titanate have been reported²² with a dielectric constant value of 110. High dielectric constant ceramics employed to develop nanocomposites have been derived by the impregnation of niobates, titanates, zirconia (ZrO_2), tantalum oxide (Ta_2O_5), aluminum oxide (Al_2O_3), *etc.* However, the interface adhesion between the ceramics and polymer matrix is poor, especially when ceramic loading is high.^{23,24} Over the past decades, polyaniline has emerged as one of the most promising organic conducting polymers, owing to its high polymerization yield and good chemical stability, combined with moderate electrical conductivity and relatively low cost.^{25,26} Nevertheless, some studies have indicated that polyaniline and polyaniline/polymer blends are capable of enhancing the dielectric constant up to 10^4 times in a partially crystalline polyaniline.²⁷ The present investigation involved a simple, yet elegant method to prepare bare polyaniline that could exhibit a very high dielectric constant (representative 1 M acetic acid media prepared sample) and low loss at lower frequency (see Fig. 10).

The basic function of a capacitor is to store opposite polarity electrostatic charges on a pair of electrically insulated conductive surfaces. The quantity of charge stored on each of these surfaces is directly proportional to their surface areas and inversely proportional to the distance between the surfaces. The dielectric constant is a measure of the degree to which the insulating material's surface interacts with the electric field set up between the charged plates. The constant is dependent on two molecular level properties: the permanent "dipole moment" and the "polarizability" or the induced change in dipole moment due to the presence of an electric field. The permanent dipole moment is the average over the various dipole moments given rise to by structural charge density differences over intramolecular distances. The charge density differences result from the electronegativity differences between the various atoms which comprise the molecular structure of the insulator. Polarizability is the property which arises from changes in the molecular electron distribution induced by the applied electric field. In the present case, the dielectric constant arises due to polarization of the negatively charged acetate molecules present in the polyaniline. The dielectric constant is relatively high (≈ 3500) when compared with HCl based polyaniline.²⁸ It is interesting to note that dielectric loss is low at higher frequency, whereas the dielectric constant is very high at higher frequency.

In order to understand the crystallinity of polyaniline, we have recorded an XRD pattern for the product obtained using 1 M acetic acid (Fig. 11). The polyaniline nanofibers are highly crystalline in nature when compared with the polyaniline prepared using regular HCl media.²⁹ The crystalline peaks at 2θ values 15° , 20° and 25° correspond to polyaniline nanofibers, and are very much comparable to the literature reported pattern of polyaniline in the metallic state.³⁰ The additional high intensity peak observed at lower angle and the minor peaks, other than those from the polyaniline nanofibers, correspond to sodium acetate which is formed during the preparation.

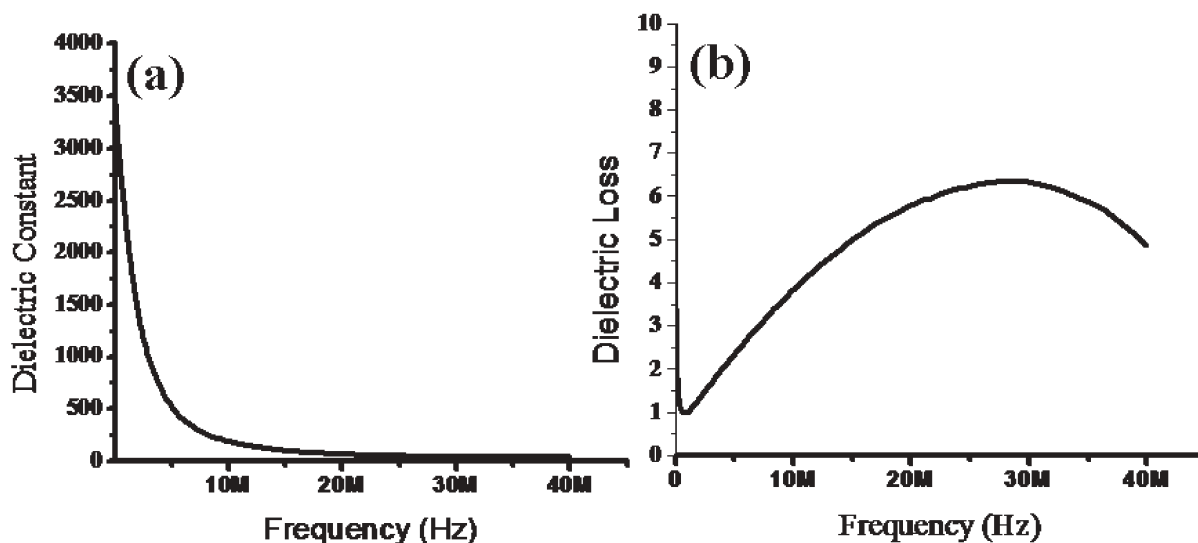


Fig. 10 (a) Dielectric constant and (b) dielectric loss for polyaniline synthesized using 1 M acetic acid.

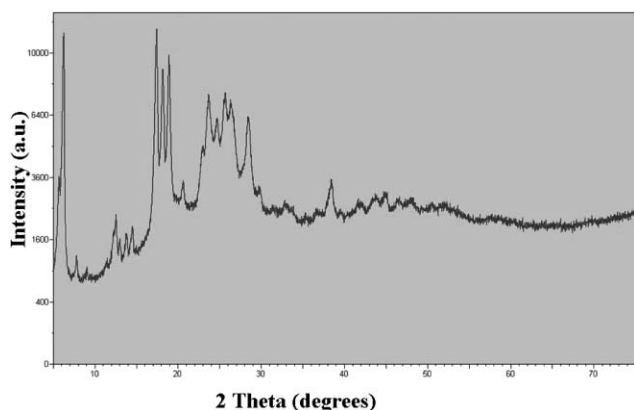


Fig. 11 XRD pattern of polyaniline nanofibers synthesized in 1 M acetic acid media at room temperature.

Conclusions

In summary, we have shown the synthesis of emerging nanostructures of electronic polymers over multiple length scales that are triggered by the ionic strength of the acids used. Specifically, we describe (i) the use of low ionic strength acid *i.e.* acetic acid in a single-step bulk synthesis of leucoemeraldine polyaniline (completely reduced state) nanofibers without the need for reducing agent, template and or seed at room temperature, (ii) a convenient method to obtain very thin nanofibers of leucoemeraldine polyaniline with diameters from 20 nm up to 50 nm, (iii) spontaneous redox reactions of nanofibers with noble metal ions under mild aqueous conditions, resulting in deposition of various shapes, such as leaf, particulate, nanowires and cauliflower for Ag, Pd, Au, and Pt, respectively, and (iv) that the polyaniline nanofibers exhibit crystallinity and high thermal stability with a broad decomposition temperature which is at least 120 °C higher when compared with reported reduced polyaniline. They have a very high dielectric constant (≈ 3500) and low loss at lower frequency, which could open a myriad of applications, such as energy storage systems, capacitors, catalysis, fuel cell membranes, and nanodevices.

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Production of olefins from ethanol by Fe-supported zeolite catalysts†

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Ethanol conversion to C_{3+} olefins over Fe/H-ZSM-5 catalysts was investigated. Fe is a non-toxic and cheap metal. C_{3+} olefins are useful not only as fuels but also chemicals. Fe catalysts are fully effective even in the presence of water in EtOH. Therefore, there is no need to remove water from water-containing ethanol, such as bio-ethanol. The initial selectivity of C_{3+} olefins was not affected by the kind of Fe source and calcination temperature significantly, except in the case of iron phosphate used as the iron source, which showed low C_{3+} olefins selectivity. In general, the selectivity of C_{3+} olefins was slightly decreased with time-on-stream. As causes of catalytic deactivation, carbon deposition on the catalyst and framework collapse of the zeolite support can be considered. However, in the cases of $Fe_2(SO_4)_3$ - and $FeCl_3$ -derived catalysts, calcined at 700 °C, the decrease in C_{3+} olefins selectivity could be suppressed. In general, selectivity of aromatics was decreased and selectivity of ethylene was increased with time-on-stream. Used catalyst can be regenerated by air treatment at 500 °C, but the degree of regeneration was dependent on the kind of iron starting materials and the calcination temperature. An $FeCl_3$ -based catalyst, calcined at 700 °C, and catalysts calcined at 900 °C (irrespective of iron source) can be almost completely regenerated, while $Fe(NO_3)_3$ - or $Fe_2(SO_4)_3$ -based catalyst, calcined at 700 °C, cannot be completely regenerated by this treatment.

Introduction

Currently, major compounds in the petrochemical industry, for example, ethylene, propylene, benzene and toluene, are synthesized by cracking of the naphtha fraction. However, the amount of petroleum resource is limited and cannot be obtained everywhere. Moreover, the combustion of petroleum produces CO_2 , which causes global warming. Therefore, much attention has been paid to alternative resources to petroleum. Biomass is one candidate, since biomass is a renewable resource and can be obtained everywhere on earth. Moreover, the combustion of biomass does not lead to an increase of CO_2 in the atmosphere, since the biomass can be photo-synthesized from CO_2 in atmosphere, whether directly or indirectly.

Transformation of oxygenate components of biomass pyrolysis oil into hydrocarbons by using H-ZSM-5 zeolite has been reported by Gayubo *et al.*^{1,2} and ethanol is one of the main biomass products. Our interest is to develop catalytic processes for producing these bulk chemicals from ethanol. Berrier *et al.* reported the transformation of ethanol into higher hydrocarbons on Co- Al_2O_3 catalysts.³ We have attempted the production of hydrocarbons from ethanol using zeolite catalysts. We found that H-ZSM-5 zeolite with a low SiO_2/Al_2O_3 ratio favours the formation of higher hydrocarbons, for example BTX (benzene, toluene, xylenes), in high selectivity, as has been reported elsewhere,^{4–12} while other

zeolites form ethylene exclusively. Moreover, Ga or noble metal catalysts supported on H-ZSM-5 zeolite with a low SiO_2/Al_2O_3 ratio showed higher selectivity of BTX, while Fe or Cr loading raised the selectivity of C_{3+} olefins (C_3 – C_7),^{13,14} which are useful not only as fuels but also chemicals. In this study, we investigated the effect of synthesis condition on the production of C_{3+} olefins over iron catalysts, since iron is a non-toxic and cheap metal.

Experimental

Catalyst preparation

As the zeolite support, H-ZSM-5 ($SiO_2/Al_2O_3 = 29$, Tosoh) was used. The zeolite was calcined at 500 °C in a muffle furnace for 6 h (heating rate was 200 °C h^{-1}) prior to use. Iron catalysts were prepared by an impregnation method (Fe = 10 wt%). As sources of Fe, iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, Wako Pure Chemicals), iron(III) sulfate *n*-hydrate ($Fe_2(SO_4)_3 \cdot nH_2O$, Wako Pure Chemicals), iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, Iwai Chemicals), iron(II) oxalate dihydrate ($FeC_2O_4 \cdot 2H_2O$, Kanto Chemicals) and iron(III) phosphate *n*-hydrate ($FePO_4 \cdot nH_2O$, Wako Pure Chemicals) were used. Iron(III) sulfate *n*-hydrate contains 60.0–80.0% of $Fe_2(SO_4)_3$. In this study, the content of $Fe_2(SO_4)_3$ was assumed to be 70.0%, where the value of *n* was *ca.* 9.5. In the case of iron(III) phosphate *n*-hydrate, the value of *n* was assumed to be 2. Iron(II) oxalate dihydrate was dissolved with nitric acid. Iron(III) phosphate *n*-hydrate was dissolved with hydrochloric acid. After impregnation, the wet catalysts were dried at 120 °C, followed by a calcination step in a flow of air, where the calcination temperature was varied from 500 to 900 °C (in every case the heating rate was 200 °C h^{-1}).

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Catalytic activity

The catalytic activity was measured in a fixed-bed reactor (0.2 g of catalyst), using a vaporized EtOH–N₂ flow (60 cm³ min^{−1}), without or with water (N₂:EtOH = 82.1:17.9 vol% and 82.1:16.1:1.8 vol%, respectively), at a temperature of 400 °C, and the change in catalytic performance with time-on-stream was investigated. The effluent gas was analyzed by gas chromatography (GC) equipped with Molecular Sieve 5A and Parapak Q columns. Two detectors were used: a TCD was used to detect light products (hydrogen, carbon monoxide, and carbon dioxide), and an FID to detect hydrocarbons, alcohols, aldehydes and ethers.

Catalytic activity may decrease with time-on-stream. Therefore, regeneration treatment of used catalyst after 7 h reaction was carried out by calcinations at 500 °C in a flow of air for 1 h on a used catalyst, and the secondary catalytic performance was examined.

Characterization

As a cause of catalytic deactivation, carbon deposition during reaction can be considered, since in the case of H-ZSM-5 zeolite used as the catalyst, carbon deposition caused catalytic deactivation.^{7,10,11} Therefore, in order to estimate carbon deposition on catalysts, thermogravimetric (TG) analyses of catalysts after reaction were carried out (Mac Science, TG-DTA2000) in the flow of air with the temperature varying from room temperature to 800 °C at 10 °C min^{−1}.

Moreover, as a cause of catalytic deactivation, as well as change in product selectivities, sintering and transformation of supported FeO_x species can be considered. Therefore, X-ray diffraction (XRD) measurements of catalysts before and after reaction were carried out (Mac Science, M18XHF²²-SRA) and the size of the metal crystallite was calculated by Sherrer's formula.

Framework collapse of the zeolite support, due to dealumination of the zeolite framework during reaction, may have some relation to catalytic deactivation, since the solid acidity of zeolite, essential for this reaction, is generated by the existence of Al atoms incorporated into zeolite framework. Therefore, in this case XRD measurements were also carried out, and the intensities of the XRD peak of zeolite framework before and after reaction were compared to investigate the framework collapse of zeolite during reaction.

NH₃–temperature-programmed desorption (TPD) experiments of zeolite support and Fe catalysts supported on zeolite were carried out in a special NH₃–TPD apparatus (Nihon Bell, BEL-CAT) connected to a Q-Mass analyzer (Pfeiffer Vacuum, Omnistar GCD301), to measure the solid acidity of the support and catalysts. After pre-treatment in a flow of He at 500 °C for 60 min, adsorption of NH₃ at 100 °C for 90 min, and desorption of weak adsorbed NH₃ in the flow of He at 100 °C for 30 min, TPD profiles were obtained under the conditions of He flow with the temperature varying from 100 to 800 °C at 10 °C min^{−1}.

Fourier transform infrared (FT-IR) spectra of zeolite support and Fe catalysts were recorded with a JASCO FT/IR 7000 spectrometer, using KBr pellets under atmospheric conditions, to measure the change of acidic site of

zeolite and catalysts. To eliminate distortions of the fundamental hydroxyl-stretching region due to water adsorption, before analyses vacuum treatment to sample pellets was carried out with heating at about 200 °C for several days.

XPS measurements of Fe catalysts were carried out (ESCA-850, Shimadzu) to investigate the effect of remaining minor elements, for example, N, P, S and Cl, contained in Fe sources (Fe(NO₃)₃·9H₂O, FePO₄·*n*H₂O, Fe₂(SO₄)₃·*n*H₂O and FeCl₃·6H₂O, respectively).

Results and discussion

Catalytic performance

Conversion of EtOH and the selectivity of each product among the gaseous products are shown in Table 1: the main gaseous products were ethylene, C₃₊ olefins (C₃–C₇ olefins were detected), paraffins and aromatics (benzene, toluene, xylenes, mesitylene and pseudocumene). In most cases, EtOH conversion was almost 100%. In general, Fe-loading suppressed the formation of aromatic compounds but enhanced the formations of ethylene and C₃₊ olefins. Paraffins yields were not always inhibited, while the C₃₊ olefins/paraffins ratio was increased by Fe-loading. In most cases, the selectivity of C₃₊ olefins was within 20–28%. Increasing the calcination temperature caused increased ethylene selectivity and decreased aromatics selectivity: for example, in the case of Fe₂(SO₄)₃ and reaction without water, the selectivity of ethylene was increased (from 22.2 to 52.5%) with increase in calcination temperature from 500 to 900 °C. On the other hand, the selectivity of aromatic compounds was decreased (from 35.1 to 10.4%). The effect of the Fe source was not distinguished so much, except for the case of FePO₄, which showed especially high selectivity of ethylene (55–88%) and low selectivity of other products (the selectivity of C₃₊ olefins was 1–20%). In general, the higher the selectivity of aromatics, the lower the selectivity of C₃₊ olefins.

On the other hand, the presence of water affected the selectivity of each product only slightly, probably due to an interaction of surface OH group with water (see Fig. 7). The selectivity of propylene seems to be slightly enhanced by adding water: for example, in the catalyst (Fe(NO₃)₃, 500 °C), the selectivity of propylene was increased (from 9.5 to 11.2%), and in the catalyst (Fe(NO₃)₃, 700 °C), the selectivity was increased (from 10.1 to 11.8%). Moreover, for 500 and 700 °C-calcined catalysts, the selectivity of ethylene was slightly decreased or kept almost constant by adding water, while the ethylene selectivity was increased for 900 °C-calcined catalysts. In most cases, the selectivities of C₃₊ olefins and paraffins were slightly increased by adding water. The selectivity of aromatic compounds was slightly increased by water for 500 °C-calcined catalysts, while the selectivity was decreased by water for most other catalysts.

The selectivity of each product changed with time-on-stream, although ethanol conversion remained constant at *ca.* 100%. The time dependence of the product selectivity could also be associated with a change in the amount of surface OH group and/or acidity. In general, the selectivity of aromatic compounds was decreased with time-on-stream, while the selectivity of ethylene was increased, and in most cases, the

Table 1 Catalytic activity of H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 29$) zeolite and Fe-H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 29$) catalysts

Fe source	Calc. temp./ $^{\circ}\text{C}$	Water	Ethanol conv. (%)	C selectivity (%)				
				Ethylene	C_{3+} olefins	(Propylene)	Paraffins	Aromatics
No Fe loaded	500	No	100.0	6.9	11.9	(5.0)	20.4	59.6
		+H ₂ O	100.0	6.0	13.1	(5.6)	26.0	53.7
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	500	No	100.0	22.4	22.4	(9.5)	20.2	35.0
		+H ₂ O	96.3	21.8	23.6	(11.2)	19.0	35.5
	700	No	97.0	24.9	23.2	(10.1)	20.4	31.5
		+H ₂ O	96.3	24.0	24.6	(11.8)	19.0	31.4
$\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$	900	No	91.5	22.9	26.8	(8.6)	37.3	13.0
		+H ₂ O	100.0	45.2	25.0	(11.9)	14.6	14.6
	500	No	99.6	22.2	23.3	(10.0)	19.4	35.1
		+H ₂ O	100.0	12.5	22.8	(10.8)	22.5	41.8
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	700	No	92.3	18.4	25.8	(11.5)	21.9	33.9
		+H ₂ O	97.0	17.6	24.3	(11.3)	20.7	37.5
	900	No	98.2	52.5	23.7	(11.0)	12.8	10.4
		+H ₂ O	99.9	52.4	24.9	(11.6)	13.5	8.9
$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	500	No	99.6	30.9	19.5	(9.0)	18.5	30.8
		+H ₂ O	100.0	24.2	21.7	(9.7)	20.2	34.0
	700	No	100.0	29.8	25.0	(12.0)	15.6	29.6
		+H ₂ O	100.0	30.6	27.1	(12.5)	17.5	24.8
$\text{FePO}_4 \cdot n\text{H}_2\text{O}$	900	No	99.9	39.0	25.3	(10.8)	14.6	20.9
		+H ₂ O	100.0	45.8	26.5	(11.9)	15.1	12.2
	700	No	95.6	33.9	25.1	(12.0)	15.9	25.2
		+H ₂ O	100.0	32.0	26.5	(12.4)	16.5	24.6
$\text{FePO}_4 \cdot n\text{H}_2\text{O}$	900	No	100.0	38.2	28.7	(12.8)	16.0	17.2
		+H ₂ O	95.60	55.5	17.4	(8.1)	9.6	17.2
	900	No	100.00	60.9	19.5	(9.1)	11.0	8.5
				97.6	1.5	(0.8)	0.7	0.0

selectivity of C_{3+} olefins was slightly decreased. Fig. 1 shows the plots of the initial selectivity of C_{3+} olefins *versus* the decrease in the selectivity of C_{3+} olefins between 0 and 7 h after starting the reaction. In this reaction, neat ethanol was used. For 500 $^{\circ}\text{C}$ -calcined catalysts, having IR-detectable surface OH groups (Fig. 7), there seems to be a correlation between initial selectivity of C_{3+} olefins and decrease in C_{3+} olefins selectivity. On the other hand, 700- and 900 $^{\circ}\text{C}$ -calcined

catalysts showed no correlation: the initial selectivities of C_{3+} olefins did not differ so significantly, except for the case of FePO_4 -derived catalyst showing low initial selectivity. Similarly, two exceptional catalysts ($\text{Fe}_2(\text{SO}_4)_3$, 700 $^{\circ}\text{C}$, and FeCl_3 , 700 $^{\circ}\text{C}$) with weak OH absorptions showed extremely small decreases (between 0 and 7 h after starting reaction) in the C_{3+} olefins selectivity (-0.8 and 0.8% , respectively) even at the high initial selectivity of C_{3+} olefins (25.3 and 25.0%, respectively). Moreover, in most cases, the decrease in C_{3+} olefins selectivity was slightly increased by adding water, while the increase in ethylene selectivity and the decrease in aromatics selectivity were enlarged by adding water.

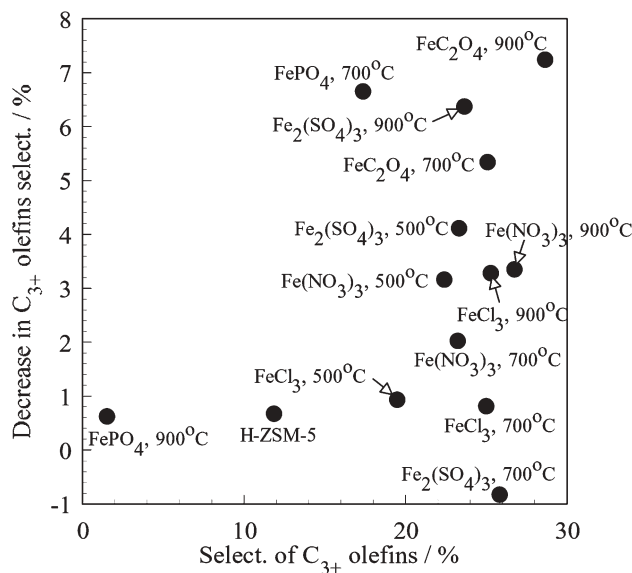


Fig. 1 Plots of the initial selectivity of C_{3+} olefins *versus* the decrease in selectivity of C_{3+} olefins over H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 29$) zeolite and Fe-H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 29$) catalysts. Reaction gas: $\text{N}_2 + \text{EtOH}$ (without H_2O).

Carbon deposition

In order to estimate carbon deposition on the catalyst surfaces, TG analyses were carried out and the mole number of C atoms in deposited carbon was calculated from the weight loss due to combustion of deposited carbon. Fig. 2 shows the plots of deposited carbon/total EtOH ratio in the mole number of C atoms *versus* the decrease in C_{3+} olefins selectivity between 0 and 7 h after starting the reaction. Here, neat ethanol was used. There was a small difference in the deposited carbon/total EtOH ratio between each catalyst, ranging from 0.07 to 0.14, except for $\text{Fe}_2(\text{SO}_4)_3$, 500 $^{\circ}\text{C}$ (0.2%) and FePO_4 , 900 $^{\circ}\text{C}$ (0.0%). In general, 500 $^{\circ}\text{C}$ -calcined catalysts showed a large amount of deposited carbon: the decrease in C_{3+} olefins selectivity as well as carbon deposition was larger than H-ZSM-5 support. 900 $^{\circ}\text{C}$ -calcined catalysts showed a small amount of carbon deposition (smaller than H-ZSM-5 support) and a large decrease in selectivity except for FePO_4 -derived catalyst, which showed a small decrease in selectivity. On the other hand, 700 $^{\circ}\text{C}$ -calcined catalysts showed a moderate

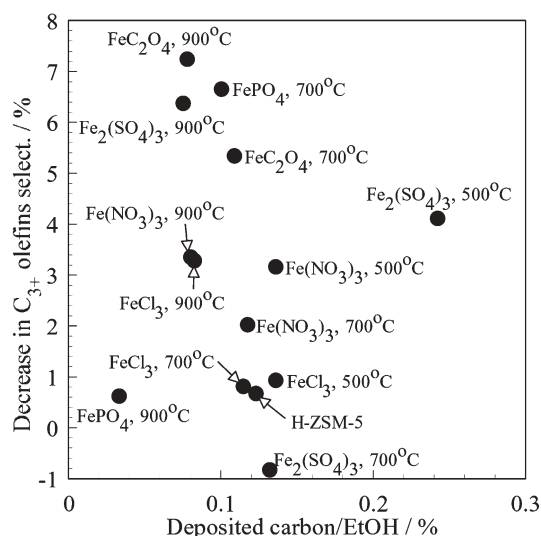


Fig. 2 Plots of deposited carbon/total EtOH ratio in mole number of C atoms calculated by result of TG analysis *versus* the decrease in C_{3+} olefins selectivity over H-ZSM-5 ($SiO_2/Al_2O_3 = 29$) zeolite and Fe-H-ZSM-5 ($SiO_2/Al_2O_3 = 29$) catalysts. Reaction gas = $N_2 + EtOH$ (without H_2O).

amount of carbon deposition, near H-ZSM-5 support. Moreover, there seems to be a weak inverse correlation between the amount of carbon deposition and the decrease in C_{3+} olefins selectivity. Although the deposited carbon/total EtOH ratio was low and negligible for the selectivity of each product and carbon balance, the effect on catalytic activity was not negligible.

Fig. 3 shows the plots of deposited carbon/total EtOH ratio in mole number of C atoms *versus* the decrease in the selectivity of aromatic compounds. It is suggested that the lower calcination temperature leads to not only a larger

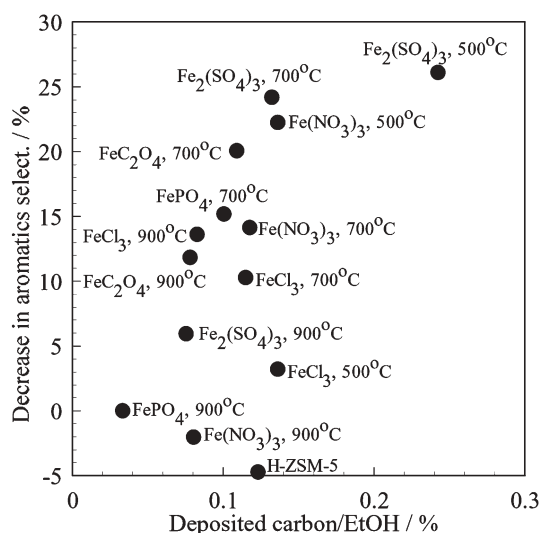


Fig. 3 Plots of deposited carbon/total EtOH ratio in mole number of C atoms calculated as a result of TG analysis *versus* the decrease in aromatics selectivity over H-ZSM-5 ($SiO_2/Al_2O_3 = 29$) zeolite and Fe-H-ZSM-5 ($SiO_2/Al_2O_3 = 29$) catalysts. Reaction gas = $N_2 + EtOH$ (without H_2O).

amount of carbon deposition but also a larger decrease in the selectivity of aromatic compounds: for example, the average decrease in selectivity for 700 °C-calcined catalysts was larger than that for 900 °C-calcined catalysts. As was previously reported,^{13,14} the catalysts yielding aromatic compounds in high selectivity tend to deposit large amounts of carbon, suggesting that aromatic compounds can be converted to deposited carbon. On the other hand, only a weak correlation between the deposited carbon/total EtOH ratio and the initial selectivity of C_{3+} olefins was recognized. Therefore, carbon deposition can be responsible for catalytic deactivation. However, this is not the only cause. In general, acidic sites of zeolite support are essential to the formation of aromatic compounds.^{4,7} When the acidic sites were covered with deposited carbon, the formation of aromatic compounds was suppressed, but the formation of C_{3+} olefins was not inhibited so significantly. The amount of carbon deposition was slightly decreased by adding water, suggesting that gasification of deposited carbon to H_2 and CO may occur by addition of water. However, water can be obtained from ethanol *via* dehydration. Therefore, the effect of water addition on carbon deposition was not significant.

Change in phase and crystallite diameter of loaded iron

Fig. 4 shows XRD patterns of Fe_2O_3 , Fe_3O_4 and Fe/H-ZSM-5 catalysts before and after reaction (without water). In the cases of $Fe(NO_3)_3$ -derived catalysts, before reaction, the loaded Fe exists as Fe_2O_3 . However, in the case of 500 and 700 °C-calcined catalysts, Fe_2O_3 species were partially reduced to Fe_3O_4 during reaction, while Fe_2O_3 on 900 °C-calcined catalyst was almost unchanged without reduction even after reaction. On the other hand, catalyst ($Fe_2(SO_4)_3$, 500 °C) does not show the XRD pattern of FeO_x before reaction, suggesting

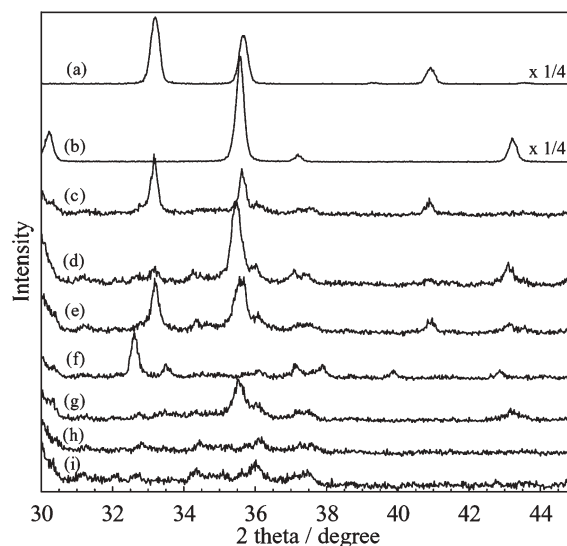


Fig. 4 XRD patterns of Fe_2O_3 , Fe_3O_4 and Fe-H-ZSM-5 ($SiO_2/Al_2O_3 = 29$) catalysts before and after reaction (without H_2O). (a) Fe_2O_3 , (b) Fe_3O_4 , (c) $Fe(NO_3)_3$, 900 °C, before reaction, (d) $Fe(NO_3)_3$, 700 °C, after reaction, (e) $Fe(NO_3)_3$, 900 °C, after reaction, (f) $Fe_2(SO_4)_3$, 500 °C, before reaction, (g) $Fe_2(SO_4)_3$, 500 °C, after reaction, (h) $FePO_4$, 700 °C, before reaction, (i) $FePO_4$, 700 °C, after reaction.

Table 2 Phase and crystallite size of FeO_x on Fe-H-ZSM-5 catalysts before and after reaction (without H₂O)

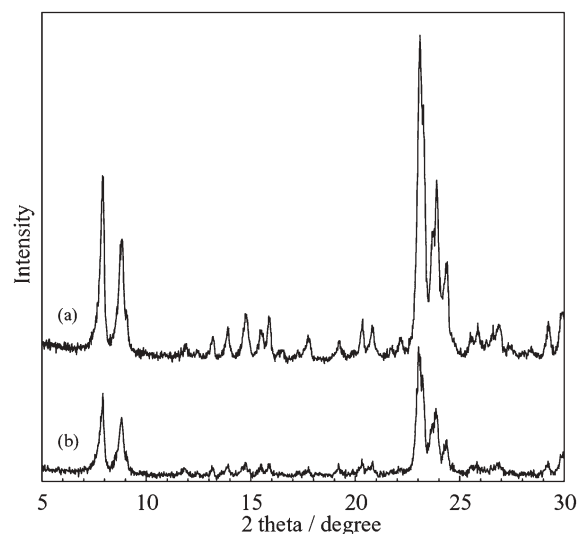
Fe source	Calc. temp./°C	Phase (crystallite size/nm)	
		Before reaction	After reaction
Fe(NO ₃) ₃ ·9H ₂ O	500	Fe ₂ O ₃ (22.2)	→ Fe ₃ O ₄ (18.3)
	700	Fe ₂ O ₃ (29.1)	→ Fe ₃ O ₄ (27.2)
	900	Fe ₂ O ₃ (34.9)	→ Fe ₂ O ₃ (33.2)
Fe ₂ (SO ₄) ₃ ·nH ₂ O	500	FeSO _x	→ Fe ₃ O ₄ (20.8)
	700	Fe ₂ O ₃ (35.6)	→ Fe ₃ O ₄ (29.4)
	900	Fe ₂ O ₃ (38.4)	→ Fe ₂ O ₃ (40.2)
FeCl ₃ ·6H ₂ O	500	Fe ₂ O ₃ (45.1)	→ Fe ₃ O ₄ (42.4)
	700	Fe ₂ O ₃ (45.2)	→ Fe ₃ O ₄ (39.7)
	900	Fe ₂ O ₃ (41.8)	→ Fe ₂ O ₃ (39.7)
FeC ₂ O ₄ ·2H ₂ O	700	Fe ₂ O ₃ (32.3)	→ Fe ₃ O ₄ (25.6)
	900	Fe ₂ O ₃ (29.6)	→ Fe ₂ O ₃ (29.7)
FePO ₄ ·nH ₂ O	700	FePO _x	→ FePO _x
	900	FePO _x	→ FePO _x

that Fe may exist as FeSO_x species, which is effective for the formation of aromatic compounds and carbon deposition, while after reaction, the XRD pattern of Fe₃O₄ was observed. The catalyst (FePO₄, 700 °C) showed no FeO_x pattern both before and after reaction. Fe may exist as FePO_x species, effective for ethylene formation, but not effective for the formation of C₃₊ olefins and aromatic compounds.

Phase and crystallite diameter of FeO_x on Fe catalysts before and after reaction are summarized in Table 2. Except for the cases of catalyst (Fe₂(SO₄)₃, 500 °C) and FePO₄-derived catalysts, FeO_x existed as Fe₂O₃ before reaction, while after reaction, Fe₂O₃ was partially reduced to Fe₃O₄ for 500 and 700 °C-calcined catalysts, but Fe₂O₃ was unchanged for 900 °C-calcined catalysts. In the cases of Fe(NO₃)₃-derived and Fe₂(SO₄)₃-derived catalysts, the higher calcination temperature led to larger crystallite diameter both before and after reaction. In most cases, the crystallite diameter of FeO_x on 500 and 700 °C-calcined catalysts became smaller during reaction, perhaps due to removal of O atoms during reaction. On the other hand, in the case of 900 °C-calcined catalysts, the crystallite diameter of Fe₂O₃ was not decreased so significantly, suggesting that removal of O atoms scarcely occurred. From these results, it appeared that the sintering of supported Fe was not very prevalent. However, there seems to be a poor correlation between the crystallite diameter before reaction and the selectivity of each product. In general, a larger decrease in FeO_x crystallite diameter resulted in a lower decrease in C₃₊ olefins selectivity and a higher decrease in aromatics selectivity.

Framework collapse of zeolite

Fig. 5 shows XRD patterns of the catalyst (Fe(NO₃)₃, 700 °C) before and after reaction, where all XRD peaks are due to the framework of H-ZSM-5 zeolite, excluding the peak of FeO_x: the intensity of XRD patterns was weakened during reaction, suggesting that framework collapse, at least in part, proceeded during reaction. The after reaction/before reaction ratio in intensity of XRD pattern detected at 7.9° is summarized in Table 3, showing that framework collapse scarcely occurred on 500 °C-calcined catalysts and, in general, a higher calcination temperature led to collapse to a greater degree. However, the

**Fig. 5** XRD patterns of Fe-H-ZSM-5 (SiO₂/Al₂O₃ = 29) (Fe(NO₃)₃, 700 °C) catalysts before and after reaction (without H₂O). (a) Before reaction, (b) after reaction.

catalyst (Fe(NO₃)₃, 700 °C) showed an especially low ratio (0.42), lower than Fe₂(SO₄)₃, 700 °C (0.62) and FeCl₃, 700 °C (0.70), suggesting that remaining S or Cl species can inhibit framework collapse in some degree. These findings could be consistent with the fact that the decrease in selectivity of C₃₊ olefins in Fe₂(SO₄)₃- or FeCl₃-derived catalysts was lower than that in Fe(NO₃)₃-derived catalysts (Fig. 1).

Solid acidity of catalysts

NH₃-TPD profiles of zeolite support and Fe catalysts are shown in Fig. 6. H-ZSM-5 support showed a desorption peak at about 400 °C. Fe(NO₃)₃-derived catalysts, calcined at 500 and 700 °C, showed an NH₃ desorption peak at about 400 °C, while the calcination at 900 °C led to the disappearance of NH₃ desorption peak. The catalyst (Fe₂(SO₄)₃, 500 °C) showed an NH₃ desorption peak at 370 °C: this peak may have been due to FeSO_x species. With calcination at a higher temperature, the NH₃ desorption peak decreased. In the cases of FeCl₃ and FeC₂O₄, NH₃ desorption peaks were not clear. On the other hand, in the case of FePO₄, the NH₃ desorption peak

Table 3 Ratio of intensity of X-ray diffraction peaks (at 7.9°) of Fe-H-ZSM-5 (SiO₂/Al₂O₃ = 29) catalysts before and after reaction (without H₂O)

Fe source	Calc. temp./°C	Ratio of intensity (after reaction/before reaction)
Fe(NO ₃) ₃ ·9H ₂ O	500	0.81
	700	0.42
	900	0.61
Fe ₂ (SO ₄) ₃ ·nH ₂ O	500	0.98
	700	0.62
	900	0.59
FeCl ₃ ·6H ₂ O	500	0.94
	700	0.70
	900	0.47
FeC ₂ O ₄ ·2H ₂ O	900	0.72
FePO ₄ ·nH ₂ O	900	0.56

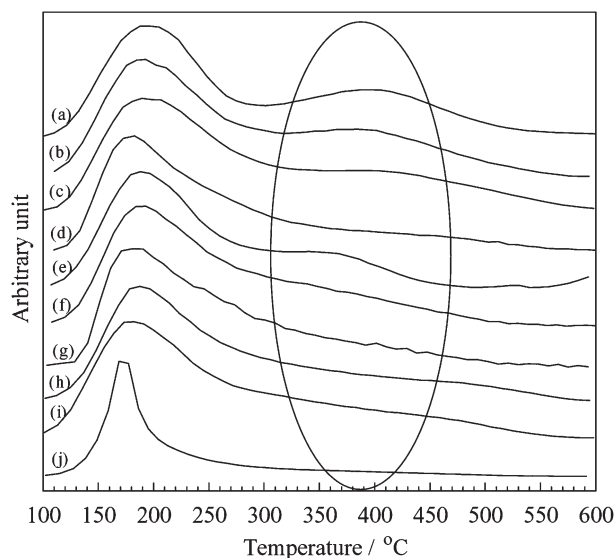


Fig. 6 NH_3 -TPD profiles of H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 29$) zeolite and Fe-H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 29$) catalysts. (a) H-ZSM-5, (b) $\text{Fe}(\text{NO}_3)_3$, 500 °C, (c) $\text{Fe}(\text{NO}_3)_3$, 700 °C, (d) $\text{Fe}(\text{NO}_3)_3$, 900 °C, (e) $\text{Fe}_2(\text{SO}_4)_3$, 500 °C, (f) $\text{Fe}_2(\text{SO}_4)_3$, 700 °C, (g) $\text{Fe}_2(\text{SO}_4)_3$, 900 °C, (h) FeCl_3 , 700 °C, (i) FeC_2O_4 , 700 °C, (j) FePO_4 , 700 °C.

disappeared completely, suggesting that FePO_x species block the acidic site of zeolite and suppress the formation of aromatic compounds and C_{3+} olefins. From these results, it is suggested that solid acidity showing an NH_3 desorption peak at about 400 °C is essential for the formation of aromatic compounds, and calcination at higher temperature may weaken this solid acid by framework collapse or/and ion-exchange with iron cation: the higher calcination temperature resulted in the lower selectivity of aromatic compounds, as shown in Table 1.

FT-IR spectra of H-ZSM-5 support and Fe catalysts are shown in Fig. 7. The absorption peak due to O–H appeared at 3600–3700 cm^{-1} . H-ZSM-5 showed clear absorption peaks.¹⁵ On the other hand, catalyst ($\text{Fe}(\text{NO}_3)_3$, 500 °C) showed the same peaks, while catalyst ($\text{Fe}(\text{NO}_3)_3$, 900 °C) showed weak peaks. Moreover, $\text{Fe}_2(\text{SO}_4)_3$ -, FeCl_3 -, FeC_2O_4 - and FePO_4 -derived catalysts showed very weak peaks. These results suggest that a proton in a zeolite framework may be exchanged with iron cations and/or framework collapse of zeolite may occur during preparation: calcination at a higher temperature led to a higher rate of ion-exchange and/or framework collapse and, as a result, the solid acidity of H-ZSM-5 zeolite may be reduced to a greater extent.

Results of XPS measurement

XPS measurement of $\text{Fe}(\text{NO}_3)_3$ -derived catalysts showed a peak due to N_{1s} at 402 eV of binding energy. Moreover, in the cases of $\text{Fe}_2(\text{SO}_4)_3$ -, FeCl_3 - and FePO_4 -based catalysts, S_{2p} (169 eV), Cl_{2p} (199 eV) and P_{2p} (134 eV) peaks were observed, respectively. These results suggest that minor elements due to Fe sources remain even after calcination and these minor elements may affect the natures of Fe catalysts and zeolite frameworks.

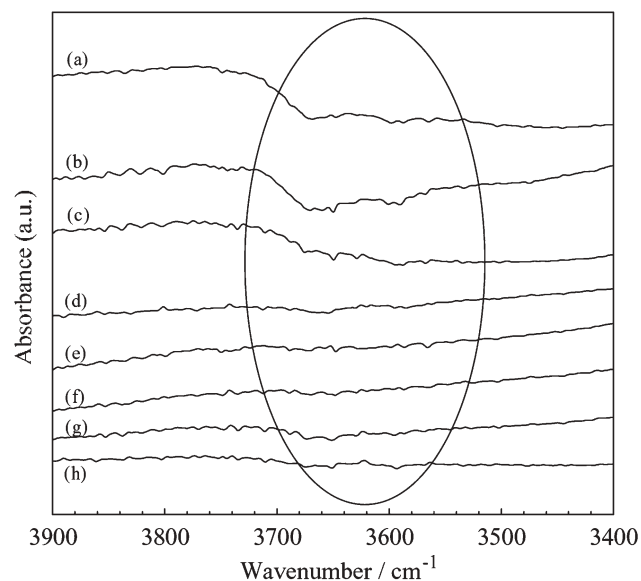


Fig. 7 FT-IR spectra of H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 29$) zeolite and Fe-H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 29$) catalysts. (a) H-ZSM-5, (b) $\text{Fe}(\text{NO}_3)_3$, 500 °C, (c) $\text{Fe}(\text{NO}_3)_3$, 900 °C, (d) $\text{Fe}_2(\text{SO}_4)_3$, 500 °C, (e) $\text{Fe}_2(\text{SO}_4)_3$, 900 °C, (f) FeCl_3 , 700 °C, (g) FeC_2O_4 , 700 °C, (h) FePO_4 , 700 °C.

Catalyst performance as a function of time and regeneration treatment

The selectivity of each product changed with time-on-stream. Therefore, catalytic performance as a function of time and the effect of regeneration treatment were investigated in the absence of water. Fig. 8 shows the catalytic performance of the catalyst ($\text{Fe}(\text{NO}_3)_3$, 700 °C) as a function of time. The selectivity of aromatic compounds was decreased (40.7 → 23.7%) and of ethylene was drastically increased (22.7 → 43.9%). The selectivity of C_{3+} olefins and paraffins were slightly decreased (20.2 → 19.6% and 14.9 → 12.5%, respectively). To regenerate the used catalyst, combustion treatment was carried out in the air-flow at 500 °C for 1 h. By means of this treatment, ethylene selectivity was decreased to 32.9% and aromatics selectivity was increased to 34.6%. However, the ethylene selectivity obtained by this treatment was higher than the initial selectivity, and the aromatics selectivity was lower than the initial selectivity. It is suggested that this air treatment alone was insufficient to fully regenerate the catalyst. Perhaps it was due to irreversible deactivation by framework collapse of the H-ZSM-5 support. As is shown in Table 2, this catalyst showed a lower ratio of intensity of XRD peaks (after reaction/before reaction = 0.42) than other kinds of 700 °C-calcined catalysts: $\text{Fe}_2(\text{SO}_4)_3$ - and FeCl_3 -derived catalysts showed intensity ratios of 0.62 and 0.70, respectively. By this regeneration treatment, combustion of deposited carbon and re-oxidation of reduced Fe_3O_4 to Fe_2O_3 could be performed almost completely.

In the catalyst ($\text{Fe}(\text{NO}_3)_3$, 900 °C), the ethylene selectivity was increased (35.5 → 49.3%), and the aromatics selectivity was decreased (15.8 → 8.7%). The selectivity of C_{3+} olefins and paraffins was slightly decreased (31.1 → 27.4% and 17.2 → 14.3%, respectively). Changes in the selectivity of each product

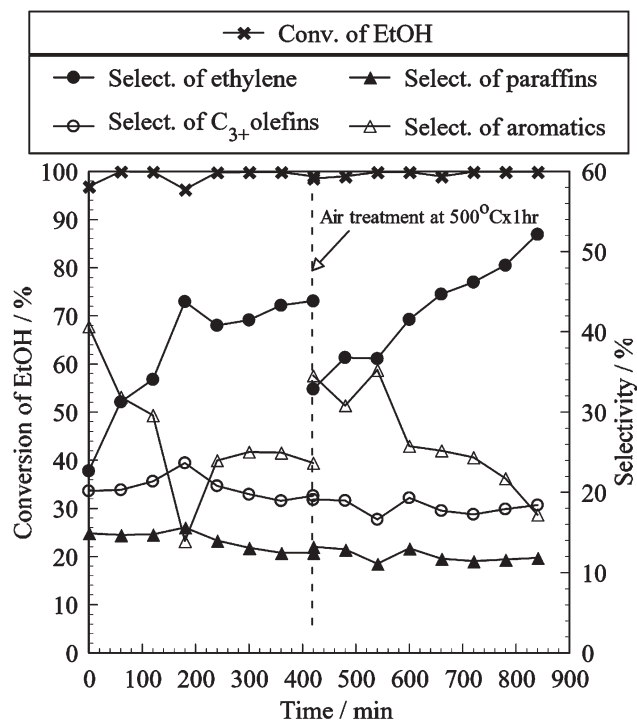


Fig. 8 Catalytic performance of Fe-H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 29$) ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 700°C calc.) catalyst as a function of time: effect of air treatment at 500°C on used catalyst. Reaction gas: $\text{N}_2 + \text{EtOH}$ (without H_2O).

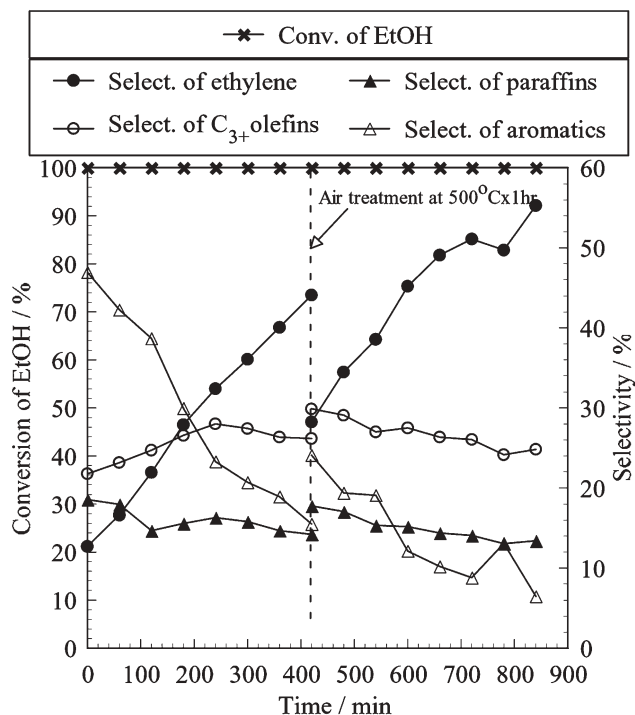


Fig. 9 Catalytic performance of Fe-H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 29$) ($\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, 700°C calc.) catalyst as a function of time: effect of air treatment at 500°C on used catalyst. Reaction gas: $\text{N}_2 + \text{EtOH}$ (without H_2O).

were smaller than in the case of 700°C -calcined catalyst. Moreover, by the combustion treatment, catalytic activity was almost restored: the selectivities of ethylene, C_{3+} olefins, paraffins and aromatics were recovered to 37.3, 30.4, 17.0 and 15.2%, respectively. It is suggested that the degree of irreversible deactivation due to framework collapse of H-ZSM-5 support was smaller than in the case of the catalyst ($\text{Fe}(\text{NO}_3)_3$, 700°C), since moderate framework collapse already occurred during catalyst preparation.

Fig. 9 shows the catalytic performance of the catalyst ($\text{Fe}_2(\text{SO}_4)_3$, 700°C) as a function of time. The pronounced increase in the ethylene selectivity (12.7 $\rightarrow$ 44.1%), as well as the marked decrease in aromatics selectivity (47.0 $\rightarrow$ 15.5%) were observed, and catalytic activity could not be restored by this combustion treatment completely. For example, by the regeneration treatment, the selectivity of ethylene was restored to 28.2%, higher than the initial selectivity in the first reaction (12.7%). However, the selectivity of C_{3+} olefins was increased with time-on-stream in the first reaction, and the selectivity of C_{3+} olefins in the second reaction (29.9%) was higher than the first reaction (21.8%), suggesting that combustion treatment enhanced the formation on C_{3+} olefins. In this case also, framework collapse may occur. However, as is shown in Table 2, the degree of collapse seems to be smaller than the case of the catalyst ($\text{Fe}(\text{NO}_3)_3$, 700°C). Therefore, remaining S may play a role in the deposition of carbon which cannot be combusted easily.

Fig. 10 shows the catalytic performance of the catalyst (FeCl_3 , 700°C) as a function of time. The increase in the

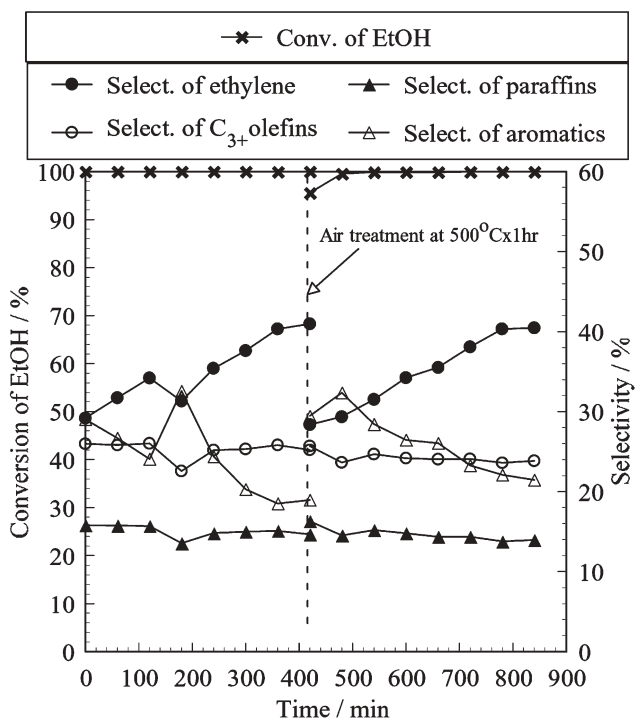
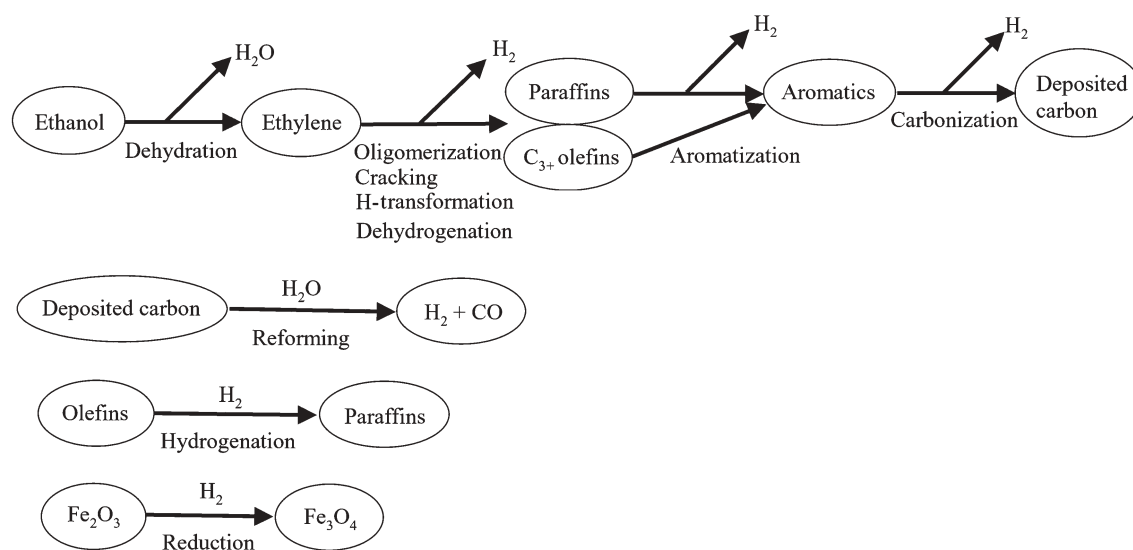


Fig. 10 Catalytic performance of Fe-H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 29$) ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 700°C calc.) catalyst as a function of time: effect of air treatment at 500°C on used catalyst. Reaction gas: $\text{N}_2 + \text{EtOH}$ (without H_2O).



Scheme 1 Supposed reaction pathway.

ethylene selectivity (29.3 → 41.0%) and the decrease in aromatics selectivity (29.0 → 19.0%) were small. The selectivities of C₃₊ olefins and paraffins were almost constant (26.0 → 25.2% and 15.8 → 14.7%, respectively). Moreover, by the combustion treatment, catalytic activity was restored almost completely: the selectivity of ethylene, C₃₊ olefins, paraffins and aromatics was recovered to 28.4, 25.7, 16.3 and 29.5%, respectively. As is shown in Table 3, the degree of framework collapse was smaller than in the cases of Fe(NO₃)₃, 700 °C and Fe₂(SO₄)₃, 700 °C. Remaining Cl species played a role in preventing framework collapse. Further study is required to elucidate the effects of S and Cl on the catalytic performance.

Reaction pathway

Scheme 1 shows the supposed reaction pathway. First, ethanol is converted to ethylene by dehydration: this reaction can proceed on an acidic site. Successive reactions, such as oligomerization, cracking, dehydrogenation and H-transformation occur on an acidic site of zeolite support,^{6,8–10} and C₃₊ olefins and paraffins are formed. Ingram reported that propylene is formed from the cracking of larger olefins, possibly 4-methylpentene, and not as an intermediate between C₂ and C₄ production.¹² It is suggested that other olefins are formed *via* these several reactions. Aromatic compounds are formed by further oligomerization and dehydrogenation of C₃₊ olefins and paraffins. Furthermore, the compounds can undergo carbonization to give deposited carbon. Fe species may inhibit the formation of aromatics in some degree.

In the case of catalysts calcined at higher temperature, the amount of acidic site may be decreased by ion-exchange with iron cation or framework collapse of the zeolite support, which leads to a decrease in both aromatics selectivity and carbon deposition and an increase in ethylene selectivity.

Water can easily be obtained by dehydration of ethanol. This water can react with deposited carbon to give CO and H₂. Moreover, H₂ can be formed *via* dehydrogenation in aromatization and carbonization. H₂ can hydrogenate olefins

to paraffins. However, the hydrogenation to paraffins can be suppressed by reduction of Fe₂O₃ to Fe₃O₄. In fact, as is shown in Table 1, generally Fe catalyst showed a higher C₃₊ olefins/paraffins ratio in selectivity than H-ZSM-5 support (no metal loaded).

In the case of 900 °C-calcined catalysts, Fe₂O₃ was unchanged without reduction, since the aromatics formation and the carbonization scarcely proceed, resulting in very little H₂ being formed.

As reaction proceeds, the carbon deposition and the framework collapse lead to significant decrease in aromatics selectivity and a slight decrease in C₃₊ olefins selectivity. Maybe the carbon deposition suppresses the aromatics formation predominantly over C₃₊ olefins, since it is suggested that aromatics formation needs a strong acidic site not covered with deposited carbon.

In the presence of water, carbon deposition can be inhibited by steam-combustion in some degree, but framework collapse can be enhanced, resulting in an enlarged decrease in aromatics selectivity and an enlarged increase in ethylene selectivity.

Conclusions

Fe–H-ZSM-5 catalysts were efficient for EtOH conversion to C₃₊ olefins, which are useful not only as fuels but also chemicals. Moreover, Fe is a cheap and non-toxic metal. Initial selectivity of C₃₊ olefins over Fe catalysts was little affected by adding water, suggesting that these Fe catalysts are fully effective even in the presence of water in EtOH. In most cases, the initial selectivity of C₃₊ olefins was not affected by the kind of iron source and calcination temperature significantly. However, in general, the selectivity of C₃₊ olefins was slightly decreased with time-on-stream, and the degree of the decrease was affected by these conditions. Among Fe catalysts, Fe₂(SO₄)₃- or FeCl₃-based catalyst calcined at 700 °C showed a low decrease in C₃₊ olefins selectivity. As causes of catalytic deactivation, carbon deposition on catalyst and framework collapse of zeolite support can be considered. An acidic site of

support was essential for the formation of olefins, paraffins and aromatics, and Fe species can inhibit the aromatics formation in some degree. H_2 was formed by steam-combustion of deposited carbon and dehydrogenation *via* aromatization and carbonization, and can hydrogenate olefins to paraffins. However, Fe_2O_3 can suppress the olefins hydrogenation by reduction to Fe_3O_4 , resulting in a higher olefins/paraffins ratio than H-ZSM-5 support (without Fe). Air treatment at 500 °C to used catalysts can restore catalytic activity and the degree of regeneration was affected by the kind of catalysts: in the $FeCl_3$ -based catalysts calcined at 700 °C and the 900 °C-calcined catalysts (irrespective of iron source), catalytic activity can be restored almost completely. On the other hand, the $Fe(NO_3)_3$ - or $Fe_2(SO_4)_3$ -derived catalysts calcined at 700 °C cannot restore the catalytic activity by this treatment completely. In any case, Fe-H-ZSM-5 catalysts are promising candidates for the production of C_{3+} olefins from ethanol. Further investigation is now in progress to find better catalysts, which can yield olefins in higher selectivity and retain their catalytic activity for a longer period.

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A process for a high yield of aromatics from the oxygen-free conversion of methane: combining plasma with Ni/HZSM-5 catalysts†

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A process for a high yield of aromatics and co-produced hydrogen from the oxygen-free conversion of methane using a two-stage plasma-followed-by-catalyst (PFC) reactor at atmospheric pressure and low temperature is reported. Pure methane and a methane and hydrogen mixture as the feed gas for the two-stage PFC process were investigated, respectively. Using the methane and hydrogen mixture as the feed gas into the two-stage PFC reactor, Ni/HZSM-5 catalysts keep stable catalytic activity for a much longer on-stream time than that using pure methane as the feed gas. The maximum aromatic yield may be achieved using low Ni-loading Ni/HZSM-5 catalysts and at a suitable catalyst temperature.

Introduction

Oxygen-free conversion of methane, simultaneously producing higher hydrocarbons and CO_x-free hydrogen, is an environmentally benign and efficient utilization for the resources of carbon and hydrogen in methane molecules. The oxygen-free dehydroaromatization of methane is of great scientific importance and potential industrial benefit for the effective utilization of natural gas and biogas to provide alternative petrochemical feed stocks and bulky CO_x-free hydrogen production for fuel cells.¹ Methane oxygen-free conversion into aromatics and hydrogen is not thermodynamically favorable at low temperatures (<773 K). The equilibrium methane conversion at 973 K is *ca.* 12% and benzene and naphthalene, in approximately equimolar amounts, are the thermodynamically preferred hydrocarbon products.² The thermodynamic limitation is the main barrier for this process. To enhance the conversion of methane into aromatics beyond thermodynamic equilibrium, studies using H₂-permeation membrane catalytic reactors are already under way with several research groups.^{3,4} However, the preliminary reports on this approach are not very optimistic and catalyst deactivation was more pronounced in a membrane catalytic reactor than in a fixed-bed reactor because of continuous withdrawal of the co-produced hydrogen.³ Atmospheric non-thermal equilibrium plasma has been used as an efficient method for oxygen-free conversion of methane into C₂ hydrocarbons (mainly acetylene) and hydrogen by using pulsed corona/streamer discharges or pulsed spark discharges.^{5–10} Only a small amount of C₃–C₅ hydrocarbons and trace amount of aromatics were usually co-produced. Recently,

Heintze and Magureanu reported the conversion of methane into aromatics in pulsed microwave plasma at atmospheric pressure in the presence of a heterogeneous catalyst.¹¹ In their work, the authors suggested that methane aromatization was very likely to be catalyzed on the coke surface and highly unlikely by acetylene trimerization. The most abundant aromatic formed was benzene and *ca.* 5% of a maximum benzene yield was obtained. In a previous short report,¹² we showed a two-stage plasma-followed-by-catalyst (PFC) reactor for the oxygen-free conversion of methane into aromatic-rich hydrocarbons and co-produced hydrogen. Methane is converted to acetylene by plasma in the first stage, with the second stage for acetylene trimerization on nickel-loaded HZSM-5 catalysts. In this paper, this two-stage PFC process for a high yield of aromatics from the feeding gas of pure methane or a methane and hydrogen mixture is elaborated.

Experimental

The two-stage PFC reactor used in this work has been described in the literature.¹² Briefly, the first stage of the PFC reactor, for generating pulsed spark discharge, was located in the upper part of a quartz tube (i.d. 10 mm) and consists of a stainless steel wire (2 mm diameter) as the high-voltage electrode and a perforated iron plate (9 mm diameter) as the ground electrode. The distance between the two electrodes was 10 mm. The high-voltage power supply for generating the pulsed spark discharge has been described in the literature.¹⁰ The second stage of the PFC reactor was filled with 0.5 g of HZSM-5 or Fe, Co, Ni, Cu, Zn metal-loaded HZSM-5 pellets of 20–40 mesh.

The metal-loaded HZSM-5 catalysts were prepared by the incipient wetness impregnation method using HZSM-5 or NaZSM-5 (SiO₂/Al₂O₃ = 25, Nankai University, China) and an aqueous solution of the corresponding metal nitrates. The metal loading of the catalysts was calculated according to the used amounts of metal nitrate. It should be mentioned that the metal loading given in this paper is only a calculated

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and not an experimentally verified value. All the impregnated samples for loading Fe, Co, Ni, Cu or Zn on HZSM-5 were dried at 393 K for 4 h, and calcined at 723 K for 4 h in air. Before the reactions, the catalysts were reduced at 673 K for 2 h in hydrogen in the PFC reactor.

The flow rates for methane, hydrogen and nitrogen were controlled through a mass flow controller. Pure methane (99.99%) and the methane (99.99%) and hydrogen (99.99%) mixture with a molar ratio of $\text{CH}_4/\text{H}_2 = 1$ were used as the feed gas introduced into the PFC reactor, respectively. Nitrogen (99.99%) at a flow rate of $2.2 \text{ cm}^3 \text{ min}^{-1}$ was used as the internal standard for analysis and introduced into the effluent gas from the PFC reactor to avoid conversion of nitrogen in the plasma.

Hydrocarbon products were sampled by a first six-way valve heated at 473 K and on-line analyzed by a first gas chromatograph (Agilent 1790F) equipped with a flame ionization detector (FID) and a 2 mm (i.d.) $\times$ 3 m Porapak-P or Porapak-Q column with N_2 as the carrier gas. Nitrogen and methane were sampled by a second six-way valve heated at 473 K and on-line analyzed by a second gas chromatograph (Agilent 1790 T) equipped with a thermal conductivity detector (TCD) and a 2 mm (i.d.) $\times$ 1 m carbon molecular sieve 601 column using hydrogen as the carrier gas. Hydrogen in the effluent gas was sampled by a third six-way valve and on-line analyzed by a third gas chromatograph equipped with a TCD and 2 mm (i.d.) $\times$ 1 m carbon molecular sieve 601 column using nitrogen as the carrier gas. To avoid electromagnetic noises from the pulsed discharges, the three on-line gas chromatographs were placed in a shielding room.

The conversion of methane (X_{CH_4}) and the selectivities of hydrocarbon products ($S_{\text{C}_x\text{H}_y}$) were evaluated using the internal standard analyzing method.¹³ In terms of the flow rate of nitrogen (F_{N_2}) used as the internal standard and the molar concentration of nitrogen (C_{N_2}) in the effluent gas given by second gas chromatograph, the total effluent gas flow rate (F^{out}) can be calibrated by the following equation:

$$F^{\text{out}} = \frac{F_{\text{N}_2}}{C_{\text{N}_2}}$$

Then, the conversion of methane and the selectivities of the hydrocarbon products were calculated from the following equations:

$$X_{\text{CH}_4} = \frac{F_{\text{CH}_4}^{\text{in}} - F_{\text{CH}_4}^{\text{out}}}{F_{\text{CH}_4}^{\text{in}}} = 1 - \frac{F_{\text{CH}_4}^{\text{out}} C_{\text{CH}_4}^{\text{out}}}{F_{\text{CH}_4}^{\text{in}}} = 1 - \frac{F_{\text{N}_2}}{F_{\text{CH}_4}^{\text{in}}} \frac{C_{\text{CH}_4}^{\text{out}}}{C_{\text{N}_2}}$$

$$S_{\text{C}_x\text{H}_y} = x \frac{F_{\text{CH}_4}^{\text{out}} C_{\text{C}_x\text{H}_y}^{\text{out}}}{F_{\text{CH}_4}^{\text{in}} X_{\text{CH}_4}} = x \frac{F_{\text{N}_2} C_{\text{C}_x\text{H}_y}^{\text{out}}}{F_{\text{CH}_4}^{\text{in}} X_{\text{CH}_4} C_{\text{N}_2}}$$

Here, x and y represent carbon-atom number and hydrogen-atom number in a molecule of hydrocarbon product, respectively. $F_{\text{CH}_4}^{\text{in}}$ and $F_{\text{CH}_4}^{\text{out}}$ represent the flow rate of methane at the inlet and outlet of the PFC reactor, respectively; $C_{\text{C}_x\text{H}_y}^{\text{out}}$ and $C_{\text{CH}_4}^{\text{out}}$, given by first and second gas chromatographs, represent the molar concentrations of hydrocarbon and methane products in the effluent gas, respectively.

Hydrogen selectivity was calculated using the external standard analyzing method from the following equation:

$$S_{\text{H}_2} = \frac{2(F_{\text{H}_2}^{\text{out}} C_{\text{H}_2}^{\text{out}} - F_{\text{H}_2}^{\text{in}})}{4F_{\text{CH}_4}^{\text{in}} X_{\text{CH}_4}} = 0.5 \frac{F_{\text{H}_2}^{\text{out}} C_{\text{H}_2}^{\text{out}} - F_{\text{H}_2}^{\text{in}}}{F_{\text{CH}_4}^{\text{in}} X_{\text{CH}_4}}$$

Here, $F_{\text{H}_2}^{\text{in}}$ represents the flow rate of hydrogen at the inlet of the PFC reactor; $C_{\text{H}_2}^{\text{out}}$, given by third gas chromatograph, represents the molar concentration of hydrogen in the effluent gas.

Coke deposited on the spent catalysts was investigated by continuously monitoring evolved CO and CO_2 during temperature-programmed oxidation (TPO) in a 5% O_2/N_2 mixed gas stream. The 20 mg of spent catalysts was diluted with 20 mg of quartz sand and placed in a quartz tube reactor (i.d. 4 mm) for TPO studies. A linear temperature program from room temperature to 1073 K with a ramp rate of 10 K min^{-1} was used. The concentrations of CO and CO_2 in the outflow gas from the TPO studies were measured with an infrared absorption spectrometer (IRAS, SICK-MAIHAK, S710).

The energy density was defined as the discharge power per feed flow. The energy cost for methane conversion, calculated by energy consumed per molecule of methane converted, was given in eV molecule^{-1} .

The temperature-programmed reaction experiments for acetylene conversion were carried out using a fused silica tube reactor (i. d. 4 mm). Samples (100 mg catalyst pellets, diluted by 100 mg quartz sand, 40–60 mesh) were pre-treated in a H_2 (99.99%) stream at 673 K for 2 h, and then cooled to room temperature. The gas was then switched to a mixture flow of 2% $\text{C}_2\text{H}_2/\text{N}_2$ ($25 \text{ cm}^3 \text{ min}^{-1}$) or 2% $\text{C}_2\text{H}_2/\text{N}_2$ ($25 \text{ cm}^3 \text{ min}^{-1}$) + H_2 ($1.5 \text{ cm}^3 \text{ min}^{-1}$). The temperature was programmed from 300 to 773 K at a rate of 10 K min^{-1} . The mass spectrometric signals of the outflow gas at $m/z = 16$ (CH_4^+), 26 (C_2H_2^+), 41 (C_3H_5^+), 78 (C_6H_6^+), 92 (C_7H_8^+) and 106 ($\text{C}_8\text{H}_{10}^+$) were scanned and recorded by a capillary-tube-sampled quadrupole mass spectrometer with two-stage differential pumping (Pfeiffer Vacuum, OmniStarTM).

Results and discussion

Pure methane as the feed gas into the two-stage PFC reactor

Using pure methane as the feed gas into the two-stage PFC reactor, the oxygen-free conversions of methane in the cases of plasma alone (without any catalysts), plasma followed by non-loaded HZSM-5 catalysts or Fe, Co, Ni, Cu, or Zn metal-loaded HZSM-5 catalysts were investigated, respectively. As shown in Fig. 1, the plasma alone case gives 41% of methane conversion at 680 kJ mol^{-1} of energy density and thus the energy cost for methane conversion was $17 \text{ eV molecule}^{-1}$. Acetylene (selectivity 84%) and hydrogen (selectivity 75%) were the dominant products, with only extremely small amount of aromatic product ($<1\%$ of benzene selectivity).

In the two-stage PFC reactor using non-loaded HZSM-5 as catalyst, aromatics were produced with 15% of selectivity at 15 min on-stream time. It was found that serious carbonaceous deposition resulted in rapid deactivation of HZSM-5 catalyst. This is in agreement with the relevant literature^{14–16} on acetylene conversion. It has been reported that metal-modified

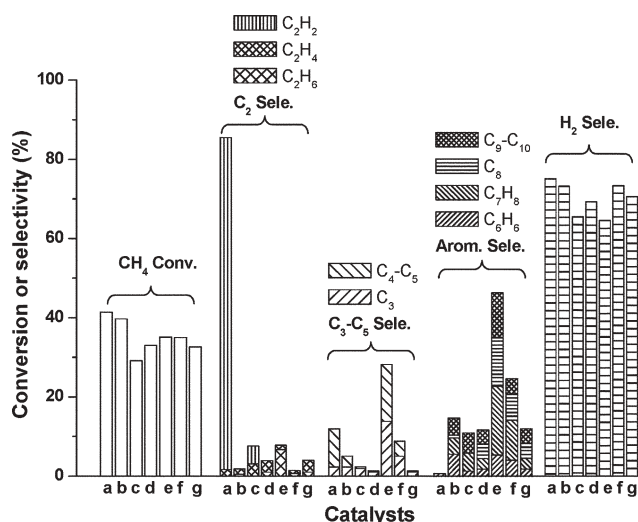


Fig. 1 Comparison of methane conversion and product selectivity in the plasma alone case, and in the PFC reactor using HZSM-5 or metal-loaded HZSM-5 catalysts (pure methane as the feed gas): (a) plasma alone; (b) HZSM-5; (c) Fe(1 wt%)/HZSM-5; (d) Co(1 wt%)/HZSM-5; (e) Ni(1 wt%)/HZSM-5; (f) Cu(1 wt%)/HZSM-5; (g) Zn(1 wt%)/HZSM-5. Catalyst temperature: 623 K, methane flow rate: $15 \text{ cm}^3 \text{ min}^{-1}$, 100% CH_4 , $W/F = 1.4 \text{ s g ml}^{-1}$, discharge power: 7.6 W, data collection time: 15 min.

HZSM-5 catalysts can promote aromatics production in the aromatization of light hydrocarbons and improve catalyst stability.^{17–20} Therefore, Fe, Co, Ni, Cu, or Zn metal-loaded HZSM-5 catalysts were investigated here. Compared with Fe, Co, Cu, or Zn metal-loaded HZSM-5 catalysts, Ni/HZSM-5 catalysts give the highest aromatics selectivity (47%) in the PFC reactor. The obtained aromatic products mainly consisted of BTX, that is, benzene (B), toluene (T) and xylene (X, some styrene and ethylbenzene). BTX selectivity ($S_{\text{BTX}} = S_{\text{C}_6\text{H}_6} + S_{\text{C}_7\text{H}_8} + S_{\text{C}_8\text{H}_{10}}$) accounts for approximately 76% of

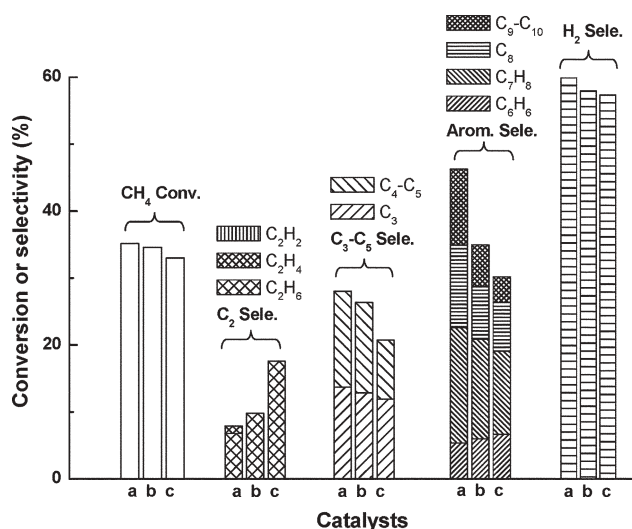


Fig. 2 Effect of Ni loading on methane conversion and product selectivities in the PFC reactor (pure methane as the feed gas). Ni loading: (a) 1 wt%; (b) 2 wt%; (c) 4 wt%. Catalyst temperature: 623 K, methane flow rate: $15 \text{ cm}^3 \text{ min}^{-1}$, 100% CH_4 , $W/F = 1.4 \text{ s g ml}^{-1}$, discharge power: 7.6 W, data collection time: 20 min.

aromatic selectivity ($S_{\text{arom.}} = S_{\text{BTX}} + S_{\text{C}_{9-10}}$). Also, hydrogen was co-produced with 65% of selectivity for Ni/HZSM-5 catalysts.

Fig. 2 presents the effect of Ni loading of Ni/HZSM-5 catalysts on methane conversion and product selectivity in the PFC reactor at 680 kJ mol^{-1} of energy density and at a catalyst temperature of 623 K. In increasing the Ni loading from 1 to 4 wt%, there is an obvious increase in ethane selectivity (from 7 to 18%), whereas aromatic selectivity decreases from 46 to 30%. This suggests that hydrocarbon products, including aromatics, may undergo decomposition to carbon and hydrogen, resulting from the nickel sites of the

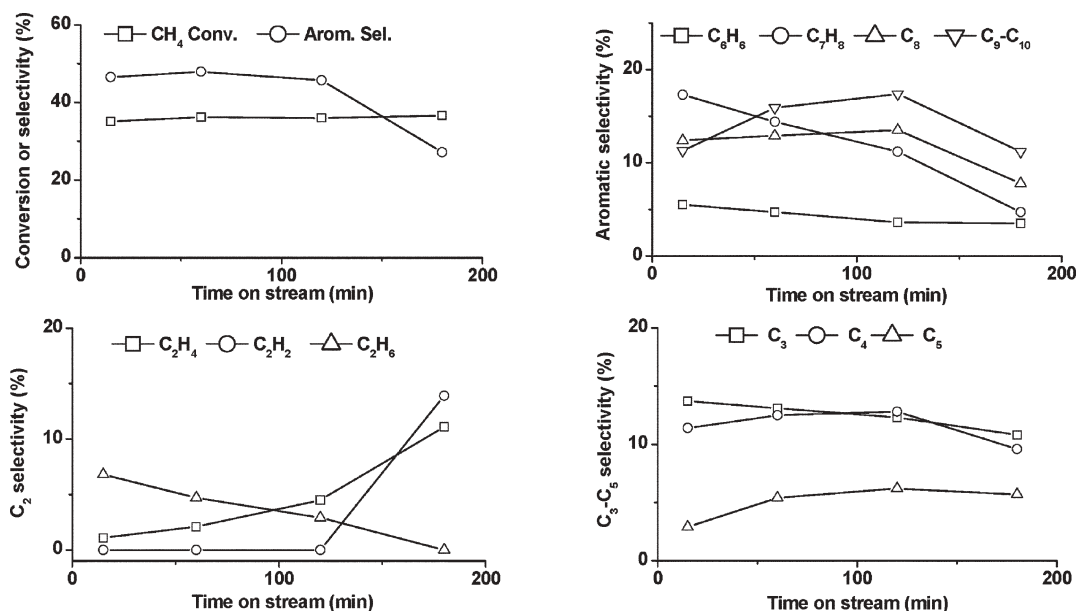


Fig. 3 Variation in methane conversion and product selectivities vs. on-stream time in the PFC reactor using Ni(1 wt%)/HZSM-5 catalysts (pure methane as the feed gas). Catalyst temperature: 623 K, methane flow rate: $15 \text{ cm}^3 \text{ min}^{-1}$, 100% CH_4 , $W/F = 1.4 \text{ s g ml}^{-1}$, discharge power: 7.6 W.

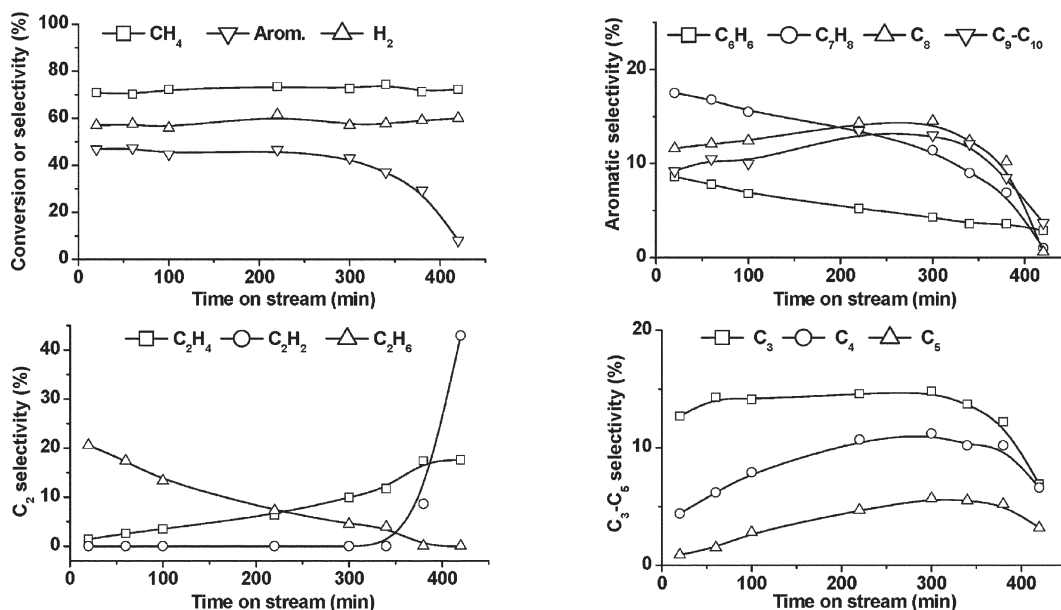


Fig. 4 Variation in methane conversion and product selectivities vs. on-stream time in the PFC reactor using Ni(1 wt%)/HZSM-5 catalyst at 673 K (methane and hydrogen mixture as the feed gas). Total flow rate: $8.4 \text{ cm}^3 \text{ min}^{-1}$, 50% CH_4 + 50% H_2 , $W/F = 2.6 \text{ g ml}^{-1}$, discharge power: 9.6 W.

Ni/HZSM-5 catalyst.²¹ In addition, the increase in ethane selectivity with Ni loading may be ascribed to the enhancement in hydrogenation activity of acetylene from the nickel sites of the Ni/HZSM-5 catalyst.

It is worth noting that, using pure methane as the feed gas, deactivation to some extent occurred on the Ni/HZSM-5 catalysts at an on-stream time of 3 h, as shown in Fig. 3. After an elapse of a 2 h on-stream time, although methane conversion was still stable, the aromatic selectivity decreased from 46% at an on-stream time of 2 h to 27% at an on-stream time of 3 h. Moreover, after 2 h on-stream time, there is a sudden rise in acetylene selectivity from 0 to 14%. This means

that, for Ni/HZSM-5 catalysts in the second stage, the acetylene produced in the plasma stage cannot be 100% converted after an on-stream time of 2 h.

Additionally, using pure methane as the feed gas, low energy density in the first stage (plasma stage) is required to avoid unstable discharge derived from serious coke deposition and low methane conversion can only be obtained. As reported in our previous paper,¹⁰ high energy density can give high methane conversion. To stabilize the discharge at high energy density and to keep the catalytic activity of Ni/HZSM-5 for acetylene conversion to aromatics during a longer on-stream time, a methane and hydrogen mixture with a molar ratio of

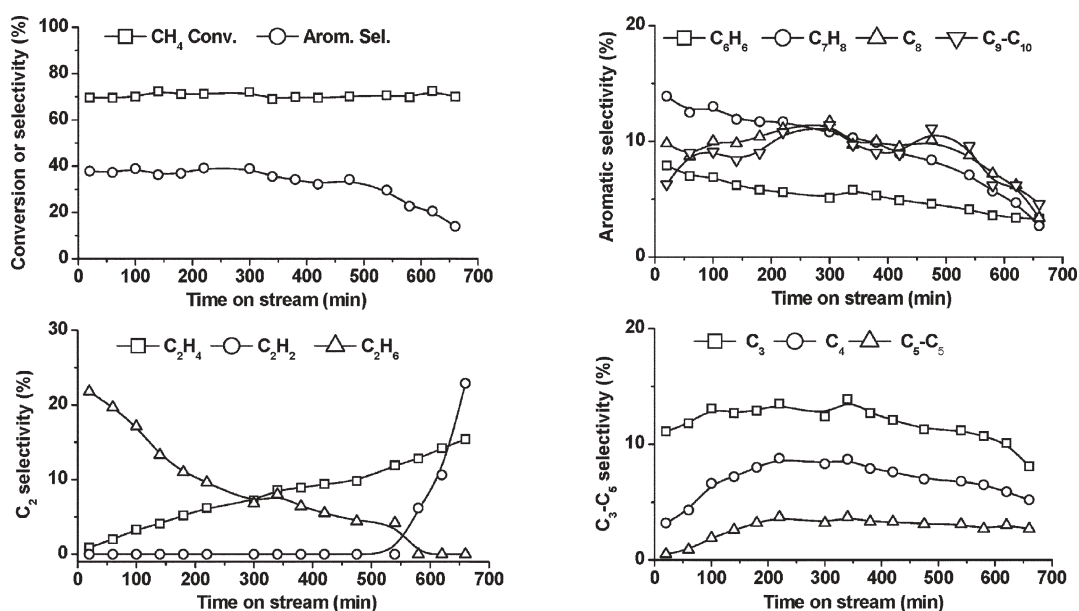


Fig. 5 Variation in methane conversion and product selectivities vs. on-stream time in the PFC reactor using Ni(2 wt%)/HZSM-5 catalyst at 673 K (methane and hydrogen mixture as the feed gas). Total flow rate: $8.4 \text{ cm}^3 \text{ min}^{-1}$, 50% CH_4 + 50% H_2 , $W/F = 2.6 \text{ g ml}^{-1}$, discharge power: 9.6 W.

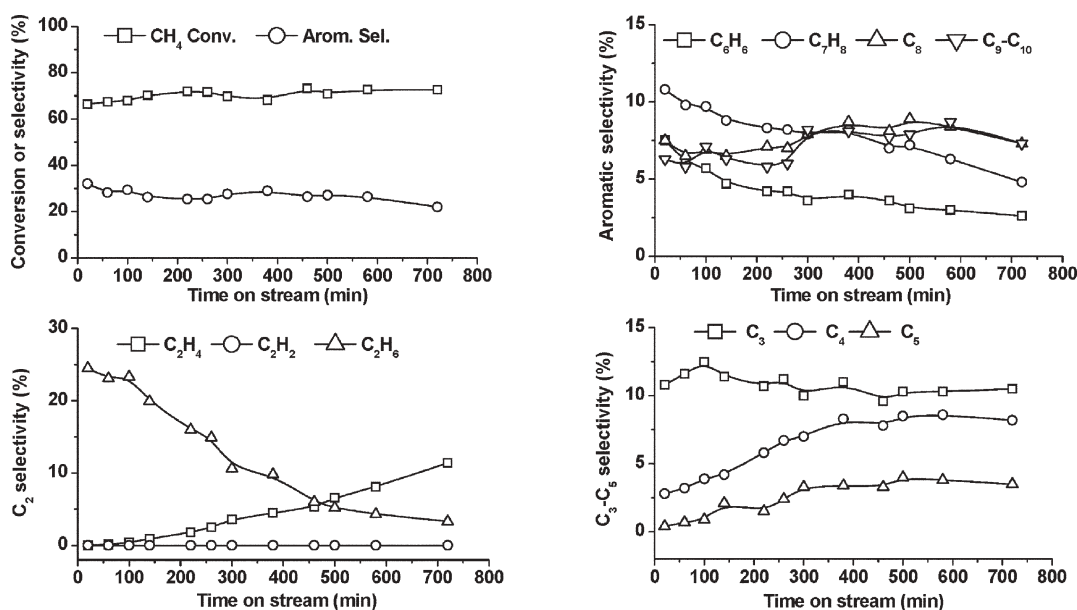


Fig. 6 Variation in methane conversion and product selectivities vs. on-stream time in the PFC reactor using Ni(4 wt%)/HZSM-5 catalyst at 673 K (methane and hydrogen mixture as the feed gas). Total flow rate: $8.4 \text{ cm}^3 \text{ min}^{-1}$, 50% CH_4 + 50% H_2 , $W/F = 2.6 \text{ s g ml}^{-1}$, discharge power: 9.6 W.

$\text{CH}_4/\text{H}_2 = 1$ was used as the feed gas introduced into the two-stage PFC reactor and examined as follows.

Methane and hydrogen mixture as the feed gas into the two-stage PFC reactor

Using a methane and hydrogen mixture as the feed gas (50% CH_4 + 50% H_2), the plasma stage gives 78% of methane conversion at 1400 kJ mol^{-1} of energy density and thus the energy cost for methane conversion was $37 \text{ eV molecule}^{-1}$. The molar ratio of $\text{C}_2\text{H}_2 : \text{H}_2 : \text{CH}_4$ in the effluent gas from the plasma stage can be calculated as approximately 1.6 : 10 : 1. This means that, in the second stage of the PFC reactor, acetylene conversion to aromatics proceeds in the presence of a large amount of hydrogen. To the best of our knowledge, studies on acetylene conversion to aromatics in an atmosphere containing a large amount of hydrogen have not yet been reported. Similar to the results of pure methane as the feed gas, the Ni/HZSM-5 catalyst showed a better performance than that of HZSM-5 for feeding with the methane and hydrogen mixture. It was reported that the incorporation of Ni in the HZSM-5 leads to a decrease in the total acidity and acidic strength of HZSM-5.²²

The effect of catalyst temperature was investigated in the PFC reactor using Ni(1 wt%)/HZSM-5 catalysts, and the data were taken at 100 min of on-stream time. From 573 to 723 K, methane conversion changed slightly in the range of 72–76% and no acetylene was detected in the products from the PFC reactor (that is, acetylene produced in the first stage was 100% converted over Ni/HZSM-5 catalysts). In the temperature range of 573–673 K, it was found that the selectivities for BTX plus $\text{C}_4\text{--C}_5$ remained nearly constant. For example, BTX selectivity and $\text{C}_4\text{--C}_5$ selectivity were 14 and 32% at 573 K and 35 and 11% at 673 K, respectively. As a result, the total selectivity of BTX plus $\text{C}_4\text{--C}_5$ was 46% at 573 K and 46% at 673 K. Thereby, it can be implied that $\text{C}_4\text{--C}_5$ species play an

intermediate role in the formation of BTX from acetylene. The aromatic selectivity exhibits a clear dependence on the catalyst temperature and a maximum aromatic selectivity

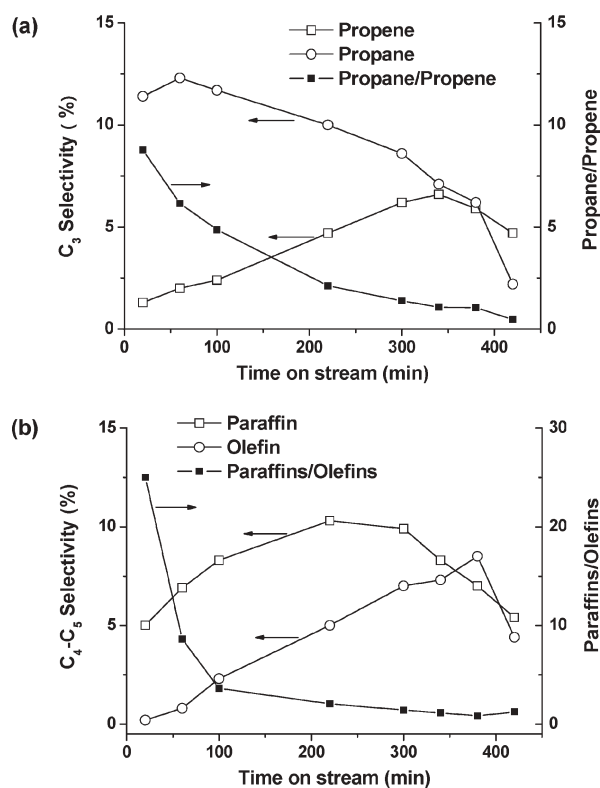


Fig. 7 Selectivities of $\text{C}_3\text{--C}_5$ paraffins and olefins and the ratio of paraffin/olefin in the PFC reactor using Ni(1 wt%)/HZSM-5 catalyst at 673 K (methane and hydrogen mixture as the feed gas). Total flow rate: $8.4 \text{ cm}^3 \text{ min}^{-1}$, 50% CH_4 + 50% H_2 , $W/F = 2.6 \text{ s g ml}^{-1}$, discharge power: 9.6 W.

was achieved at a catalyst temperature of 673 K. Therefore, the following experiments were carried out at a catalyst temperature of 673 K.

Fig. 4, 5 and 6 show methane conversion and product selectivity as a function of on-stream time in the PFC reactor using Ni/HZSM-5 catalysts with different Ni loadings (1, 2, and 4 wt%). For the PFC reactor using the Ni(1 wt%)/HZSM-5 catalyst (Fig. 4), on average during 5 h of on-stream time, 33% of aromatics yield, 41% of hydrogen yield with 72% of methane conversion have been achieved at 1400 kJ mol⁻¹ of energy density and a 673 K catalyst temperature. The ratio of C₃–C₅ paraffins to olefins decreased dramatically during 100 min on-stream time and then decreased slightly (Fig. 7), which reflects the decrease in hydrogenation activity from the nickel sites of the Ni/HZSM-5 catalyst. The change in hydrogenation activity was very likely caused by the coke deposited on the catalysts. The coke deposited on the catalysts used in Fig. 4 was determined by the TPO method. The total amount of coke on the catalysts for 7 h of on-stream time was determined to be 8.9 mmol. From the total amounts of carbon atoms in methane converted (57.0 mmol) and hydrocarbon products (49.5 mmol), the total amount of coke can also be calculated as 7.5 mmol. It can be easily seen that the coke amount determined and the calculated one are very close, which provides a direct assessment of the carbon balance. For the cases using Ni(2 wt%)/HZSM-5 and Ni(4 wt%)/HZSM-5 catalysts, the coke selectivities calculated based on the carbon

balance of reaction were also in reasonable agreement with those determined by the TPO method.

Comparing Fig. 3 and Fig. 4, it can be concluded that, using a methane and hydrogen mixture as the feed gas into the two-stage PFC reactor, the Ni/HZSM-5 catalyst maintains a stable catalytic activity for much a longer on-stream time than using pure methane as the feed gas. Increasing the Ni loading there was a decrease to some extent in the selectivities for the aromatics, but the life of the Ni/HZSM-5 catalyst was further prolonged. Using the Ni(4 wt%)/HZSM-5 catalyst in the PFC reactor, the selectivities for the aromatics and methane conversion remain almost constant during the 12 h on-stream time (see Fig. 6).

The temperature-programmed reactions for acetylene conversion were investigated over quartz sand, HZSM-5 catalysts, Ni/NaZSM-5 and Ni/HZSM-5, respectively (Fig. 8). For quartz sand, in the entire temperature range investigated, hardly any acetylene was converted and hardly any product was observed. For HZSM-5 catalysts, the acetylene MS signal decreased slowly with the increase in temperature when temperature < 700 K. At temperatures > 700 K, the acetylene MS signal fell rapidly. For the Ni/HZSM-5 catalysts in C₂H₂ + H₂, acetylene may be completely converted at > 500 K and aromatics begin to be produced. At temperatures > 673 K, the aromatic MS signals decreased remarkably due to decomposition and hydrogenolysis. Therefore, the optimum temperature for acetylene aromatization was 600–673 K. This is in

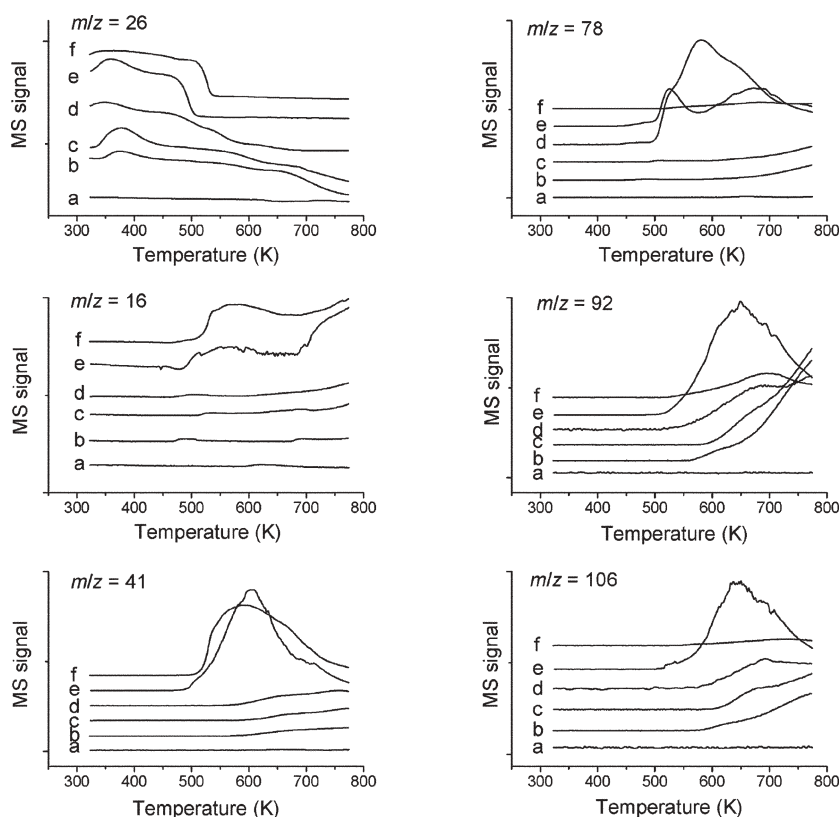


Fig. 8 MS signals for the temperature-programmed reaction of acetylene in C₂H₂/N₂ or C₂H₂/N₂ + H₂ over samples of quartz sand, HZSM-5, Ni(2 wt%)/HZSM-5 or Ni(2 wt%)/NaZSM-5. Flow rate in C₂H₂/N₂ case: 25 cm³ min⁻¹ of 2% C₂H₂/N₂; flow rate in C₂H₂/N₂ + H₂ case: 25 cm³ min⁻¹ of 2% C₂H₂/N₂, 1.5 cm³ min⁻¹ of H₂. (a) Quartz sand, C₂H₂/N₂ + H₂; (b) HZSM-5, C₂H₂/N₂; (c) HZSM-5, C₂H₂/N₂ + H₂; (d) Ni(2 wt%)/HZSM-5, C₂H₂/N₂; (e) Ni(2 wt%)/HZSM-5, C₂H₂/N₂ + H₂; (f) Ni(2 wt%)/NaZSM-5, C₂H₂/N₂ + H₂.

good agreement with the above-mentioned results of the investigations into the effect of temperature. For the Ni/NaZSM-5 catalyst in $C_2H_2 + H_2$, only trace amount of aromatics were produced and non-aromatics were mainly obtained. Thereby, it can be deduced that the Brønsted acid sites on HZSM-5 catalysts played a key role in the conversion of acetylene into aromatics.

Conclusion

In conclusion, this paper reports a novel process for a high yield of aromatics and co-produced hydrogen from the oxygen-free conversion of methane using a two-stage PFC reactor composed of pulsed spark discharge plasma and Ni/HZSM-5 catalyst at atmospheric pressure and low temperature. BTX molecules are the major aromatic products. Using a methane and hydrogen mixture as the feed gas into the two-stage PFC reactor, the Ni/HZSM-5 catalyst maintains a stable catalytic activity for a much longer on-stream time than that using pure methane as the feed gas. The maximum aromatics yield may be achieved using low Ni-loading Ni/HZSM-5 catalysts and at a suitable catalyst temperature. This study shows very encouraging progress in overcoming the thermodynamic barrier for oxygen-free conversion of methane into aromatics and hydrogen. It should also be noted that, at present, this technology is quite some distance from being useful to industry.

Acknowledgements

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Process design simulation of H₂ production by sorption enhanced steam methane reforming: evaluation of potential CO₂ acceptors†

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A concept for pure H₂ production with CO₂ capture by sorption enhanced steam methane reforming (SESMR) has been investigated. Conventional steam reforming with CO₂ capture has been used as a base case for comparison. SESMR resulted in competitive thermal efficiencies, which were highly dependent on the CO₂ acceptor material. Thus, CaO and other more novel solid acceptors such as Li₂ZrO₃, K-doped Li₂ZrO₃, Na₂ZrO₃ and Li₄SiO₄ were screened in terms of thermodynamics, kinetics and stability. It was concluded that higher H₂ yields and efficiencies can be obtained for the acceptors that have good ability for removing CO₂ at low partial pressures. The best efficiencies were obtained using CaO as acceptor due to its more favourable thermodynamics and high reaction rates; however, the stability of CaO has to be improved. On the other hand, Na₂ZrO₃ is a promising alternative due to the good kinetics for CO₂ removal and the stability.

1 Introduction

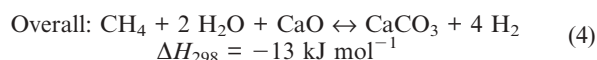
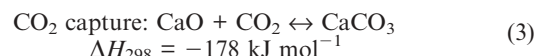
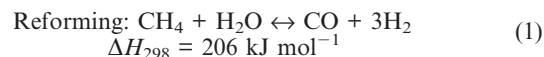
Fossil fuels are the dominant form of energy utilised in the world (86%), and account for about 75% of the current anthropogenic CO₂ emissions. Thus, there is a need for developing technologies that allow the use of fossil fuels while reducing the carbon dioxide emissions. At this point, the capture and storage of CO₂ may play a crucial role.

Hydrogen is an important raw material in the chemical and petroleum industries. Moreover, hydrogen might become a new generation of clean energy carrier for transport, especially for fuel cell applications, which would cause a huge increase in the hydrogen demand. The dominant industrial process for large scale hydrogen production is steam methane reforming (SMR). The steam reforming process involves multiple steps and severe operating conditions. The reformer is normally operated at 1073–1123 K and 20–35 bar. In addition, the reformer is followed by high and low temperature shift reactors, and carbon dioxide removal.¹

In the last years, increasing attention has been given to the study of sorption enhanced steam methane reforming (SESMR) for the production of hydrogen with CO₂ management.^{2–11} In this process, a CO₂ acceptor is installed together with the reforming catalyst in the reactor bed for removal of the carbon dioxide from the gas phase during reaction. Thus, the equilibrium of steam methane reforming and water-gas shift (WGS) reactions is shifted towards hydrogen production. As a result, high H₂ yields (>90%) are

obtained at lower temperatures (723–873 K) than conventional SMR (1073–1300 K). In addition, the process layout is simplified; there is no need for water-gas shift reactors or absorption columns and also less demanding requirements for the high temperature reactor materials. Consequently, the investment and operation costs for hydrogen production can possibly be reduced.

Eqn (1)–(4) show the reactions taking place in the catalytic bed when, for instance, CaO is used as CO₂ acceptor:



The H₂ yield depends strongly on the properties of the CO₂ acceptor. Different materials have been reported as candidates for application in SESMR. However, the selection of an appropriate acceptor is not straightforward and several requirements have to be fulfilled. The acceptor should have a large CO₂ capacity and adequate kinetics for both capture and regeneration. In addition, high cycle stability is required. SESMR is a batch process that requires regeneration of the acceptor after saturation with CO₂. The regeneration can be carried out by a temperature swing or pressure swing. In the case of a temperature swing process, it is desired to reduce the temperature gap between capture and regeneration.

Metal oxides such as CaO can react with CO₂ in the required range of temperatures, showing a good capacity and kinetics, but unfortunately poor stability.² More recently, Li and Na metal oxides have been reported as very good candidates for

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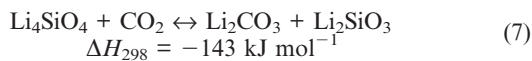
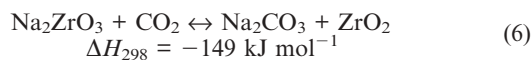
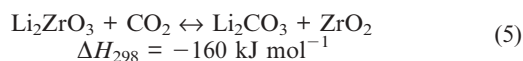
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CO₂ removal, with both fast kinetics and high stability.^{12–17} Examples of these materials are shown in eqn (5)–(7):



All the acceptors presented above are preferably regenerated by a temperature swing. If a pressure swing regeneration configuration is preferred, hydrotalcite-like compounds are currently the most promising candidates. These materials can take CO₂ at temperatures up to 773 K, showing good kinetics and stability, but poor capacity especially at high temperatures.^{18,19}

A large number of experimental and reactor modelling studies on SESMR have been reported, especially by application of CaO and hydrotalcite-like acceptors.^{2–11} However, little attention has been given to optimise the system configuration and the properties of the acceptor. In the present study, hydrogen production with CO₂ capture by SESMR is evaluated according to a multiscale approach. First, a process configuration has been proposed, simulated and discussed in terms of energy efficiency. Conventional steam methane reforming has been used as a base case for comparison. In addition, an evaluation of CaO, Li₂ZrO₃, K-doped Li₂ZrO₃, Na₂ZrO₃ and Li₄SiO₄ as potential CO₂ acceptors for SESMR has been carried out. The different candidates have been screened by means of thermodynamic analysis, kinetic measurements and the process design simulations.

2 Experimental

2.1 Synthesis and characterisation of the CO₂ acceptors

Li₂ZrO₃, Na₂ZrO₃ and K-doped Li₂ZrO₃ have been prepared by a novel soft chemistry route. Zirconyl nitrate, lithium acetate, sodium citrate and potassium nitrate were used as Li, Zr, Na and K precursors, respectively. In all cases, appropriate amounts of the precursors were dissolved in deionised water and mixed for several hours. The resulting solutions were dried by heating to 373 K in an oil bath under continuous stirring. Finally, Li₂ZrO₃ and K-doped Li₂ZrO₃ were obtained by calcination in air of the solid dried products at 873 K for 6 h. A two-step calcination was carried out in the case of Na₂ZrO₃; first, the sample was heated to 1073 K under an Ar atmosphere and then calcined at this temperature for 3 h in air. More details about the preparation and properties of the ceramic oxides have been reported elsewhere.^{14–16} CaO was obtained by calcination of CaCO₃, prepared as described by Andreassen *et al.* using calcium nitrate and sodium carbonate as precursors.²⁰ Li₄SiO₄ is a commercial sample provided by Toshiba.

X-Ray diffraction patterns were recorded at room temperature on a Siemens D5005 X-ray diffractometer using CuK α radiation ($\lambda = 1.54 \text{ \AA}$). The scans were recorded in the 2θ range between 20 and 85° using a step size of 0.03°. The average crystallite thickness or grain size was calculated from the Scherrer

Table 1 Physical properties of the acceptors

Sample	Crystallite size ^a /nm	BET surface area/m ² g ⁻¹	Stoichiometric capacity ^b (%)	Experimental capacity ^b (%)
CaO	64	3	78.6	49.5
Li ₂ ZrO ₃	13	5	28.8	27.1
K-doped Li ₂ ZrO ₃ ^c	15	<2	26.6	20.7
Na ₂ ZrO ₃	30	5	23.4	16.3
Li ₄ SiO ₄	37	2	36.6	22.9

^a X-ray diffraction. ^b Capacity: (gCO₂/g acceptor) $\times$ 100. ^c K : Li : Zr 0.2 : 2.2 : 1

equation.²¹ Lanthanum hexaboride, LaB₆, was used as a reference material to determine the instrumental line broadening.

Nitrogen adsorption–desorption isotherms were measured with a Micromeritics TriStar 3000 instrument, and the data were collected at 77 K. The samples were out-gassed at 573 K overnight prior to measurement. The surface area was calculated from the Brunauer–Emmett–Teller (BET) equation.²²

A summary of the main physical properties of the acceptors is presented in Table 1.

2.2 Thermodynamic modelling

FactSageTM 5.0²³ and HSC Chemistry²⁴ were used to calculate the equilibrium partial pressure of carbon dioxide on the selected materials at different temperatures. Furthermore, a thermodynamic study of the SESMR process has been carried out in an equilibrium of steam methane reforming and the WGS reaction. The equilibrium concentrations of the different reaction components have been calculated in Matlab using thermodynamic data originating from FactSageTM 5.0 and HSC Chemistry.

2.3 Kinetic measurements

CO₂ capture and regeneration properties were evaluated using a tapered element oscillating microbalance (TEOM).²⁵ A scheme of the TEOM reactor set-up has been reported previously.²⁶ The tapered element was loaded with 20 mg of the CO₂ acceptor together with quartz particles. The samples were heated to 848 K at a heating rate of 10 K min⁻¹ in pure argon and held for 60 min. The CO₂ capture was initiated by switching from Ar to the reaction mixture at the same temperature. The different partial pressures of CO₂ in the reaction mixture were obtained by adjusting the flow rates of Ar and CO₂ at a constant total flow rate of 100 ml min⁻¹. After saturation of the acceptor, the temperature was increased at 10 K min⁻¹ to the selected regeneration temperature and the flow gas was changed from CO₂ to Ar to release the CO₂. The capture reaction was carried out at 848 K for all the samples, while the regeneration was carried out at 953 K for CaO, Na₂ZrO₃ and Li₄SiO₄ and at 923 K for Li₂ZrO₃ and K-doped Li₂ZrO₃. A detailed description of the testing procedure has been reported elsewhere.²⁵

2.4 Process simulation

The H₂ production by a conventional steam reformer with CO₂ capture and a sorption enhanced steam reformer has been simulated in Hysys.²⁷ The performance of the different cases

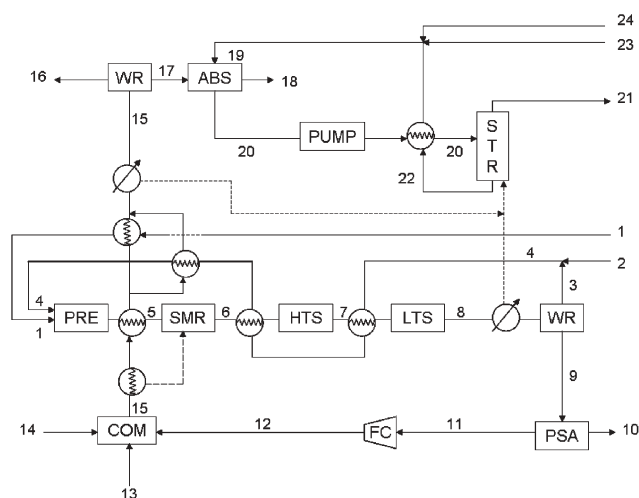


Fig. 1 Flow diagram of the simulated steam methane reforming process with CO₂ capture. PRE: pre-reformer, SMR: steam reformer, HTS: high-temperature shift reactor, LTS: low-temperature shift reactor, WR: water removal, PSA: pressure swing adsorption unit, FC: fuel compressor, COM: combustor, ABS: absorber, PUMP: pump, STR: stripper.

has been evaluated in basis of thermal and net efficiency. Fig. 1 and 2 show the process lay-out of the two simulated cases.

2.4.1 Case A: SMR. Natural gas (NG) and water are preheated before entering the adiabatic pre-reformer (PRE) at 783 K. All higher hydrocarbons are converted, and the reforming and water gas shift reactions (WGS) are basically at equilibrium. The resulting stream is preheated to 823 K before entering the tubular steam reformer (SMR). Heat to the reactor is indirectly provided by firing supplementary NG outside the tubes. A hydrogen rich process gas leaves the reactor at 1193 K and 25 bar. This gas is heat-exchanged with the water feed to 623 K before entering the high-temperature shift reactor (HTS). Later, the gas is further heat-exchanged

with the water feed to 473 K before entering the low-temperature shift reactor (LTS). The resulting gas leaves the LTS at 523 K and heat is extracted in a boiler to produce some steam for the later CO₂ capture. Further cooling to 303 K is carried out in a condenser. At this time, the condensate water is removed in a separator (WR). Further purification of the gas is carried out in a pressure swing adsorption unit (PSA). The hydrogen recovery in the PSA was 90% and the hydrogen purity 99.9%. Waste gases from the PSA and supplementary NG are burned with air in burners located on the outside of the tubes in the tubular steam reformer (COM). Around 50% of the provided heat is used in the reformer, while the rest of heat is used to preheat the feed streams of the pre-reformer, reformer and for the generation of steam. The removal of the flue gas CO₂ is carried out in an monoethanol amine (MEA) absorption plant (ABS). The flue gas is cooled to 313 K in a direct contact cooling tower before entering the absorption column. A lean MEA stream is entering the top of the column and absorbs the CO₂ from the gas that rise through the column. The CO₂ rich MEA stream leaving the column is pressurised to 2.3 bar and heat-exchanged before entering the stripper (STR). Heat is added through a reboiler at the bottom which reverses the reaction between CO₂ and MEA. Thus, an almost pure CO₂ stream leaves the top of the stripper while a lean MEA solution leaves at 398 K. This stream is further cooled to 313 K with cold water and recirculated to the absorber completing the cycle.

2.4.2 Case B: SESMR. NG and water are preheated before entering the reformer (SESMR). In this case, the reformer is filled with a CO₂ acceptor and a reforming catalyst. The capture of CO₂ shifts the reforming and WGS reactions towards hydrogen production. This allows the reformer to be operated at a much lower temperature than the conventional case. Accordingly, the reformer is operated at 848 K, 10 bar and a steam-to-carbon ratio (S/C) of 5. These conditions are chosen to maximise the conversion at the outlet of the reactor when Li₂ZrO₃ is used as acceptor.²⁵ The hydrogen rich gas leaves the adiabatic reactor with some unreacted methane and traces of CO and CO₂. This gas is heat exchanged with feed water before cooling to 303 K. While condensate water is removed in a separator, the hydrogen rich gas is cooled and compressed (FC) to the feed pressure (25 bar) of the PSA. A pure hydrogen stream leaves the PSA unit while the waste gas from the PSA is combusted with oxygen from an air separation unit (ASU). The resulting flame temperature is too high due to the burning with pure oxygen; some flue gas is therefore recycled to cool the flame. In this process configuration the regeneration is based on a thermal-pressure swing process. The hot flue gas is used to increase the temperature and regenerate the acceptors. The regeneration temperature was selected based on the thermodynamic properties of the acceptor and the amount of steam generated during the combustion. The regeneration pressure was 1 bar. Supplementary methane was necessary for the combustion in some of the studied cases when high conversions are achieved in the reformer. Finally, the regenerator flue gas consisting of a mixture of steam and CO₂ is heat exchanged and water is removed. The resulting stream is wet CO₂ ready for compression and storage.

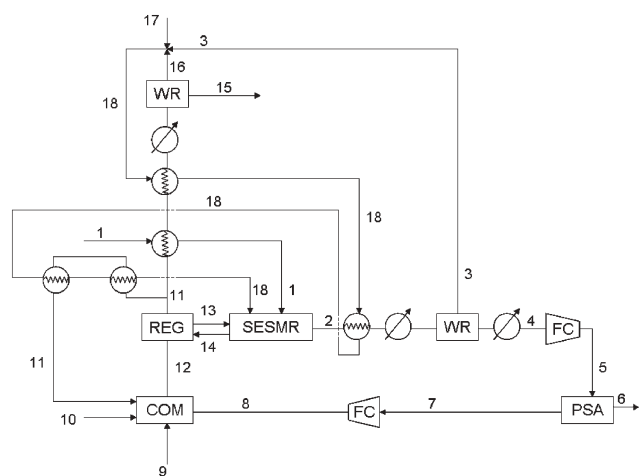


Fig. 2 Flow diagram of the simulated sorption enhanced steam methane reforming process. REG: regenerator, SESMR: sorption enhanced reforming reactor, WR: water removal, FC: fuel compressor, PSA: pressure swing adsorption unit, COM: combustor.

2.4.3 Hysys simulation. A conventional steam reformer with CO₂ capture and a sorption enhanced steam reformer have been simulated in Hysys. Both CaO and Li₂ZrO₃ have been used as acceptors in the SESMR case. The Soave–Redlich–Kwong (SRK) state equation was selected for the reforming section while the amine package was used in the MEA section. The thermochemical properties of the acceptors^{23,24} were also included in the Hysys simulations. All the reactors were simulated as equilibrium reactors with all reactions in equilibrium, except the water–gas–shift reactors where only the WGS reaction was in equilibrium. The ASU was not modelled, but the cost for oxygen production was set to 1.0 MJ kg⁻¹ O₂.²⁸ The natural gas was approximated as pure methane and pressure drop in the units was not considered. The final pressure for hydrogen and CO₂ was set to 25 bar and 1 bar, respectively. No further compression was included. The PSA was modelled as a component splitter with 90% hydrogen recovery and a product purity of 99.9% for all cases.²⁹

The SMR case was based on an ordinary steam reformer with 80% CO₂ capture of the flue gas. A steam/carbon ratio of 2.3 and process gas temperature of 1193 K was selected. These are typical working conditions used in a modern steam reformer today. The inlet temperature to the shift reactors was set to be 623 and 473 K for the high and low temperature shift reactors, respectively. Boilers were installed to meet the steam demand in the CO₂ stripper.

The SESMR case was modelled as a thermal–pressure swing process, where the reformer operated at 10 bar and the regenerator at 1 bar. The reformer was modelled as a reactor with continuous regeneration of the acceptor. Generally, the reactor and the regenerator have to operate at the same pressure, but were modelled at different pressures in order to avoid the dynamic nature of SESMR in the simulation. The regeneration temperature was 993 K and 1143 K for Li₂ZrO₃ and CaO, respectively. Formation of Ca(OH)₂ was not considered. Compression of the process gas from 10 bar to 25 bar was selected for direct comparison with the SMR case and meet the pressure specification of the PSA.

3 Results and discussion

3.1 Thermodynamic analysis

Fig. 3 shows the equilibrium partial pressures of carbon dioxide for the acceptors selected in this study in the temperature interval from 725–1000 K. CaO shows more favourable thermodynamics than the Li and Na based mixed oxides. Accordingly, CaO can remove lower concentrations of CO₂ compared to the others from a thermodynamic point of view. Doping of the mixed oxides might shift the equilibrium concentration; for example, doping Li₂ZrO₃ with K enhances the equilibrium with CO₂ due to the formation of a molten carbonate phase between K₂CO₃ and Li₂CO₃.³⁰ As a result, the K-doped material can take CO₂ in a broader range of pressures and temperatures. For instance, the partial pressure of CO₂ in the equilibrium of LiKZrO₃ (Li : K, 1 : 1) at 850 K is 0.02 bar *versus* 0.05 bar for pure Li₂ZrO₃.

The equilibrium concentration of H₂ when operating under SESMR conditions depends strongly on the thermodynamic properties of the acceptor. Higher H₂ yields will be obtained

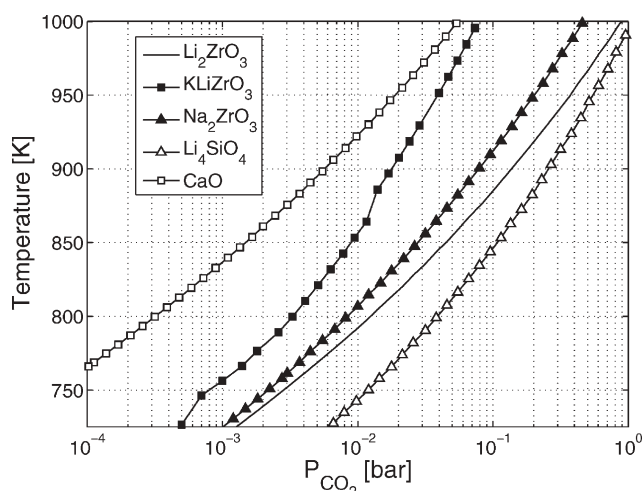


Fig. 3 Equilibrium partial pressure of carbon dioxide for the different studied acceptors.

with the more thermodynamically favoured acceptors. Fig. 4 shows the dry H₂ yield that can be obtained at equilibrium in SESMR at different reaction temperatures and pressures at a constant steam to carbon ratio of 5 for CaO, Li₂ZrO₃, Na₂ZrO₃ and Li₄SiO₄, respectively. A H₂ yield close to 90% can be achieved when the process is operated at 848 K, total pressure of 10 bar and Li₂ZrO₃ as acceptor. Similar yields can be obtained with Na₂ZrO₃. On the other hand, a yield higher than 98% can be achieved if Li₂ZrO₃ is replaced with CaO at the same working conditions, while only 82% will be obtained by using Li₄SiO₄. It is interesting to note that up to 99.5% H₂ can be obtained using CaO in SESMR at 1 bar. In addition, it is possible to use lower S/C ratios with CaO and still achieve similar or higher conversion than with the other selected acceptors.

Summarising, CaO is the most favourable CO₂ acceptor from the thermodynamic point of view among the studied acceptors, followed by K-doped Li₂ZrO₃ (Li : K, 1 : 1, 93% H₂), Na₂ZrO₃ (90% H₂), Li₂ZrO₃ (89% H₂) and Li₄SiO₄ (82% H₂). The H₂ yields are given on a dry basis and at the operation conditions of 10 bar, 848 K and S/C = 5. On the other hand, at identical conditions only 62% of H₂ can be obtained without an acceptor in the reactor and when the thermodynamics of steam reforming are governing, indicating the potential of SESMR.

3.2 Process design

As described earlier, the H₂ production by a conventional steam reformer with CO₂ capture and a sorption enhanced steam reformer have been simulated in Hysys. The performance of the different cases has been evaluated by means of thermal and net efficiency. The lower heating value (LHV) based thermal efficiency was defined as:

$$\text{Thermal efficiency} = \frac{\text{LHV}_{\text{out}}}{\text{LHV}_{\text{in}}} \quad (8)$$

$$\text{Net efficiency} = \frac{\text{LHV}_{\text{out}}}{\text{LHV}_{\text{in}} + \text{Work}_{\text{in}}} \quad (9)$$

The main process stream data for both the base case and SESMR are shown in Tables 2 and 3, respectively. The

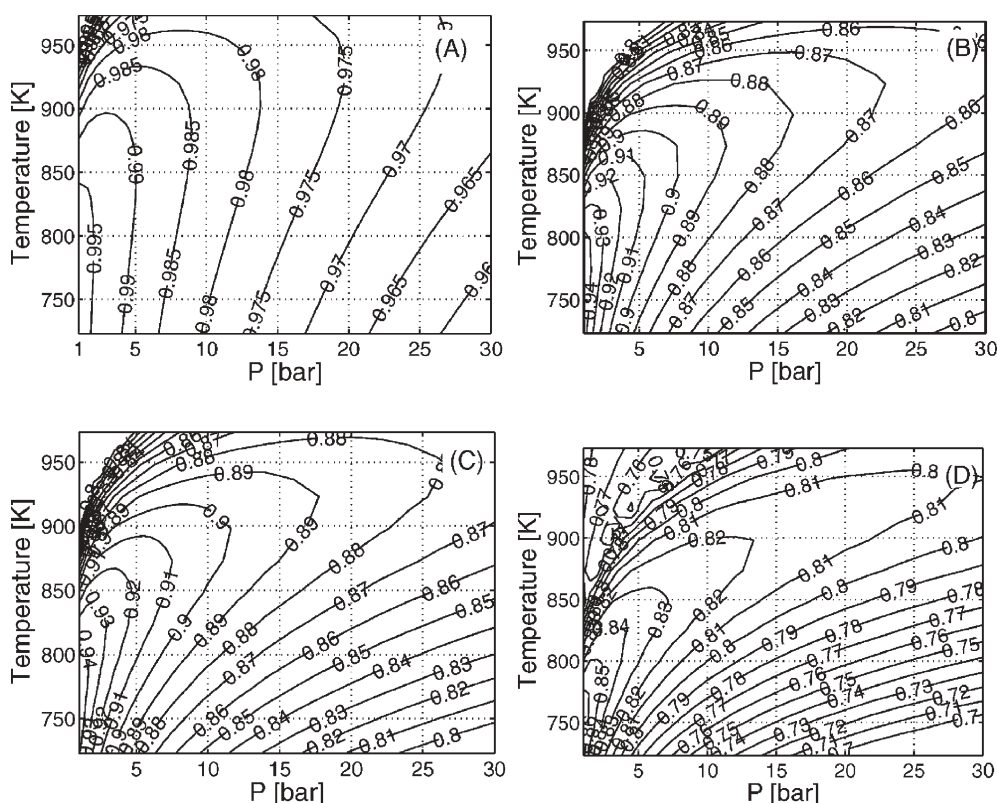


Fig. 4 Thermodynamic simulation of the hydrogen yields obtained by application of SESMR when: (A) CaO, (B) Li_2ZrO_3 , (C) Na_2ZrO_3 , (D) Li_4SiO_4 are used as acceptors, respectively. $S/C = 5$. The numbers stated in the Figures are the mole fraction of hydrogen in a dry basis.

influence of the CO_2 acceptor on the efficiency of the SESMR process was evaluated by the study of two different acceptors: Li_2ZrO_3 and CaO. The working conditions for the different studied cases and efficiencies are summarised in Table 4.

Special attention has been given to the thermal management of the processes. SMR is highly endothermic while SESMR is close to thermo-neutral. The reaction heat of the SESMR depends on the used acceptor. For example, by using CaO as acceptor the process is weakly exothermic ($\Delta H_{298} = -13 \text{ kJ mol}^{-1}$), while by using Li_2ZrO_3 the overall reaction is weakly endothermic ($\Delta H_{298} = 5 \text{ kJ mol}^{-1}$).

Therefore, the need of additional heat into the reaction zone is smaller in the SESMR case. However, the regeneration step is a highly endothermic reaction, requiring a large energy input. Still, this energy demand for the studied acceptors is lower than the energy required to carry out the reforming in the SMR case. Thus, improved heat integration is possible in the SESMR process.

A modern steam reformer is reported to have a thermal efficiency of 88% with steam credit.¹ This value is comparable with the thermal efficiency calculated in this study for the SMR case when no CO_2 capture is included in the simulation

Table 2 Composition for selected positions in the flow sheet in Fig. 1. SMR case: reaction temperature 1193 K, 25 bar and S/C : 2.3

Stream	Molar flow/ kmol s^{-1}	H_2 (%)	CH_4 (%)	CO (%)	CO_2 (%)	H_2O (%)	N_2 (%)	O_2 (%)	MEA (%)
1, 13	1, 0.27	—	100	—	—	—	—	—	—
2, 3, 4, 16	1.66, 0.63, 2.3	—	—	—	—	100	—	—	—
17, 24	0.88, 0.57	—	—	—	—	100	—	—	—
5	3.43	7.54	27.26	0.02	1.90	63.27	—	—	—
6	5.00	56.17	3.01	12.80	4.22	24.80	—	—	—
7	5.00	62.91	3.01	5.05	11.96	17.06	—	—	—
8	5.00	67.05	3.01	0.91	16.10	12.92	—	—	—
9	4.36	76.87	3.45	1.05	18.43	0.20	—	—	—
10	3.02	99.94	—	—	—	0.06	—	—	—
11, 12	1.34, 1.34	24.97	11.22	3.40	59.89	0.52	—	—	—
14	5.45	—	—	—	—	—	79	21	—
15	6.89	0.03	—	0.12	18.38	17.30	62.58	1.59	—
17	6.00	0.03	—	0.14	21.01	5.12	71.79	1.82	—
18	5.45	0.03	—	0.16	5.24	13.40	79.11	2.01	0.05
20	25.49	—	—	—	2.13	86.88	—	—	10.98
21	1.03	—	—	—	97.99	1.99	0.02	—	—
22	24.91	—	—	—	2.18	86.59	—	—	11.23
23	0.003	—	—	—	—	—	—	—	100

Table 3 Composition for selected positions in the flow sheet in Fig. 1. SESMR-Li₂ZrO₃ case: reaction temperature/regeneration 848/1003 K, 10 bar and S/C: 5. SESMR-CaO case: reaction/regeneration temperature 848/1143 K, 10 bar and S/C: 3

Stream	Molar flow/kmol s ⁻¹	H ₂ (%)	CH ₄ (%)	CO (%)	CO ₂ (%)	H ₂ O (%)	O ₂ (%)	Li ₂ ZrO ₃ (%)	Li ₂ CO ₃ (%)	ZrO ₂ (%)	CaCO ₃ (%)	CaO (%)
SESMR-Li ₂ ZrO ₃	1, 9	1, 0.05	—	100	—	—	—	—	—	—	—	—
	2	6.73	41.48	4.48	0.07	0.30	53.66	—	—	—	—	—
	3, 16, 17, 18	3.59, 0.94, 0.46, 5	—	—	—	—	100	—	—	—	—	—
	4, 5	3.13, 3.13	89.13	9.64	0.16	0.65	0.42	—	—	—	—	—
	6	2.51	99.79	—	—	—	0.21	—	—	—	—	—
	7, 8	0.61, 0.61	45.44	49.14	0.81	3.31	1.30	—	—	—	—	—
	10	0.85	—	—	—	—	100	—	—	—	—	—
	12	10.37	—	—	—	48.13	51.43	0.44	—	—	—	—
	13	1	—	—	—	—	—	100	—	—	—	—
	14	1.63	—	—	—	—	—	19.51	40.24	40.24	—	—
	15	1.10	—	—	—	95.08	4.16	0.76	—	—	—	—
	1, 9	1, 0.05	—	100	—	—	—	—	—	—	—	—
	2	4.80	66.22	4.29	0.02	0.02	29.45	—	—	—	—	—
	3, 16, 17, 18	1.40, 0.81, 0.79, 3	—	—	—	—	100	—	—	—	—	—
	4, 5	3.39, 3.39	93.56	6.06	0.03	0.03	0.32	—	—	—	—	—
SESMR-CaO	6	2.86	99.81	—	—	—	0.19	—	—	—	—	—
	7, 8	0.53, 0.53	59.83	38.78	0.17	0.21	1.01	—	—	—	—	—
	10	0.68	—	—	—	—	100	—	—	—	—	—
	12	10.11	—	—	—	51.95	47.67	0.38	—	—	—	—
	13	1.5	—	—	—	—	—	—	—	—	—	100
	14	1.5	—	—	—	—	—	—	—	—	52.83	47.17
	15	1.09	—	—	—	96.28	3.10	0.62	—	—	—	—

Table 4 Simulation conditions and main results for the studied cases

Case	S/C ratio	P/bar	React./Regen. T/K	X _{CH₄} (%)	H ₂ before PSA (%)	Thermal efficiency (%)	Electric work	Net efficiency (%)
SMR	2.3	25	1193	85	77	71 (86) ^a	<1% LHV	71
SESMR-Li ₂ ZrO ₃	5	10	848/1003	70	89	72	4% LHV	69
SESMR-CaO	3	10	848/1143	79	94	82	4% LHV	79

^a Efficiency before CO₂ capture.

(86%). On the other hand, a penalty in the efficiency from 86 to 71% is obtained as a result of the CO₂ removal. This decrease is mainly related to the thermal energy required for stripping of CO₂ from the amine solution.

A similar thermal efficiency was calculated for the SESMR-Li₂ZrO₃ case when it was operated at 10 bar, 848 K and S/C: 5. The selection of the working temperature was based on an optimum value derived from kinetic studies,³¹ while the steam-to-carbon ratio was adjusted to enhance the conversion. The reforming of NG is thermodynamically favoured by low pressures. However, high pressures are generally used because compression of gases for downstream applications is not economically attractive. The SMR case was operated at 25 bar. Nevertheless, lower pressures had to be used in the SESMR-Li₂ZrO₃ case in order to reach a competitive conversion. These conditions lead to a methane conversion of 70%, lower compared to the SMR case. However, a relatively pure hydrogen stream (89% H₂ in dry basis) was obtained with CH₄ as the main impurity.

Higher thermal efficiencies are obtained with CaO (82%) due to the lower S/C ratio used in this case. The equilibrium hydrogen yields using CaO as acceptor at S/C ratio 3 are shown in Fig. 5. High S/C ratios are necessary in order to maintain a competitive conversion when Li₂ZrO₃ is used as acceptor, as indicated by the thermodynamic analysis. The same can be applied to the other mixed oxides. However, the ability of CaO to remove CO₂ at lower concentrations makes

the acceptor better suited from the thermal efficiency point of view and operation at lower S/C ratios is possible. It should be noticed that even though a lower S/C ratio is used in the SESMR-CaO case, larger conversions and H₂ yields are obtained than for SESMR-Li₂ZrO₃.

Note that in both cases, the addition of around 5% of supplementary methane is necessary for complete combustion of the PSA waste gases. Since lower conversion is achieved by

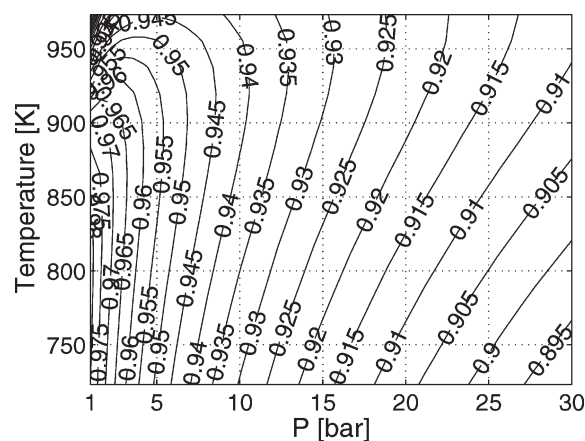


Fig. 5 Thermodynamic simulation of the hydrogen yields obtained by application of SESMR when CaO is used as acceptor. S/C = 3. The numbers stated in the Figure are the mole fraction of hydrogen in a dry basis.

SESMR- Li_2ZrO_3 , a smaller amount of supplementary CH_4 would be expected. However, this value is enhanced due to the higher S/C ratio necessary in SESMR- Li_2ZrO_3 ; extra fuel is necessary for heating of the water feed. The amount of supplementary methane could be minimised by working at lower conversions, for example by working away from the equilibrium. This will also reduce the size of the reactor; however, larger PSA units will be needed. This design parameter has to be optimised by taking into account economic factors.

Note that in this study, all the thermal efficiencies are calculated considering that the reactors are working at equilibrium. However, in a industrial process, the real conversion can be lower than the equilibrium. The conversion will depend on the reactor size, the kinetics of CO_2 capture and the capacity of the CO_2 acceptors. The kinetic behaviour of the CO_2 acceptors at SESMR conditions is an important parameter for selection of acceptors and is discussed in the following section.

In general, SESMR presents a simpler process layout than SMR. This can be observed from direct comparison of Fig. 1 and 2. The PRE, SMR, HTS, LTS, ABS and STR are substituted by the SESMR and the REG. The regenerator may be omitted in the case of a batch operation process or in the case of a reformer with continuous regeneration. In addition, the high H_2 yields obtained by SESMR will result in smaller PSA units than SMR. The amount of gas entering the PSA unit for the SMR and the SESMR cases are given in Table 2, stream 9 and Table 3, stream 5, respectively. The results show that a total molar flow of 1.01 kmol s^{-1} has to be adsorbed in the PSA unit per mol of CH_4 during SMR operation, while in the SESMR case the amount is reduced to 0.34 kmol s^{-1} . However, a compression stage will be required to meet the PSA specification and exit pressure of 25 bar in this case. This compression will cause a penalty in the net efficiency of SESMR because of the induced electric work. The regeneration of the acceptor in the SESMR case was done by a pressure-temperature swing at 1 bar and 1003 K. In order to provide heat for the regeneration, the waste gases from the PSA are combusted with oxygen. The need for electric work for oxygen production and compression makes the net efficiency of SESMR- Li_2ZrO_3 low compared to conventional SMR, whereas the values for SESMR- CaO are still higher than SMR. It should be mentioned that the compression stage will only be necessary for some downstream applications and it is included in this case for direct comparison with the SMR case.

3.3 Kinetic behaviour of CO_2 capture

In addition to favourable thermodynamics, appropriate CO_2 capture kinetics and stability are also important properties for the application of CO_2 acceptors in SESMR.

In a previous study, the H_2 production by SESMR has been simulated by a dynamic one-dimensional pseudo-homogeneous model.¹¹ It was shown that SESMR is an appropriate route for direct production of a hydrogen-rich stream. In addition, simulation results showed that the CO_2 capture kinetics are very important, in many cases being the rate limiting step. Therefore, the removal of CO_2 at low partial pressures is critical for a high efficiency of the process and reducing the reactor size.

Fig. 6 shows in detail the uptake profiles for the studied acceptors at 848 K under (A): 100% CO_2 and (B): 30% CO_2 . As discussed above, CaO shows a high capacity and fast CO_2 uptakes, both at high and low CO_2 concentrations. Li_2ZrO_3 also showed good behaviour at 100% CO_2 , while very slow kinetics were observed when the partial pressure of CO_2 was low. The doping of the material with K enhanced the kinetics considerably, although, the doping results in a decrease in the capacity. This decrease is directly related to the amount of doping agent; the sample presented here has a molar composition K : Li : Zr, 0.2 : 2.2 : 1. It should be noticed that this sample differs in composition with the K-doped sample presented in the thermodynamic analysis, where K : Li : Zr 1 : 1 : 1 was used. The addition of K has a positive effect on the capture rate because of the formation of an eutectic molten carbonate at high temperatures. The molten carbonate can reduce the diffusion resistance of CO_2 on the acceptor.³⁰ On the other hand, Li_4SiO_4 performed similar kinetics and capacity as K-doped Li_2ZrO_3 (K : Li : Zr, 0.2 : 2.2 : 1). Finally, Na_2ZrO_3 showed the fastest kinetics among its ceramic counterparts,

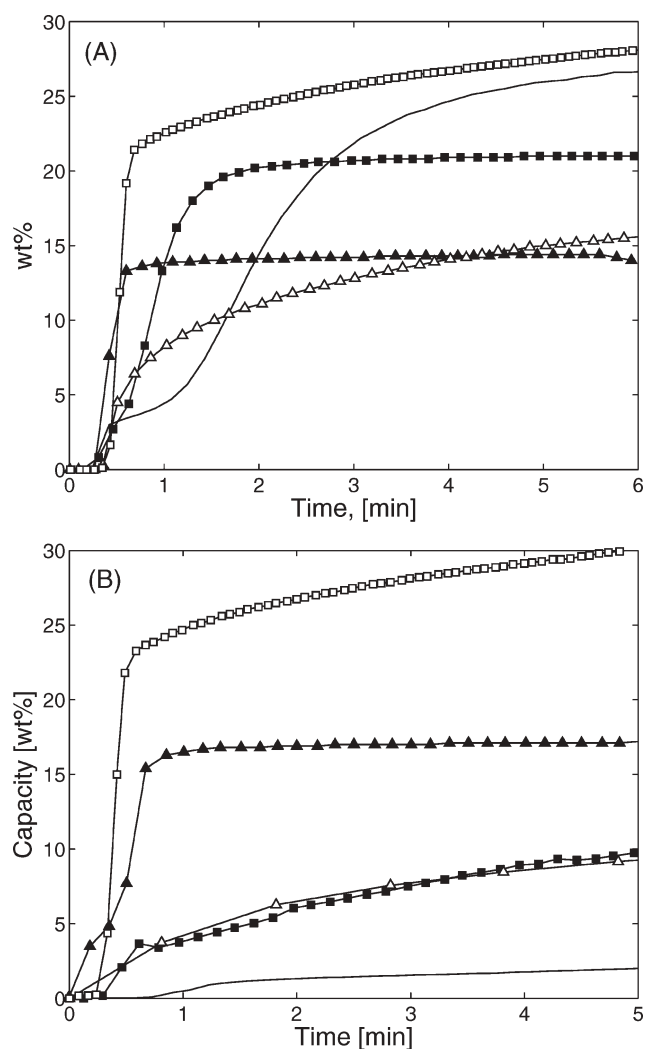


Fig. 6 CO_2 uptake profiles for the studied acceptors at 848 K and under 100 ml ml^{-1} of (A): pure CO_2 and (B): a mixture of Ar/CO_2 , P_{CO_2} : 0.3 bar. (—) Li_2ZrO_3 , (▲) Na_2ZrO_3 , (■) K-doped Li_2ZrO_3 (K : Li : Zr 0.2 : 2.2 : 1), (△) Li_4SiO_4 , (□) CaO .

comparable with the kinetics of CaO, even at the low partial pressures of CO₂. However, a lower total capacity is obtained.

The partial pressure of CO₂ in the reactor environment at the normal SESMR conditions is lower than 10%. Therefore, the properties of the acceptor in this range of concentrations is of special relevance. From the simulation study referred to earlier, it was concluded that the application of Li₂ZrO₃ as acceptor can lead to high H₂ yields. However, for this purpose, long contact times are necessary due to poor kinetics at working conditions, as shown in Fig. 6(B). As a result, the working capacity of the process becomes poor compared to conventional SMR.¹¹ Faster kinetics is then desirable to compete with the reforming reaction, making Na₂ZrO₃ or CaO more appropriate acceptors. In addition, reactor simulations indicated that the sorbent capacity also has a significant effect on the reactor size. Therefore, a CO₂ acceptor with large capacity and fast kinetics at relatively low CO₂ partial pressures is highly desirable for sorption enhanced steam reforming.

A better understanding of the relationship between chemical and physical properties of the materials and their activity for CO₂ capture is essential for the development of CO₂ acceptors. As previously reported,²⁵ the crystal size of Li₂ZrO₃ is a very important parameter for the CO₂ capture kinetics, and improved kinetics can be obtained with nanosized Li₂ZrO₃. This conclusion is valid also for the other oxides. Although the crystal or grain sizes measured by XRD are in the nanometre range, all acceptors have small surface areas, as presented in Table 1. A scanning electron microscopy study indicates that the single crystals aggregate in larger particles in the µm range for all the samples, resulting in the relatively low surface area. The final degree of reaction of the solid acceptors can be calculated from the ratio between the experimental and stoichiometric capacity indicated in Table 1. It can be observed that the degree of reaction depends significantly on the crystal size of the materials. The acceptor with smallest crystal size, Li₂ZrO₃, has the highest degree of reaction.

However, the higher reaction rate for CaO than other materials can not be ascribed to the crystal size, since CaO has the largest crystallite size. The chemical properties of the solid acceptor must play a significant role in determining the activity. Recently, quantum chemical cluster studies have been used to understand the mechanism of CO₂ adsorption on MgO and CaO surfaces.³² The reactivity towards CO₂ of the acceptors can be related to the Madelung potential, which varies with the lattice constant. Lowering the Madelung potential leads to a more diffuse electron cloud of the O²⁻ site on the CaO surface, which facilitates overlapping of orbitals from the adsorbing molecules.³² Thus, a comparison of the lattice parameters can give an indication of the reactivity towards CO₂ for the different acceptors. The materials in the present study have inherently different structures, and a simple comparison based on lattice parameters alone is questionable. CaO is cubic with a lattice parameter $a = 4.81 \text{ \AA}$. Li₂ZrO₃ has a tetragonal structure, while Na₂ZrO₃ and Li₄SiO₄ are monoclinic. Quantum chemical calculations are most likely necessary for an improved understanding.

The introduction of K in the Li₂ZrO₃ does not result in significant variations in particle size or surface area. However, as discussed above, the improved kinetics are likely due to the

formation of a molten carbonate that will be in the liquid phase at the reaction conditions. As a result, the diffusion of CO₂ in the oxide is faster than in pure Li₂ZrO₃.³³

Detailed kinetic study has been previously performed on Li₂ZrO₃, Li₄SiO₄ and CaO.^{11,34,35} The results clearly indicate that the reaction order on CO₂ depends significantly on the materials used. The reaction order varies from 2 for Li₂ZrO₃ to lower than 1 for Li₄SiO₄. This indicates that different acceptors give rise to different reaction mechanism or/and different rate limiting steps. The presence of a complicated mechanism of CO₂ capture on Li₂ZrO₃ was already evidenced in an earlier study.²⁵ Kinetic modelling including detailed mechanisms of CO₂ capture on different CO₂ acceptors is in progress.

H₂ production by SESMR with the use of Li₂ZrO₃ and Na₂ZrO₃ as acceptors has been experimentally tested in a fixed-bed reactor at 848 K, 5 bar, S/C: 5, 1.9 L h⁻¹ g(cat)⁻¹, acceptor/catalyst: 5.³⁶ A hydrotalcite-like catalyst with 40% Ni has been used as reforming catalyst.³⁷ In the case of using Na₂ZrO₃, H₂ yields larger than 90% H₂ were obtained during SESMR operation. The same experiment was carried out using Li₂ZrO₃ as acceptor. However, the H₂ yield was not considerably enhanced in this case. The capture rate of Li₂ZrO₃ at low partial pressures of CO₂ is considerably slower than for Na₂ZrO₃ as observed in Fig. 6(B). As a result, at the present working conditions the capture reaction cannot compete with the reforming and the CO₂ formed in the reaction zone cannot be completely removed.

The results show that among the studied materials, CaO is the most favourable CO₂ acceptor from the thermodynamic and kinetic point of view, followed by Na₂ZrO₃. However, stability problems in the case of CaO make the material less promising. The high temperature for the regeneration of the material results in sintering and loss in porosity. As a result, the capture capacity decays dramatically after the first 10 cycles and the capacity is lower than 10% after about 50 cycles.³⁸ In addition, it is also known that CaO can react with steam leading to the formation of Ca(OH)₂, thus lowering the conversion.³⁹ Fig. 7 shows the changes in the capacity for the different acceptors after successive cycles. As observed, CaO has the highest starting capacity; however, the stability is very poor. On the other hand, the various Li and Na ceramics showed a good stability after a multicycle study. This feature can make Na₂ZrO₃ one of the most complete materials, despite its lower capacity. However, it has to be emphasised that the price of Li and Zr based materials is several orders of magnitude higher than Ca based acceptors. Therefore, long term stability is required under capture/regeneration cycles. Abanades *et al.* claimed that Li based materials must sustain several thousand cycles in order to compete with other present technologies after studying the cost and performance of various CO₂ solid acceptors in CO₂ capture cycles.⁴⁰ Table 5 summarises the properties of the studied acceptors.

4 Conclusions

The application of SESMR has been evaluated according to a multiscale approach and compared to conventional SMR. According to the thermodynamic analysis of the system, the hydrogen yield obtained by SESMR is very much dependent

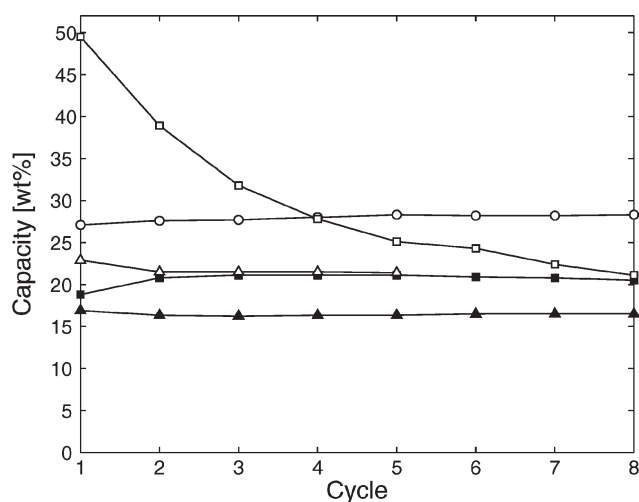


Fig. 7 CO₂ capture capacity after saturation of the different studied acceptors for successive cycles: stability plot. (○) Li₂ZrO₃, (▲) Na₂ZrO₃, (■) K-doped Li₂ZrO₃ (K : Li : Zr 0.2 : 2.2 : 1), (△) Li₄SiO₄, (□) CaO.

Table 5 Properties of the studied acceptors

	CaO	Li ₂ ZrO ₃	KLiZrO ₃	Li ₄ SiO ₄	Na ₂ ZrO ₃
Capacity	G	F	F	F	F
Thermodynamic	G	F	F	F	F
Stability	P	G	F	G	G
Kinetics	G	F/P	F	F	G
Regeneration <i>T</i>	H	M	M	M	M

^a G: good. F: fair. P: poor. H: high. M: medium.

on the CO₂ acceptor properties. An acceptor working efficiently at low partial pressures of CO₂ is required. Thus, a comparative study of five different high-temperature CO₂ acceptors has been carried out. The results show that none of the acceptors completely fulfil all the requirements for SESMR. CaO is the most favourable acceptor from the thermodynamic point of view leading to the highest H₂ yields. However, further development of the material is necessary in order to improve its stability. Na₂ZrO₃ may be a good alternative due to the good kinetics and stability, but an increase in the total capacity is desirable.

The thermal efficiencies of SESMR derived from the process simulation study are comparable to conventional steam reforming when lithium zirconate is used as acceptor. The use of an acceptor with a more favourable CO₂ equilibrium such as CaO considerably enhances this efficiency.

Thus, SESMR results in a simpler process configuration, less demand on high temperature materials, smaller PSA units and reasonable thermal efficiency. These features make SESMR a promising alternative for production of hydrogen and power generation with CO₂ management. However, a detailed economic evaluation of the system is necessary.

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Evolution of the bulk structure and surface species on Fe–Ce catalysts during the Fischer–Tropsch synthesis†

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Two Fe–Ce catalysts were prepared by wet impregnation of Ce onto iron oxyhydroxide (FeOOH) and hematite iron oxide (α -Fe₂O₃), respectively. Their performance in the Fischer–Tropsch (FT) synthesis was investigated and compared with that obtained with a Ce-free α -Fe₂O₃ catalyst. It was observed that the behavior of the different catalysts changed along the course of the FT reaction. The catalysts were tested for different periods of time, carefully passivated, recovered from the reactor and characterized by different techniques. The FT activity of the Ce-loaded and Ce-free catalysts decreased initially, but at a certain point the catalytic activity started to increase. The time needed to reach this inflection point depended on the catalyst composition, being shorter for the Ce-promoted catalysts. The catalytic activity of the Ce-free catalyst increased when the Fe₃C species were transformed into χ -Fe_{2.5}C, which are suggested to be the carbide phase present when polymerized carbon species (C_β) are formed. The addition of Ce to the iron oxyhydroxide developed solids with a higher BET surface area. Besides, these samples displayed a higher FT activity at long time-on-stream (TOS). Moreover, Ce addition also facilitated the formation of the C_β species previous to the evolution of Fe₃C into χ -Fe_{2.5}C, and therefore, promoted the FT synthesis reaction.

Introduction

The Fischer–Tropsch (FT) synthesis is a worthwhile route to produce sulfur- and aromatics-free liquid fuels along with other chemical products (mainly alcohols) from syngas mixtures (H₂ + CO). One of the challenges of the FT process is to modulate the distribution of products, which is accurately described by the Anderson–Schulz–Flory (ASF) model. According to this model, the FT synthesis is a polymerization reaction in which the chain growth occurs through the successive incorporation of a monomer building block to the previously formed oligomer. Promising results have been obtained with conventional FT catalysts (based either on Fe or Co oxides) promoted by certain additives. Thus, elements like K, Mn, Cu, Ru, Zn and Al are typically added to Fe oxide precursors. It is well established that potassium increases the olefin content and selectivity to heavier products.^{1,2} Manganese is known to increase the light olefins content;³ copper and ruthenium^{4,5} enhance the reduction–carburization rate of the catalytic precursors; and aluminium or zinc⁴ enhances the catalyst surface area and improves the structural integrity.

Recently, it has been shown that Fe–Ce mixed oxides lead to more active FT catalysts than pure α -Fe₂O₃.^{6,7} The higher catalytic activity is related to close Fe–O–Ce interactions in the oxide form and to the stabilization of Ce(III) cations on the

surface. Actually, the Ce promotion was associated with the formation of new catalytic active sites (Fe–Ce ensembles) based on the coexistence of Ce(III) and Ce(IV) cations on the catalyst surface. The CO dissociation and the Fe carburization processes are accelerated on these active sites because ceria is able to transfer the oxygen atoms rapidly from the CO molecules, increasing in that way the CO reactivity markedly.

Currently, there is not a general agreement about the nature of the real active phase in Fe-based catalysts for the FT synthesis.^{8,9} Many researchers have found a correlation between the carbide content in the catalyst and the FT activity.^{10–12} Schulz *et al.*¹³ reported that the approach to the FT steady-state with Fe-based catalysts can be divided into several episodes of distinct kinetic regimes when the catalysts are activated with H₂. These episodes consist in carbon deposition and Fe carburization processes until the totality of α -Fe (the main phase after H₂ pretreatment) is transformed into χ -Fe_{2.5}C. At this moment, the steady-state is reached and the formation of the “real” FT catalyst is supposed to occur. However, there is a lack of correlation between the amount of bulk iron carbide and the activity of the catalyst.^{14,15} According to these studies, the bulk iron carbide serves merely as a support of the actual active surface species. The exact nature of the carbide phase over which the reaction takes place remains elusive. Bartholomew *et al.*^{16,17} have recently identified and quantified different carbon and metal carbide species present on the surface of unsupported and supported Fe catalysts used in the FT synthesis by temperature-programmed surface reaction (TPSR) with hydrogen (also known as temperature-programmed hydrogenation, TPH). In either case, a correlation between the coverage of atomic surface carbon species and the catalyst activity was found.

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Herranz *et al.*¹⁸ have also identified different carbon and metal carbide species present on the surface of Mn- and Ce-promoted Fe catalysts after different activation pretreatments by using the same TPSR technique. A straightforward correlation between the concentration of the Hägg carbide (χ -Fe_{2.5}C) species and the catalytic activity was found. Furthermore, the higher activity of the catalysts was directly related to a higher coverage of polymeric surface carbon species (C_β).

Taking into account all this argumentation, the effect of Ce addition to Fe-based catalysts could be related to a faster carburization process, leading thus to an acceleration of the episodes which yield to the real active phase for the CO hydrogenation reaction. On the other hand, Ce addition could also be responsible of the formation of more reactive carbon species on the surface. Hitherto, the actual nature of the Fe–Ce active phase(s), the surface species and their evolution in the different kinetic regimes has not been unequivocally determined.

The objective of the present study was to identify the bulk and surface structural changes of the catalyst which take place during the FT reaction in order to establish a correlation between the catalytic activity and the phases present in the catalyst. In order to achieve this goal, the catalysts were characterized after being used for different periods of time-on-stream (TOS). Bulk phases and textural properties were characterized by powder X-ray diffraction (XRD), Mössbauer spectroscopy and N₂ adsorption isotherms. Carbonaceous species were identified by temperature-programmed surface reaction with hydrogen. Special attention was paid to the analysis of the different iron carbide and carbonaceous species.

Experimental

Catalyst preparation

A Ce-free iron oxide (α -Fe₂O₃) catalyst was prepared by precipitation⁶ and used as reference material. This solid was referred to as Fe. Two different Fe–Ce samples (95% Fe and 5% Ce, atomic percentages) were prepared by impregnation of iron oxyhydroxide (referred to as FeCe-I) and iron oxide (referred to as FeCe-IC), respectively, with a 1.5 M aqueous solution of Ce(NO₃)₃ (Aldrich, 99.99%) at 333 K, as has already been described in previous work.⁷ After the impregnation step, the resulting solids were treated in air at 573 K for 2 h. The iron oxyhydroxide (FeOOH) solid was prepared by fast addition of a 5.6 M NH₄OH solution to a 1.0 M aqueous solution of Fe(NO₃)₃ (Fluka 98–100%) at constant temperature (353 K). The precipitated material (iron oxyhydroxide) was filtered off and washed thoroughly with distilled water. The solid was then dried at 323 K for 24 h. The iron oxide was obtained by treating the iron oxyhydroxide previously described in air at 573 K for 2 h.

Catalytic measurements

The catalysts were tested in the CO hydrogenation reaction using a fixed-bed microreactor (stainless steel 316, 150 mm long and 9 mm i.d.). The reactor temperature was measured with a K-type thermocouple buried in the catalytic bed. Flow rates were controlled using a Brooks 5850 TR series mass flow

controllers. In order to facilitate the characterization of the catalysts after the FT reaction, the samples (400 mg, 0.25–0.30 mm particle size) were loaded in the reactor without dilution with inert materials. The catalysts were activated *in situ* at 673 K (heating rate of 2 K min^{−1}) for 16 h in 33 vol% H₂–N₂ mixture (5.9 L_{H₂} min^{−1}) at atmospheric pressure. The reactor was then cooled down in N₂ to the reaction temperature (573 K) and the system was pressurized to 1.01 MPa. Next, the flow was switched to synthesis gas (H₂–CO = 2; GHSV = 15.48 L g_{cat}^{−1} h^{−1}). This point was considered to be the start of the reaction. It was estimated that the reaction mixture would have flushed out the N₂ in *ca.* 45 min at this pressure and flow rate values. Product analysis was performed on line with a gas chromatograph (HP 6890 Plus). A Porapak Q (1/8" × 3 m) packed column connected to a thermal conductivity detector was used to analyze the inorganic gases (H₂, N₂, CO, CO₂) and water. The hydrocarbons and oxygenated compounds were analyzed in a DB-1 capillary column (60 m × 0.25 mm × 0.25 μm) connected to a flame ionization detector. The following temperature program was used: 223 K for 10 min, a ramp of 10 K min^{−1} to 523 K and then held at this temperature for 20 min. N₂ was used as an internal standard for the chromatographic analyses.

The spent catalysts were recovered for characterization after the activation process and after the catalytic test for selected time-on-stream (TOS) values. In order to avoid extensive oxidation under ambient air, the catalysts were passivated *in situ* by using an O₂–N₂ (<1 vol% O₂) flow at 298 K for 1 h, according to the method established by Datye *et al.*¹⁹ This procedure resulted in the oxidation of the outermost surface layers, thus impeding the further modification of the carbonaceous species present on the solid surface.

Catalysts characterization

XRD patterns were recorded in the 5–80° 2θ range in scan mode (0.02°, 2 s) using a Seifert 3000 XRD diffractometer equipped with a PW goniometer with Bragg–Brentano θ/2θ geometry, an automatic slit, and a bent graphite monochromator. Nitrogen adsorption isotherms were recorded at 77 K using a Micromeritics ASAP 2000 apparatus. The samples were degassed at 413 K for 12 h prior to the determination of the adsorption isotherm.

Transmission Mössbauer spectra were recorded at room temperature using a conventional constant-acceleration spectrometer equipped with a ⁵⁷Co (Rh) source. Finely ground powdered absorbers were prepared with a thickness of about 10 mg cm^{−2} of natural Fe. The spectra were computer-fitted to a sum of Lorentzian-shaped lines by applying the constraints of equal linewidth and area for the two peaks of doublets, and equal linewidth and areas in the ratio 3 : 2 : 1 : 1 : 2 : 3 for the six peaks of sextets. The relative concentrations of the different Fe species were calculated from their spectral area ratios assuming equal *f* factors (probability of Mössbauer effect) for all the Fe species present in the spectrum. Isomer shifts were referred to the center of the α-Fe sextet at room temperature.

TPH was carried out in a U-shaped quartz reactor connected to a QMS 200 Balzer Prisma quadrupole mass spectrometer for on line gas analysis. The sample (about 50 mg)

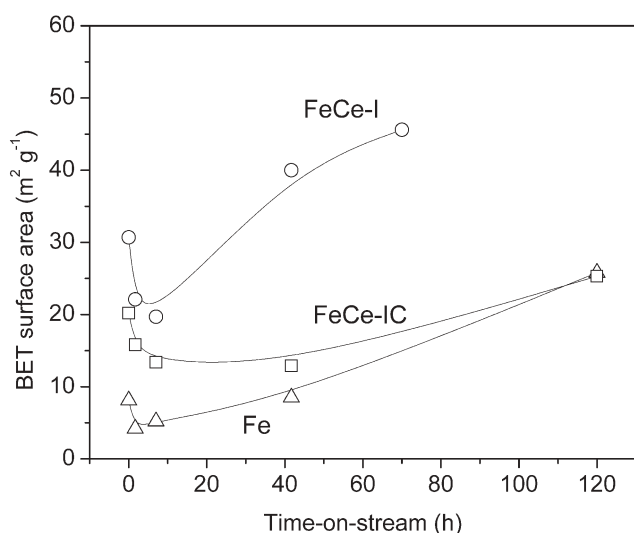


Fig. 1 Evolution of the BET surface area with TOS.

was treated with a 10 vol% H_2 -Ar mixture (50 mL min^{-1}) from 298 to 1073 K at a heating rate of 10 K min^{-1} . The fragments $m/z = 2, 16, 18, 28, 41$ and 44 and typical minor fragments from methane and small hydrocarbons were continuously recorded. Gas lines from the reactor to the inlet of the mass spectrometer were heated to 393 K to avoid water condensation.

Results and discussion

Fig. 1 and Fig. 2 depict, respectively, the evolution of the BET surface area and hydrocarbon formation rate values *versus* TOS of the different catalysts. It is clearly seen that the BET surface area and the rate of hydrocarbon formation changed in the same way as the reaction proceeded. Furthermore, it is evident that surface area and catalytic activity displayed a similar behavior. Both phenomena may be well related, probably as a result of a structural evolution of the catalysts. Two different episodes could be distinguished. During the first

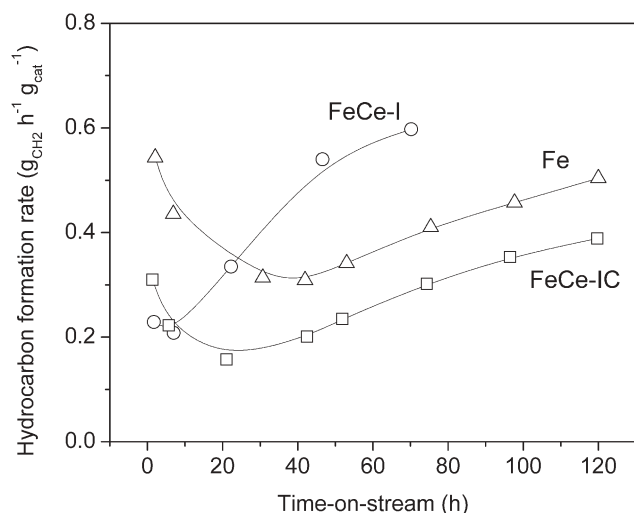


Fig. 2 Evolution of the rate of hydrocarbon formation with TOS.

one, the catalytic activity declined. At a certain TOS value, an inflection point was reached and the catalyst activity increased. Noticeably, the Ce-free catalyst displayed the highest CO conversion rate to hydrocarbons in the early stages of the reaction. This suggests a higher carburization level of the Ce-free catalyst. However, the sample FeCe-I developed a more active catalyst than the Fe material after the inflection point, probably because of the formation of more sites with higher reactivity as a consequence of the Fe-Ce interactions. The catalytic activity of the FeCe-IC sample was lower than that of the Fe sample. In that case, the material was prepared by impregnation of hematite. Therefore, Fe-Ce interactions (which are formed during the thermal treatment of Ce-impregnated iron oxyhydroxide) were not created. Probably, Ce atoms are deposited over the Fe oxide surface covering active sites. This would explain the lower catalytic activity of the FeCe-I sample.

As already mentioned, a straightforward correlation between the catalytic activity and the BET surface area as the reaction proceeded (high TOS values) can be observed. At a first glance, it seems that the role of Ce is to increase the catalyst surface area and, consequently, the number of active sites and the catalytic activity. However, this correlation does not apply in the early stages of the FT reaction. Therefore, other factors should be evoked in order to explain the lower activity of the Fe-Ce catalysts during the initial episodes of the reaction. Besides, it is also interesting to note that the Ce-free iron catalyst needs a longer reaction time to reach the above mentioned inflection point in the catalytic activity.

Fig. 3 shows the evolution of the CO_2 formation rate *versus* TOS. First of all, a parallelism between the rates of hydrocarbons and carbon dioxide formation can be seen by comparing Fig. 2 and Fig. 3. This strongly suggests that the CO_2 evolution is the result of the water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$): as the reaction proceeds, the water concentration increases and the CO_2 formation rate is also increased. In addition, Fig. 3 clearly shows that the CO_2 formation rate is higher with the Ce-containing samples, which is the result of the very well known ability of Ce-containing solids to catalyze the water-gas shift reaction.²⁰

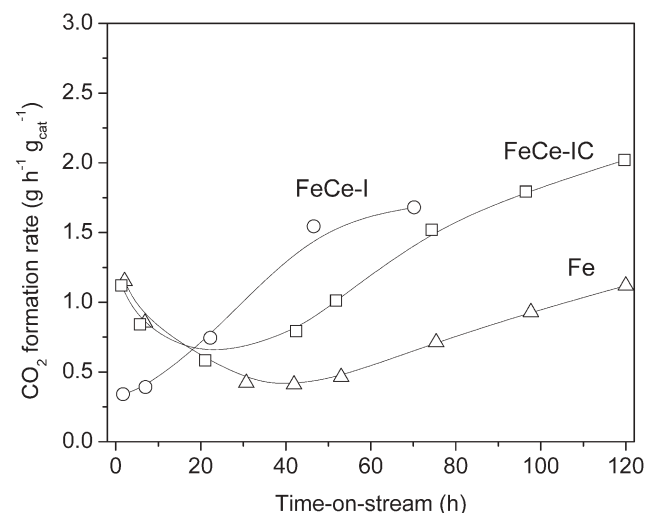


Fig. 3 Evolution of the rate of carbon dioxide formation with TOS.

The pore size distribution (not shown) corresponding to the Fe, FeCe-I and FeCe-IC catalysts after different TOS values also changed. In general, Ce addition stabilized the mesoporous structure of the solids during the first episodes of the reaction. All catalysts displayed a narrow pore distribution in the mesoporous range before the activation process. However, only the FeCe-I and FeCe-IC catalysts maintained that structure after the activation, although the average pore diameter was shifted to higher values, as it was previously described by other authors.^{14,21} Nevertheless, it is remarkable that all catalysts depicted similar textural properties for the last stages of reaction, displaying a broad pore distribution ranging from mesoporous to macroporous structures.

Fig. 4, Fig. 5 and Fig. 6 depict, respectively, the XRD patterns obtained with the FeCe-I, FeCe-IC and Fe catalysts used in the FT synthesis for the selected TOS. The species detected in the diffraction patterns of the Ce-promoted samples (FeCe-I and FeCe-IC) presented a similar evolution. During the first stages of the reaction, reflections ascribed to metallic iron (Fe^0), magnetite (Fe_3O_4) and different iron carbides ($\chi\text{-Fe}_{2.5}\text{C}$ and Fe_3C) phases were observed in the Ce-containing samples. On the contrary, Fe^0 was not detected in the Ce-free catalyst. This feature is indicative of a lower iron carburization rate of the Ce-containing samples, leading to less active materials for the FT synthesis. This feature is in good agreement with the correlation between the Fe carbide content and the FT activity found by other authors.^{10–13} For the Ce-free Fe catalyst, the reflection peaks assigned to the $\chi\text{-Fe}_{2.5}\text{C}$ phase were more evident at expense of those corresponding to the Fe_3C phase (compare the XRD patterns after 40 and 70 h on stream) as the reaction proceeds further. Besides, an increase on the catalytic activity was observed during this period of time. Therefore, it seems that the evolution of the carbide phase was responsible for the enhancement of the catalytic activity of the Fe sample after 40 h on stream.

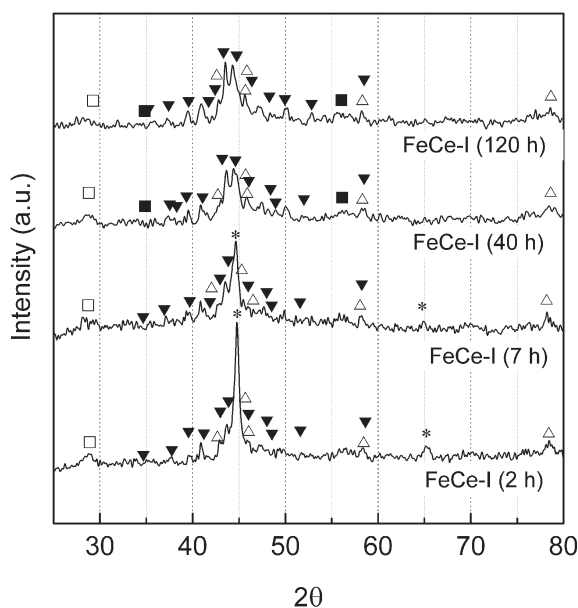


Fig. 4 XRD patterns of the FeCe-I catalyst after different TOS. Fe^0 : *; Fe_3O_4 : ■; $\chi\text{-Fe}_{2.5}\text{C}$: ▼; Fe_3C : △; c- CeO_2 : □.

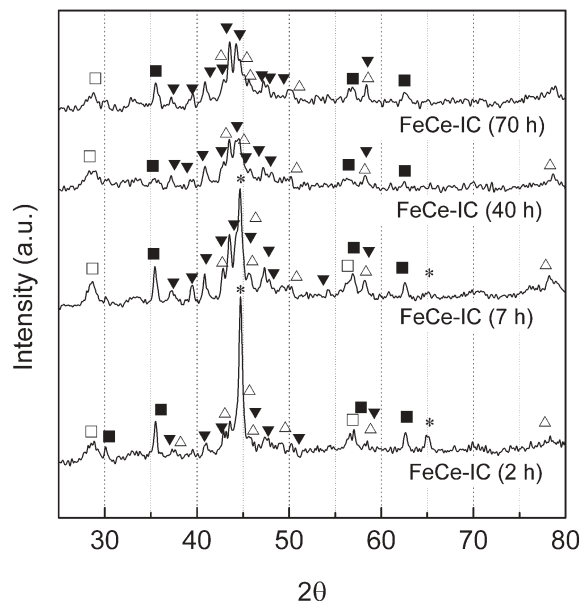


Fig. 5 XRD patterns of the FeCe-IC catalyst after different TOS. Fe^0 : *; Fe_3O_4 : ■; $\chi\text{-Fe}_{2.5}\text{C}$: ▼; Fe_3C : △; c- CeO_2 : □.

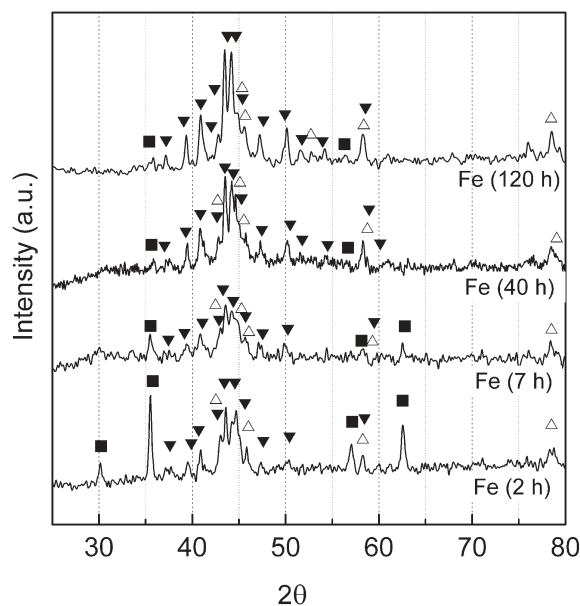


Fig. 6 XRD patterns of the Fe catalyst after different TOS. Fe_3O_4 : ■; $\chi\text{-Fe}_{2.5}\text{C}$: ▼; Fe_3C : △.

Furthermore, it pinpoints to the $\chi\text{-Fe}_{2.5}\text{C}$ phase as the actual Fischer–Tropsch active site, in agreement with Schulz *et al.*¹³ However, the picture for the promoted samples is somewhat different. In that case, the FT activity started to increase before the Fe_3C phase evolved to $\chi\text{-Fe}_{2.5}\text{C}$. It should be noted that $\chi\text{-Fe}_{2.5}\text{C}$ are detected as the major carbide species of the Fe–Ce catalysts. However, other characterization techniques were used due to the difficulty for unequivocal iron carbide phase assignments, since Fe_3C and $\chi\text{-Fe}_{2.5}\text{C}$ present some common diffraction lines and some uncertainty remains.

The Ce-containing and Ce-free catalysts were also studied by means of ^{57}Fe –Mössbauer spectroscopy. Fig. 7 and Fig. 8

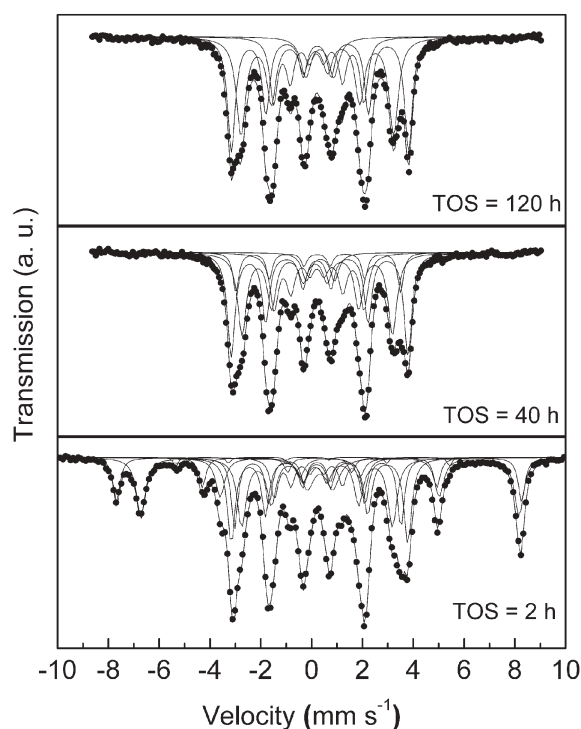


Fig. 7 Mössbauer spectra of the Fe catalyst after different TOS.

show, respectively, the spectra recorded at room temperature obtained for the Fe and FeCe–I catalysts after selected TOS values (2, 40 and 120 h).

All the spectra recorded from the Fe catalyst (Fig. 7) showed a complex pattern constituted by magnetic and paramagnetic

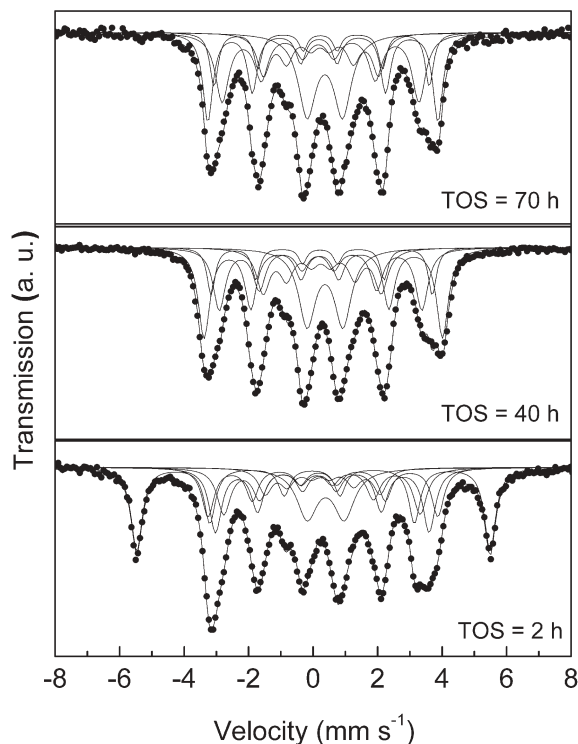


Fig. 8 Mössbauer spectra of the FeCe–I catalyst after different TOS.

components whose dominant magnetically split component presents an average hyperfine magnetic field range that is typical of iron carbides.^{22,23} The spectrum of the Fe catalyst recovered after 2 h of TOS exhibited, besides the mentioned carbide pattern, other peaks corresponding to magnetic sextets with fields higher than those of the carbides, and also a small peak, located at $v = -5.5 \text{ mm s}^{-1}$, which fitted to the first peak of the Fe^0 sextet. In principle, these peaks indicated that some oxidized Fe compounds and Fe^0 might be present in this sample. It is well established that some iron carbides yield Mössbauer spectra constituted by several sextets whose number and corresponding hyperfine magnetic fields and relative spectral areas have to be determined for accomplishing a reliable identification of the carbide phases. Thus, we proceeded with the difficult deconvolute-task by fitting up to a maximum of seven different sextets and a doublet. The spectrum recorded from the catalyst of long-lasting TOS (120 h) fitted satisfactorily to three sextets (labeled 1, 2 and 3) and a doublet D. Besides the doublet D and the sextets 1, 2, 3, a fourth sextet (labeled 4) had to be included to obtain a consistent fit of the TOS = 40 h spectrum. Finally, the adequate fitting of the spectrum corresponding to the shorter TOS (2 h) required the use of seven sextets (1–7) and a doublet. The resulting fitted spectra are shown in Fig. 7 and the Mössbauer parameters obtained from the fits are collected in Table 1. The parameters shown in Table 1 allowed us to assign the three sextets with labels 1, 2, 3 to the Hägg carbide ($\chi\text{-Fe}_{2.5}\text{C}$) and the sextet 4 to cementite (Fe_3C).^{22,23} The sextet labeled 5, whose spectral contribution to the TOS = 2 h spectrum is less than 2%, corresponded to Fe^0 , while the parameters obtained for sextets 6 and 7, present also in the TOS = 2 h spectrum, matched with those obtained for the Fe_3O_4 .²⁴ It is clear that the small amount of Fe^0 in the TOS = 2 h sample was, therefore, insignificant. Superparamagnetic or some amorphous ferric oxides²⁴ produce parameters similar to those obtained for the doublet D. A quadrupole doublet analogous to D was found as the dominant component in the spectrum of a $\text{Fe}_2\text{O}_3\text{--K}_2\text{O--SiO}_2\text{--CuO}$ catalyst after FT reaction. That doublet was attributed to a mixture of superparamagnetic particles of both magnetite and hematite phases.²⁵

The deconvolution of the spectra of the FeCe–I catalyst (Fig. 8) was carried out following the same procedure used in the case of the Fe catalyst. It is remarkable that the spectrum of the FeCe–I catalyst recovered after the shorter TOS (2 h) showed an important spectral contribution of a magnetic component with hyperfine splitting coincident with that of $\alpha\text{-Fe}$ (around 25% of the total area). Thus, the spectra corresponding to 40 and 120 h TOS were fitted to four sextets (1, 2, 3 and 4) and a doublet, whereas an additional fifth sextet (corresponding to Fe^0 , label 5) had to be included in the case of the sample recovered at 2 h of TOS. The obtained Mössbauer parameters are collected in Table 2. Similarly to the Fe-catalyst, the parameters allowed the assignment of the sextets 1, 2 and 3 to the Hägg carbide ($\chi\text{-Fe}_{2.5}\text{C}$), sextet 4 to cementite (Fe_3C).^{22,23} and sextet 5, which was only present in the TOS = 2 h spectrum, to Fe^0 . The important contribution of the Fe^0 sextet to the TOS = 2 h spectrum indicated a lower iron carburization rate for the FeCe–I catalyst, as compared with the Fe catalyst, which was almost fully carburized after 2 h on

Table 1 Mössbauer parameters obtained with the Fe catalyst after different TOS values^a

	Parameters	Fe, 2 h	Fe, 40 h	Fe, 120 h
Doublet (superparamagnetic Fe(III))	$\delta/\text{mm s}^{-1}$	0.34 (2)	0.35 (2)	0.32 (2)
	$\Delta/\text{mm s}^{-1}$	1.01 (3)	1.11 (3)	1.10 (2)
	$\Gamma/\text{mm s}^{-1}$	0.60 (6)	0.42 (5)	0.48 (3)
	$A_{\text{rel}} (\%)$	6.3	5.2	8.1
Sextet 1 ($\chi\text{-Fe}_{2.5}\text{C}$)	$\delta/\text{mm s}^{-1}$	0.18 (1)	0.18 (1)	0.19 (1)
	$2\epsilon/\text{mm s}^{-1}$	0.09 (1)	0.08 (1)	0.07 (1)
	H/T	18.4 (1)	18.4 (1)	18.6 (1)
	$\Gamma/\text{mm s}^{-1}$	0.42 (2)	0.42 (2)	0.44 (1)
Sextet 2 ($\chi\text{-Fe}_{2.5}\text{C}$)	$\delta/\text{mm s}^{-1}$	0.26 (1)	0.26 (1)	0.27 (1)
	$2\epsilon/\text{mm s}^{-1}$	0.12 (1)	0.11 (1)	0.10 (1)
	H/T	21.5 (1)	21.6 (1)	21.6 (1)
	$\Gamma/\text{mm s}^{-1}$	0.36 (1)	0.36 (1)	0.36 (1)
Sextet 3 ($\chi\text{-Fe}_{2.5}\text{C}$)	$\delta/\text{mm s}^{-1}$	0.25 (1)	0.25 (1)	0.24 (1)
	$2\epsilon/\text{mm s}^{-1}$	0.08 (1)	0.08 (1)	0.10 (1)
	H/T	10.8 (1)	10.8 (1)	11.0 (1)
	$\Gamma/\text{mm s}^{-1}$	0.34 (1)	0.34 (1)	0.38 (1)
Sextet 4 (Fe_3C)	$\delta/\text{mm s}^{-1}$	0.23 (1)	0.25 (1)	
	$2\epsilon/\text{mm s}^{-1}$	0.02 (1)	0.04 (1)	
	H/T	20.3	20.1	
	$\Gamma/\text{mm s}^{-1}$	0.32 (1)	0.28 (1)	
Sextet 5 (Fe^0)	$\delta/\text{mm s}^{-1}$	15.4	10.0	
	$2\epsilon/\text{mm s}^{-1}$	-0.06 (2)		
	H/T	33.4 (1)		
	$\Gamma/\text{mm s}^{-1}$	0.42 (2)		
Sextet 6 (Fe(III) ; Fe_3O_4)	$\delta/\text{mm s}^{-1}$	1.3		
	$2\epsilon/\text{mm s}^{-1}$	0.31 (1)		
	H/T	49.4 (1)		
	$\Gamma/\text{mm s}^{-1}$	0.32 (1)		
Sextet 7 (Fe(II/III) ; Fe_3O_4)	$\delta/\text{mm s}^{-1}$	9.7		
	$2\epsilon/\text{mm s}^{-1}$	0.71 (1)		
	H/T	0.01 (1)		
	$\Gamma/\text{mm s}^{-1}$	46.1 (1)		
	$A_{\text{rel}} (\%)$	0.42 (2)		
	$A_{\text{rel}} (\%)$	17.1		

^a δ : isomer shift (relative to $\alpha\text{-Fe}$); Δ : quadrupole splitting; 2ϵ : quadrupole shift; Γ : full linewidth at half maximum; H : hyperfine magnetic field; A_{rel} : relative spectral area. Numbers in parentheses provide the uncertainty in the last digit.

stream. The parameters of the doublet D, which was present in all the FeCe-I catalyst spectra, were similar to those obtained in the case of the Fe catalyst. Therefore, it was also suggested to be the result of a mixture of superparamagnetic particles of both magnetite and hematite phases.²⁵

In summary, the Mössbauer results were in good agreement with the XRD results. Both techniques indicated a lower iron carburization rate of the Ce-loaded catalyst in comparison to the Ce-free one. This observation justifies the lower catalytic activity of the FeCe-I and FeCe-IC catalysts during the first episodes of the reaction, as expected from the existing correlation between the iron carbide content and the FT activity of the catalyst.^{10–13} According to the Mössbauer results, a mixture of $\chi\text{-Fe}_{2.5}\text{C}$ and Fe_3C phases was developed in the Fe catalyst. The contribution of $\chi\text{-Fe}_{2.5}\text{C}$ increased in detriment of Fe_3C as the reaction proceeded. Finally, the Hägg carbide was the only iron carbide phase observed. This evolution of the carbide phases, also observed by XRD, could be responsible for the enhancement of the catalytic activity of the Fe catalyst after 40 h of reaction. In the case of Ce-loaded

Table 2 Mössbauer parameters obtained with the FeCe-I catalyst after different TOS values^a

	Parameters	FeCe-I, 2 h	FeCe-I, 40 h	FeCe-I, 120 h
Doublet (superparamagnetic Fe(III))	$\delta/\text{mm s}^{-1}$	0.39 (2)	0.36 (1)	0.37 (1)
	$\Delta/\text{mm s}^{-1}$	1.15 (3)	1.11 (3)	1.11 (2)
	$\Gamma/\text{mm s}^{-1}$	0.76 (6)	0.64 (4)	0.62 (3)
	$A_{\text{rel}} (\%)$	13.3	20.4	18.9
Sextet 1 ($\chi\text{-Fe}_{2.5}\text{C}$)	$\delta/\text{mm s}^{-1}$	0.19	0.19 (2)	0.19 (1)
	$2\epsilon/\text{mm s}^{-1}$	0.16 (2)	0.07 (2)	0.08 (1)
	H/T	18.9 (2)	18.9 (1)	19.5 (1)
	$\Gamma/\text{mm s}^{-1}$	0.50	0.50 (4)	0.45 (2)
Sextet 2 ($\chi\text{-Fe}_{2.5}\text{C}$)	$\delta/\text{mm s}^{-1}$	16.3	26.5	22.3
	$2\epsilon/\text{mm s}^{-1}$	0.24 (1)	0.24 (1)	0.26 (1)
	H/T	0.12 (2)	0.12 (1)	0.10 (1)
	$\Gamma/\text{mm s}^{-1}$	22.1 (2)	22.1 (1)	22.9 (1)
Sextet 3 ($\chi\text{-Fe}_{2.5}\text{C}$)	$\delta/\text{mm s}^{-1}$	0.45 (3)	0.36 (1)	0.44 (1)
	$2\epsilon/\text{mm s}^{-1}$	15.6	25.3	30.6
	H/T	0.26	0.23 (1)	0.26 (1)
	$\Gamma/\text{mm s}^{-1}$	0.07 (4)	0.03 (1)	0.04 (1)
Sextet 4 (Fe_3C)	$\delta/\text{mm s}^{-1}$	11.0 (3)	11.1 (1)	11.3 (1)
	$2\epsilon/\text{mm s}^{-1}$	0.50	0.46 (5)	0.50 (1)
	H/T	9.0	15.1	16.9
	$\Gamma/\text{mm s}^{-1}$	0.24 (1)	0.24 (1)	0.24
Sextet 5 (Fe^0)	$\delta/\text{mm s}^{-1}$	0.09 (2)	0.04 (1)	0.05 (1)
	$2\epsilon/\text{mm s}^{-1}$	20.6 (2)	20.7 (1)	21.3 (1)
	H/T	0.46 (6)	0.30 (1)	0.30 (1)
	$\Gamma/\text{mm s}^{-1}$	21.0	12.7	11.3
	$A_{\text{rel}} (\%)$	-0.01 (1)		
	$\delta/\text{mm s}^{-1}$	0.04 (1)		
	H/T	34.0 (1)		
	$\Gamma/\text{mm s}^{-1}$	0.42 (1)		
	$A_{\text{rel}} (\%)$	24.7		

^a δ : isomer shift (relative to $\alpha\text{-Fe}$); Δ : quadrupole splitting; 2ϵ : quadrupole shift; Γ : full linewidth at half maximum; H : hyperfine magnetic field; A_{rel} : relative spectral area. Numbers in parentheses provide the uncertainty in the last digit.

samples, both iron carbides ($\chi\text{-Fe}_{2.5}\text{C}$ and Fe_3C) were always detected. The presence of Ce resulted in an increase of the catalytic activity only when the sample was fully carburized.

The Ce-loaded and Ce-free iron catalysts were also characterized by TPH. Fig. 9 shows the evolution of selected fragments $m/z = 16$ (CH_4) and 28 (C_2H_4 , C_2H_6 and CO) with

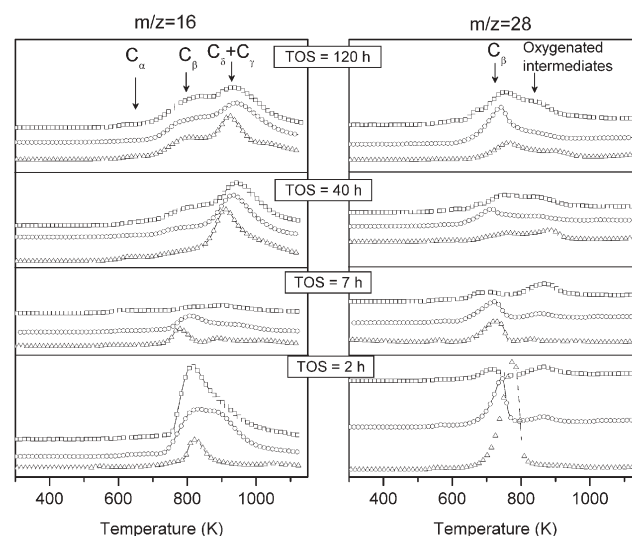


Fig. 9 TPH patterns after different TOS. Fe: Δ ; FeCe-I: $\square$; FeCe-IC: $\circ$.

temperature. The TPH experiments led to complex profiles with several peaks. The assignment of those peaks to the corresponding surface species was based on the previous work from Bartholomew *et al.*^{16,17} and Herranz *et al.*¹⁸ The following species were observed: C_α (atomic carbon), C_β , (polymerized methylene), C_γ (Fe carbides) and C_δ (graphitic species). The fragment $m/z = 28$ was ascribed to both CO-containing species and other hydrocarbons (like ethane and ethylene), which were formed from the species named C_β . The discrimination between those hydrocarbons and CO-containing species was accomplished by analyzing the fragments $m/z = 26, 27$ and 30 (results not shown). Thus, the fragment $m/z = 28$ at *ca.* 700 K was assigned to C_β , whereas the fragment $m/z = 28$ at *ca.* 900 K was ascribed to CO-containing species. A straight correlation between the amount of C_β species and the FT activity could be observed after 7 h on stream. However, such correlation was not straightforward during the initial stages of the reaction (TOS = 2 h). In spite of the higher content of carbonaceous species observed in the samples FeCe-I and FeCe-IC, these catalysts were less active than the Fe solid. It must be recalled that the Ce-loaded catalysts were not completely carburized after 2 h on stream. According to the “competition model” proposed by Niemantsverdriet *et al.*,²² the carbonaceous species diffuse preferably into the Fe^0 structure before rendering FT products. Instead, a good correlation between the FT activity and the peak intensity of CO-containing species (observed in Fig. 9 between 800 and 900 K) was found during the initial episodes of the reaction (TOS = 2 h). These species would form from oxygen-containing carbonaceous species. Nevertheless, such oxygen containing species could have also been formed during the passivation process.

As it was indicated above (Fig. 2), the CO conversion rate to hydrocarbons decreased continuously during the first stages of the reaction for all the catalysts. But at a certain point, which depended on the catalyst nature, the activity increased. We observed that the Ce-loaded iron catalysts showed a shorter induction process. As it was discussed previously, the FeCe-I and FeCe-IC catalysts were not completely carburized during the first stages of the reaction. According to the “competition model” suggested by Niemantsverdriet *et al.*,²² these catalysts were less active in the FT synthesis because the carbon atoms were consumed in order to carburize the metallic Fe species, instead of producing hydrocarbons.

However, it is important to remark that the concentration of graphitic deposits in all catalysts increased between 7 and 40 h on stream. From this point, the formation of these species reached a steady-state. Along with the formation of graphitic deposits, a decrease of the BET surface area values and a loss of the mesoporous structure were also detected (see Fig. 1). These events could also be responsible for the initial decreasing activity. The Fe catalyst was already totally carburized after 2 h on stream. Therefore, the decreasing activity observed with this sample during the first stages of the reaction should be related to the formation of graphitic deposits, which could be deposited over the active sites, as it has been described by other authors.²² In the case of the FeCe-I and FeCe-IC samples, the catalytic activity increased after 7 and 20 h on stream, respectively, while the graphitic deposits were still

forming. Consequently, it seems that the catalytic activity of the Ce-loaded catalysts increased when the solids were totally carburized, independently of the formation of graphitic deposits.

As it was pointed out above, a direct correlation between the concentration of C_β species (polymerized carbon) on the catalyst surface and the catalytic activity of all the samples for TOS values higher than 7 h was found. In addition, the increase of the concentration of this type of species was parallel with the increase of the surface area of the solids. In the case of the Ce-free iron sample, the increase of the catalytic activity was also accompanied by an increase of the concentration of $\chi\text{-Fe}_{2.5}\text{C}$ species and by a decrease of the Fe_3C concentration. According to the XRD and Mössbauer spectroscopy results, this evolution was observed continuously during the reaction. Finally, the Fe_3C phase could not be detected after 120 h on stream. The Ce-free iron catalyst underwent the increase of the catalytic activity after 40 h on stream, which coincides with the total transformation of the Fe_3C phase into $\chi\text{-Fe}_{2.5}\text{C}$ and with the stabilization of the graphitic deposits concentration on the surface. In summary, a good correlation between $\chi\text{-Fe}_{2.5}\text{C}$ and FT activity was found for the Ce-free iron catalyst. Therefore, we suggest the Hägg carbide as the active phase in FTS.

In the case of the Ce-loaded iron catalysts, we also observed the transformation of Fe_3C species into $\chi\text{-Fe}_{2.5}\text{C}$, although in this case the Fe_3C species did not evolve totally, as is indicated by the fact that they were observed after 120 h on stream. Considering that the Fe–Ce catalysts displayed a shorter induction process, Ce addition would be responsible for the formation of C_β species, independently of the graphitic deposits formation. The effect of Ce addition could also be related to the increase of the surface area. Despite the fact that the Fe_3C did not evolve totally into $\chi\text{-Fe}_{2.5}\text{C}$ in the case of the Ce-loaded iron catalysts, Ce addition originated a higher number of active sites, and consequently, the effect of graphitic deposits is less significant in absolute terms. Also, it is important to remark that we have observed in previous work⁷ the presence of Ce(III) species by XPS after reductive treatments. It has been proposed that the presence of these species may result in the formation of the so-called tilted CO adsorption mode, in which the CO molecules are attached to iron atoms by its carbon atom and to the Ce cations by its oxygen atom. This tilted adsorption mode is only possible when Ce is present as Ce(III) cations. Consequently, the CO dissociation rate is increased because the C–O bond is weakened in the CO tilted configuration^{26,27} and because the Ce(III) cations can rapidly capture the oxygen atom from CO by the fast oxidation to Ce(IV). This produces more active catalytic sites and could explain the higher CO conversion values observed with the Ce-loaded iron catalysts when compared to the Ce-free one, even without the complete evolution of Fe_3C species into $\chi\text{-Fe}_{2.5}\text{C}$ species, which are proposed to be the active phase.

Conclusions

On the basis of the results presented in this contribution, the following conclusions can be drawn: (i), the nature of the

surface species and bulk composition of both Ce-loaded and Ce-free iron catalysts is dynamic and depends on the time-on-stream; (ii), several iron phases, including iron oxides, metallic iron and different iron carbides, are observed initially. The catalytic activity is determined not only by the relative proportion of these species, but also by the catalyst surface area; (iii), the Hägg carbide species (χ -Fe_{2.5}C) seems to be the most active iron phase. There is also correlation between the catalytic activity and the presence of C_β species on the catalyst surface; and (iv), the addition of Ce to iron oxide FT catalysts increases the catalytic activity in terms of a faster activation and a higher catalytic activity level in the steady-state.

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Electrocatalytic conversion of CO₂ to long carbon-chain hydrocarbons†

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It is shown for the first time that using Pt nanoparticles on carbon-based electrodes it is possible to convert CO₂ to long carbon-chain hydrocarbons (>C₅) at room temperature and atmospheric pressure in a continuous flow cell having the working electrode directly in contact with the CO₂ in the gas phase. The performances and product distribution depend on the nature of the electrocatalyst and the reaction conditions. It is also shown that product distribution is different from that expected from Anderson–Schultz–Flory distribution for Fischer–Tropsch synthesis. This step integrates in a photoelectrochemical device to ultimately use solar energy and water to convert back CO₂ to fuels. The possibility of the use of this device for Mars missions is also mentioned.

The growing consensus that fossil-fuel use is causing climate change and the recent effort to formulate international treaties to limit greenhouse-gas emissions lend urgency to find solutions to close the carbon cycle and stabilize the CO₂ emissions. Different CO₂ mitigation technologies and strategies have been proposed to reduce the emissions, such as recovery/disposal of CO₂, bioconversion, thermochemical dissociation or chemical use, but there is still the need to find new solutions.¹

CO₂ use as feedstock for producing chemicals is a relevant part of carbon management,^{2,3} even if the possible market is significantly lower than the amount of CO₂ emitted, because it represents a way for its recycling and reuse. The possibility of converting CO₂ back to fuels using solar energy, on the contrary, has a greater potential because it provides a pathway to harvest solar energy and convert it to a form such as liquid hydrocarbons which can be exploited in the existing infrastructure for energy use and distribution. With respect to photosynthesis and the use of biomass for biofuels, the conversion of CO₂ to liquid fuels has the advantage of potential higher efficiency in the conversion of energy (typically significantly lower than 1% in photosynthesis). In comparison to H₂ production by water splitting or to the photovoltaic solar to electrical energy transformation, the conversion of CO₂ to liquid fuels allows easier storage and transport.

There is thus a relevant interest in the possibility of converting CO₂ to liquid fuels in the absence of sacrificial reagents.⁴ The photocatalytic reduction of CO₂ in aqueous slurries containing semiconductor powders such as SiC, GaP, CdS, ZnO, TiO₂, or WO₃ was first reported in 1979 by

Inoue *et al.*⁵ The products were formic acid, formaldehyde, methyl alcohol and methane. The quantum yields for the production of HCHO and methanol were estimated to be less than 10^{−3} using a TiO₂ catalyst. Later, many research groups have studied the photoreduction of CO₂. Products containing two carbon atoms such as ethyl alcohol and ethylene or ethane were also observed, but in a low amount,⁶ using some semiconductor materials. Also more recent results, using Ti-containing nanoporous catalysts for example,⁷ showed that a mixture of C₁ products is mainly produced.

An improvement is expected by physically separating the stages of oxidation and reduction, *e.g.* realizing a photoelectrochemical device instead of the direct photoreduction of CO₂. In fact, the photoreduction of CO₂ is competing with H₂ and H₂O₂ formation, which consumes H⁺ and e[−], while the indirect route allows these side reactions to be minimized better.

Taniguchi⁸ first reviewed the electrochemical and photoelectrochemical reduction of carbon dioxide. Recent reviews are those by Hori⁹ on the CO₂ electroreduction at metal electrodes and by Gattrell *et al.*¹⁰ on the aqueous electrochemical reduction of CO₂ to hydrocarbons at copper surfaces. Among the different metals studied, only copper showed significant formation of hydrocarbons.

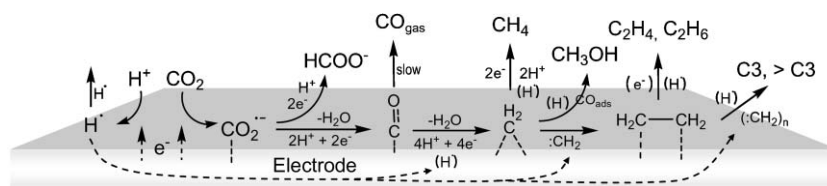
The reduction of CO₂ to hydrocarbons is a complex multi-step reaction involving shared intermediates and multiple reaction pathways.^{9–11} The initial step is the reduction of CO₂ by one electron to form the carbon dioxide anion radical (‘CO₂[−]’) which may evolve into the formate anion or by further reduction to chemisorbed CO (Scheme 1). The latter could desorb or be further reduced by four electrons in the presence of protons to give an adsorbed :CH₂ species. The surface methylene group (:CH₂) by reaction with two further electrons and protons gives CH₄ or by reaction with another :CH₂ species forms ethylene, *via* the intermediate formation of surface species such as di-σ-ethylene (or possibly ethylidyne or ethylidene species).

Alternative pathways of transformation in the carbene mechanism proposed for the electrochemical reduction of carbon dioxide are summarized in Scheme 1. The CO₂ activation step involves a reaction between a carbon dioxide anion

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Scheme 1 Simplified reaction network at the surface of electrode in the reduction of CO₂ to hydrocarbons.

radical and another CO₂ molecule to form an intermediate which upon reduction gives adsorbed CO and a carbonate anion. For the CO activation, the first oxygen abstraction may occur by either protonation of the oxygen or directly from the metal electrode forming a carbide species which is then hydrogenated to a carbyne or methylene species. For carbon chain growth, the first step may be the coupling of two adsorbed CO molecules followed then by the abstraction of the two oxygen molecules and hydrogen insertion into the carbon atoms.

Although conclusive evidence about the reaction mechanism in CO₂ electrochemical reaction is still not available, the simplified reaction network shown in Scheme 1 indicates how the reaction is highly sensitive to the electrode surface structure, local conditions such as pH and CO₂ concentration and temperature. The product distribution depends on the applied potential. At potentials less negative than about -1.0 V, CO and formate anion are the main products, while a potential more negative than -1.4 V is required to enhance the formation of CH₄ and C₂H₄. Note that the suggested reaction mechanism in the liquid phase electrocatalytic reduction of CO₂ (summarized in Scheme 1) resembles that of the Fischer–Tropsch (FT) reaction, at least in terms of the main characterizing surface reaction intermediates leading to C–C bond formation.

The main limitations in the electrochemical approach used up to now are the need to use (i) non-aqueous solvents (low-polarity) to increase CO₂ solubility and improve adsorption on the surface of CO₂^{•−} anion radicals, and (ii) corrosive media, high pressure, and metal halides. In fact, LiCl or equivalent salts are needed to enhance the adsorption of the carbon dioxide anion radical. A fast deactivation has been also reported.¹¹

A maximum faradaic efficiency for hydrocarbons (methane and ethylene) of about 10% (at polarization above -3.0 V) with the formation of HCOOH, and CO as the major products was observed¹² using the following reaction conditions: a copper electrode, LiCl/methanol as electrolyte, a pressure of 10 atm and a reaction temperature of 50 °C. Using a glassy carbon electrode and a pressure of 30 atm, the maximum faradaic efficiency for HC products was lower than 3%, but methane, ethane, ethylene, propane and n-butane were observed with a product distribution following the Schultz–Flory distribution such as in the Fischer–Tropsch synthesis.¹²

Ougitani *et al.*¹³ studying the probability of chain growth for hydrocarbon formation by electrochemical reduction of CO₂ on Fe and Ni electrodes suggested that the probability of chain growth increases with increasing temperature, but this contrasts with the productivity, because increasing the reaction temperature decreases the solubility of CO₂ in solution.

Therefore, to convert CO₂ electrocatalytically to long carbon-chain hydrocarbons (>C₅) it is necessary to use a different approach. We earlier proposed for this reaction of CO₂ conversion to higher hydrocarbons our interest in using a photoelectrocatalytic (PEC) reactor,¹⁴ which is schematically shown in Fig. 1. The PEC concept was originally proposed by “Hitachi Green Center” researchers.¹⁵

On the cathode side a photocatalyst (nanostructured titania) photodissociates water to produce protons and electrons which are used on the anode side of a membrane (on the electrocatalyst) to reduce CO₂ to hydrocarbons. The membrane is a proton-conductive membrane such as Nafion® 117. The net reaction is thus the conversion of combustion products to fuels/chemicals using solar energy. Furthermore, the pure oxygen produced on the photocatalytic side can be used to improve the efficiency of the combustion or can be used in other chemical processes.

The construction, characteristics and materials (apart the photocatalytic side) of the PEC reactor are those of PEM fuel cells. This will allow an easier scale up taking also advantage of all developments in fuel cells, especially in terms of engineering and cost.

There is no solvent on the anode side and therefore there is no need to recover the products from a liquid phase (a main problem in the conventional CO₂ photo- and electro-reduction), and there are no problems of solubility of CO₂. Instead, using electrodes based on nanostructured carbon it is possible to use the confinement effect¹⁶ inside the nanopores to create a virtual higher pressure of the reactant (CO₂) at the electrocatalyst surface and thus favour the chain growth. The use of nanostructured carbon would also favour a high mobility of hydrogen radicals that are important in the reaction mechanism (Scheme 1). These were the conceptual bases for an European funded project (ELCAT, Electrocatalytic Gas-Phase Conversion of CO₂ in Confined Catalysts, part of the

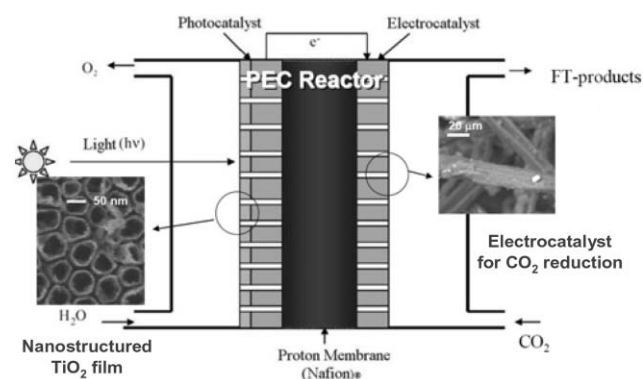


Fig. 1 Schematic cartoon of the photoelectrocatalytic (PEC) reactor.

EU programme NEST-ADVENTURE), some of which key results will be reported here.

We will show here for the first time how using catalysts based on metal particles supported on nanostructured carbon and a gas phase electroreduction it is possible to form long C-chain ($>C_5$) hydrocarbons from CO_2 , a discovery which opens interesting perspectives on using solar energy to close the cycle converting back CO_2 to liquid fuels. In fact, these results open the possibility of realizing a new gas-to-liquid process that starts directly from CO_2 . A side application may also include the possibility to generate fuels on Mars. With respect to earlier preliminary results¹⁴ obtained in a batch type reactor, the results reported in this work were obtained in a continuous flow electrocatalytic reactor simulating the anode part of the PEC reactor schematically shown in Fig. 1. However, for the sake of comparison some results using also a batch-type reactor are reported.

Experimental

Preparation of the working electrodes

The electrodes were prepared by depositing Pt nanoparticles on carbon black (Vulcan XC-72) and/or carbon cloth and then assembling the electrode by hot-pressing on a Nafion membrane. The noble metal loading is about 0.4 and 0.6 mg cm^{-2} . For reference, a commercial Pt/GDM (supplied from E-TEK) sample was also used. The latter electrode will be indicated hereinafter as Pt/GDM_{com}, where GDM indicates gas diffusion membrane and the suffix *com* that it is a commercial sample. The first two electrode will be indicated as Pt_{nano}/GDM and Pt_{nano}-C/GDM to indicate Pt nanoparticles deposited directly on a carbon cloth GDM or first on carbon black and then on the carbon cloth GDM, respectively. The Pt active phase (about 20% weight with respect to GDE) is located between the gas diffusion layer (GDE) at the direct contact with CO_2 in the gas phase and the Nafion[®] membrane layer.

Pt_{nano}/GDM is obtained by an *in-situ* reduction of the precursor (H_2PtCl_4) by bubbling H_2 through an ethanolic solution of bathophenanthroline disulfonic acid disodium salt.

Pt_{nano}-C/GDM is synthesized by a methanolic reduction. A solution of the surfactant SB12 (2.1 g) ((dodecyldimethyl 3-sulfopropyl) ammonium hydroxide) in 12 mL of methanol–water (volumetric ratio 1 : 3), is mixed with a platinum solution, (250 mg) in 12 mL of methanol–water (volumetric ratio 1 : 3). Then 600 mg of carbon black (Vulcan XC-72) are added. The resulting suspension is stirred and refluxed at 90°C for 1 h. The solid is recovered by centrifugation at 1800 rpm for 10 min, and dried overnight at 70°C . In both cases, the crude solid is then crushed, suspended in 2 mL of ethanol and sonicated for 10 minutes. After the sonication, the suspension is put onto carbon cloth GDM (E-TEK), and the solvent is allowed to evaporate at room temperature.

The electrodes are assembled by hot-pressing of the as-synthesized catalysts with a Nafion membrane, at 80 atm and 135°C for 90 s. For all these samples, the Pt loading is 20% by weight, which corresponds to a surface concentration of between 0.4 and 0.6 mg cm^{-2} .

The samples were characterized by XRD (X-ray diffraction), SEM (scanning electron microscopy) and TEM (transmission electron microscopy). The mean diameter of the Pt particles in Pt_{nano}/GDM was found to be 3.0 nm, while that of Pt_{nano}-C/GDM was 5.4 nm. However, the latter sample showed fewer aggregates of Pt particles, *i.e.* a better dispersion of the metal particles on the carbon substrate. In the case of Pt/GDM_{com} the mean diameter of the metal particles was 2.0 nm.

Electrocatalytic tests of CO_2 reduction

The catalytic tests were carried out in three type of electrocatalytic reactors (Fig. 2). The first (Fig. 2a) is a semi-half discontinuous cell. One side of the Nafion[®] membrane is in contact with a liquid acid electrolyte, where the other side (the working electrode, where the Pt/GDM layer is present) operates in contact with a gas phase containing high purity (99%) CO_2 . The geometrical area of the electrode in contact with the gas phase was *ca.* 1 cm^2 .

In the discontinuous mode, after first fluxing the cell for 30 min with a CO_2 flow, the cell is closed and then the potential starts is applied. In the semi-half continuous mode (Fig. 2c), the design is analogous to the former, but in the

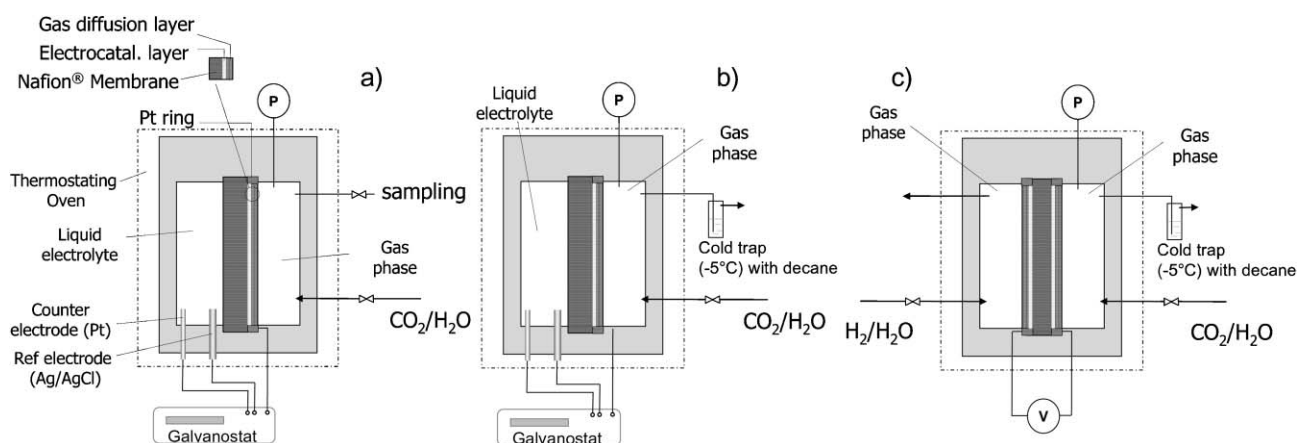


Fig. 2 Scheme of the three types of electrocatalytic cells used in the experiments (see text): a) semi-half discontinuous cell, b) full continuous cell, and c) semi-half continuous cell

presence of a continuous flux of CO₂ through the cell. The products of reaction are trapped in purified decane maintained at -5°C , while in the former case, they were sampled directly from the gas phase. The volume of the liquid side of the electrocatalytic cell is about 10 ml, while that of the gas phase side about 3 ml. The liquid side contains as electrolyte a purified 0.5 M solution of potassium bicarbonate in distilled water. This solution is used as source of H⁺ ions for the CO₂ reduction (they diffuse to the catalyst through the Nafion[®] membrane). The counter electrode (platinum wire) and the reference electrode (saturated Ag/AgCl electrode) are located in this part of the electrocatalytic reactor.

The full continuous mode electrocatalytic reactor (Fig. 2b) has both sides in contact with the gas phase, but one containing CO₂ and the other side containing H₂. The fluxes are saturated with water vapour at room temperature to preserve H⁺ conduction of the Nafion[®] membrane, because this depends considerably on its degree of humidity. Differently from the former two cases, both sides of the Nafion[®] membrane have the Pt/GDM electrocatalytic layer. A Pt ring allows the electric connection between the wires (connected to the controlling potentiostat/galvanostat—Amel mod. 2049) and the Pt/GDM to be maintained in all the reactor configurations.

Fig. 2 shows a scheme of three type of electrocatalytic cells, while Table 1 summarizes some of the parameters of the operations. Experiments are conducted galvanostatically. Typical reaction conditions, if not otherwise indicated, were the following: flow of CO₂ = 20 cm³ min⁻¹, [KHCO₃] = 0.5 M, applied current 20 mA, room temperature (22 °C), atmospheric pressure, geometrical dimension of the electrode 1 cm². Analysis of the products was made by a gas-chromatograph (GC) equipped with a FID detector and a gas-mass GC (MS-GC) apparatus.

Blank initial experiments were made to check whether in the absence of the electrocatalyst layer, of CO₂ in the gas phase or of a voltage applied across the cell, the products of reaction were detected. A negative response was obtained in all cases.

Results and discussion

Formation of long carbon chain hydrocarbons and the role of the reaction cell configuration

Reported in Fig. 3 are the results obtained for the electrocatalytic reduction of CO₂ as a function of time of reaction in the semi-half discontinuous cell using Pt/GDM_{com} as working electrode. Initially, methane is the main product of reaction,

Table 1 Reaction conditions used in the three reactor modes shown in Fig. 2

	Type of reactor (Fig. 2)		
	a	b	c
Liquid phase side	KHCO ₃ aq. 0.5 M	KHCO ₃ aq. 0.5 M	(^a)
Gas Phase side	CO ₂ -He (1 : 1)	CO ₂ + 4% H ₂ O	CO ₂
Pressure, bar	1.6	1.0	1.0
Temperature, °C	22	22	22

^a No liquid phase, gas phase H₂ + 4% H₂O

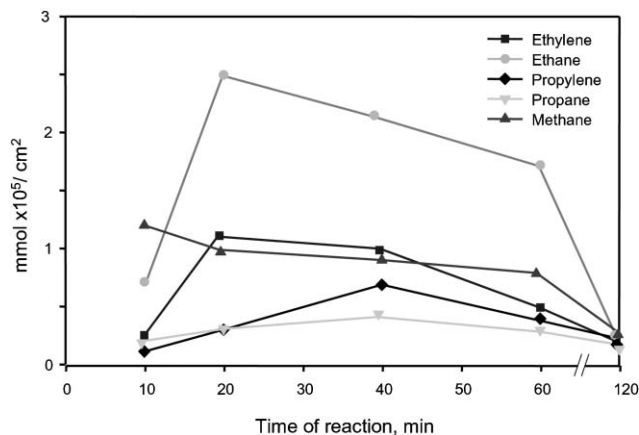


Fig. 3 Electrocatalytic reduction of CO₂ using Pt/GDM_{com} as working electrode and the semi-half discontinuous cell as reactor.

but its amount progressively decreases on increase of the time of reaction, indicating its further conversion (batch-type reactor). After 20 min, the main products observed are C2 hydrocarbons (ethane and in minor amount ethylene), but for longer times of reaction their amount also decreases. The formation of C3 hydrocarbons reaches a maximum after about 40 min of reaction and then decreases. In addition to these products, minor amounts of ethanol are also observed.

These results show that under the electrocatalytic conditions, differently from Fisher–Tropsch reaction, the desorption–readsorption and further conversion of higher C-atom number hydrocarbons may occur. The formation of alcohols occurs, but is of minor importance. Alkanes are mainly formed, but alkenes also are formed in significant amount. The lowering of the amount of all products for the longer times of reaction is mainly due to their further conversion to heavier products that remain adsorbed on the electrocatalyst.

By inverting the polarity of the electrode, in fact, desorption of significant amounts of hydrocarbons was observed. Part of the products remaining on the electrocatalyst during reaction could also be recovered by washing the electrode after reaction with an organic solvent, but the recovery was not quantitative. Due to this fact, it is not possible to determine the faradaic efficiency of the process, because the amount of products remaining adsorbed on the working electrode cannot be quantified.

CO was also detected in the gas phase in significant amounts (in an amount about $10^3 \times$ higher with respect to hydrocarbons). H₂ formation was not detected, but the limit of sensibility of the apparatus used (GC-TDC) was not very high.

Hydrocarbons having a carbon chain up to three carbon atoms were detected using the semi-half discontinuous cell for the electrocatalytic tests of CO₂ reduction. Hydrocarbons with longer carbon-atom chain were instead observed using the two continuous cell modes (full continuous cell and semi-half continuous cell) (Fig. 4). Due to the use of a trap based on cold decane (-5°C) to recover the reaction products (see Fig. 2), hydrocarbons having a maximum carbon-chain of nine carbon atoms were detectable. Possibly also heavier hydrocarbons were formed, even if it should be considered that probably they mainly remain adsorbed on the electrocatalyst, because all the

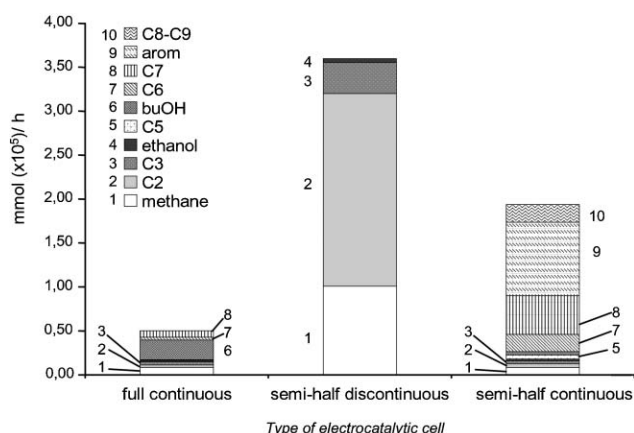


Fig. 4 Effect of the type of electrocatalytic cell on the amount of products formed in 1 h using Pt/GDM_{com} as working electrode.

system operates at room temperature. As noted above, tests either inverting the polarity of the electrode or washing the working electrode with an organic solvent at the end of the experiments showed the presence of large amounts of reaction products (heavy hydrocarbons) remaining adsorbed on the electrode. However, the recovery was not complete making thus impossible to estimate the faradaic efficiency of the process.

As far as we know, this is the first report of the possibility of forming long carbon-chain hydrocarbons (>C₅) by the electrocatalytic reduction of CO₂. This result opens new perspectives in gas-to-liquid conversion: for example, using a similar approach to convert methane to liquid hydrocarbons without passing through syn gas), and in the conversion of CO₂ back to fuels. In fact, in contrast to all the previous observations, easy to store liquid hydrocarbons could be produced, a significant step forward. This result derives from two main differences with respect to previous results on the electrochemical reduction of CO₂: the use of gas phase instead of liquid phase, and the use of a working electrode based on nanostructured carbon instead of metallic planar-type electrode.

Productivity was lower in the continuous operation with respect to the discontinuous (batch-type) operations (Fig. 4). Note that in the discontinuous apparatus the sampling of the products of reaction was made with a gas syringe, while in the continuous cells the products were collected in cold decane and then analyzed (see Fig. 2).

In the semi-half continuous cell, the main products of reaction detected were hydrocarbons with a carbon-chain higher than five C atoms. Alkyl-substituted aromatics (toluene and xylenes, in particular) were also detected as main products of reaction. Alcohols (ethanol and butanol mainly) were instead detected in small amounts. Using the full continuous configuration, the productivity was about one third. In addition, the product distribution was different, with formation mainly of n-butanol in this case. However, also in this case hydrocarbons up to seven carbon atoms in the chain were observed. This evidences that protons may be also produced by H₂ reduction, but the process is probably less efficient than supplying H⁺ directly using a liquid electrolyte. It may be

noted, however, that SEM-EDX mapping of the working electrode revealed that the K⁺ ions of the liquid electrolyte (see Table 1) crossed the Nafion[®] membrane, being present in significant amounts on the catalyst layer of the working electrode, in the case of semi-half continuous cell.

As noted in the introduction, the use of LiCl/methanol as electrolyte was necessary to increase the effectiveness in the electroreduction of CO₂ in liquid phase. Li⁺ ions probably are necessary to enhance the surface adsorption of CO₂ and/or the surface concentration of the intermediate carbon dioxide anion radical. Very reasonably, the K⁺ ions have a similar effect and for this reason, productivity of the semi-half continuous cell is higher than that of the full continuous cell. The higher flux of H⁺ in the semi-half mode also explains why alcohols are found in very low amounts in contrast with the full continuous cell case. It should also be noted that the semi-half discontinuous cell operates at slightly higher pressure than the semi-half continuous cell (Table 1), and possibly, for this reason, the crossover of K⁺ ions from the liquid to the gas side of the membrane was higher, as noted by SEM-EDX mapping. Higher productivity of the semi-half discontinuous cell with respect to the semi-half continuous cell (Fig. 4) is probably related to this effect, although further studies are necessary for a better understanding.

Role of the nature of the working electrode and of the reaction conditions

Reported in Fig. 5 are the results of the comparison of the performances of three working electrodes based on Pt particles supported on carbon using the semi-half continuous cell.

Pt/GDE_{com} is a reference sample, *e.g.* a commercial electrode from E-TEK for PEM (polymer-electrolyte membrane) fuel cells. As shown in Fig. 1 and discussed before, the PEC reactor has several characteristics analogous to PEM fuel cells. Pt_{nano}/GDE and Pt_{nano}-C/GDE are two electrodes prepared by *in-situ* reduction of H₂PtCl₄ (in an organic solvent and in the presence of surfactants) on commercial carbon-cloth (GDE, from E-TEK) or of carbon-black (Vulcan XC-72) deposited then on the carbon-cloth.

Both Pt_{nano}/GDE samples show better performances (both in terms of productivity and formation of >C₅ hydrocarbons) than the reference sample (Pt/GDE_{com}), even if the latter has

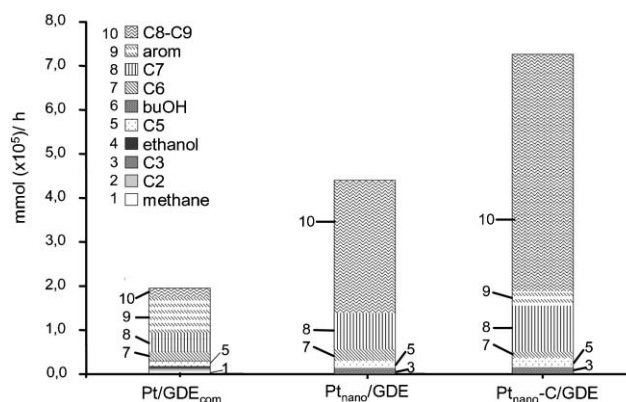


Fig. 5 Effect of the nature of the working electrode on the amount of products formed in 1 h in a semi-half continuous cell.

smaller sized Pt particles (see experimental). This could only be explained by considering that the surfactant used during the preparation of these samples allows a better interaction between the Pt particles and the carbon substrate. These samples also show better performances than the commercial reference electrode in PEM fuel cell tests. In all cases, hydrocarbons (alkanes, in particular) are the main products, while alcohols form only in low amounts.

When the Pt particles are deposited first on carbon black and then onto the carbon cloth, instead of directly onto the latter (Pt_{nano}-C/GDE and Pt_{nano}/GDE, respectively), there is a better productivity and especially amount of C8–C9 hydrocarbons which become the major product of reaction.

This suggests that the initial hypothesis of a possible confinement of CO₂ inside the nanoporous carbon as a key factor leading to the formation of long carbon-chain hydrocarbons is probably correct, even if further studies are necessary to demonstrate the concept.

The effects of the flow rate of CO₂, *e.g.* of the contact time, and the influence of the current applied to the cell are summarized in Fig. 6 for the Pt/GDE_{com} working electrode. Decreasing the flow rate of CO₂ from 20 to 10 ml min⁻¹, an increase of the total amount of products from about 2.0×10^{-5} to 2.6×10^{-5} mmol h⁻¹, and an increase of the formation of hydrocarbons with higher C-atom number are observed. The fraction of hydrocarbons $\geq$ C5 increases from about 90% to about 96% on decreasing the flow rate of CO₂. Note that, due to the fluidodynamic configuration of the electrochemical flow cell, it is not fully correct to speak of residence or contact time. In fact, the results may be more appropriately interpreted, considering that the products of reaction may be further converted to hydrocarbons with a higher carbon-atom, in agreement with the results of Fig. 3. Therefore, by decreasing the flow rate of CO₂ the probability that the products of reaction may be further converted is higher. This is in agreement with the observation that the fraction of heavier products ($\geq$ C5) increases from 90% to 96% on decreasing the flow rate of CO₂.

Increasing instead the applied current to the cell from 20 mA to 40 mA a worsening of the productivity is noted, although further slightly increasing the fraction of heavier products

($\geq$ C5) to about 97–98%. The effect is probably related to the enhanced formation of hydrocarbons $>$ C9 which were not detected in our experimental conditions, because decane was used as solvent for the trapping of the products of reaction. On the other hand, the volatility of hydrocarbons $>$ C9 is so low that probably, when formed, they remain adsorbed on the electrocatalyst.

Hara *et al.*^{12b} observed that the efficiency of CO₂ electrochemical reduction in liquid phase, high pressure (30 bar) and using a glassy carbon electrode shows a maximum for a current density of 100 mA cm⁻², but the amount of hydrocarbons $>$ C2 becomes nearly negligible on increasing the current density above about 20 mA cm⁻². In general, on Cu electrodes, where hydrocarbons are mainly produced, the more negative potentials, *i.e.* larger current densities, favour the reaction, differently from electrodes where CO is the main product of reaction. On the glassy carbon electrode, the hydrocarbons are instead preferentially produced at less negative potentials, *i.e.* smaller current densities. It is probable that our Pt/GDE is in between these two cases and a maximum activity is shown for a current density of about 20 mA cm⁻². In fact, on decreasing the current density below this value, the productivity of CO₂ electrocatalytic reduction significantly decreases.

Reaction mechanism

The present data cannot clarify the reaction mechanism and network in the electrocatalytic conversion of CO₂ to high carbon-chains, but do give some useful indication for further studies. In fact, as pointed out in the introduction and also outlined in Scheme 1, the reaction mechanism and key surface reaction intermediates suggested in the literature for the electrochemical reduction of CO₂ resemble those of the Fischer–Tropsch reaction,¹⁷ even if only short C-chain hydrocarbons (C2, and traces C3 and C4) were detected. It is thus necessary to discuss whether our results, which evidence also the formation of longer C-chain hydrocarbons, are in accordance with previous suggestions on the reaction mechanism or instead indicate a different reaction mechanism, which should deserve investigations that are more specific.

Hara *et al.*^{12b} observed on their glassy carbon (GC) electrodes working at high pressure a product distribution which followed the Anderson–Schultz–Flory (ASF) distribution typical for a Fischer–Tropsch reaction mechanism, although they observed only hydrocarbons up to four carbon atoms. They thus concluded that the reaction mechanism of hydrocarbon formation on a GC electrode (planar-type) was similar to that on Fe, Ni, and Co Fischer–Tropsch catalysts. In agreement, also on Fe, Ni, and Co electrodes they observed an ASF distribution for the hydrocarbons.¹⁸

In our case, the results of Fig. 2 pointed out that the hydrocarbons desorbing to the gas phase may further react and be transformed to higher carbon-atom chain hydrocarbons. The results of the effect of the reaction conditions (Fig. 6) are consistent with this indication. The comparison of Pt_{nano}/GDE and Pt_{nano}-C/GDE (Fig. 5) suggests in agreement that a more nanoporous structure, which limits the rate of diffusion of the reaction products to the gas phase and thus

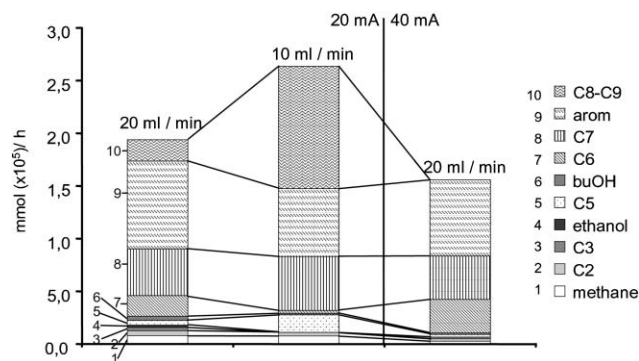


Fig. 6 Influence of the flow of CO₂ at 20 mA, and influence of the current with [CO₂] = 20 ml min⁻¹ on the products formed after 1 h of reaction, using Pt/GDE_{com} as the working electrode. Semi-continuous cell.

favours their consecutive transformation, effectively favours the productivity and especially the formation of heavier hydrocarbons. Desorption and consecutive readsorption–transformation of hydrocarbons to form heavier products is not consistent with a Fischer–Tropsch (FT) like mechanism. It is thus interesting to analyze whether the product distribution in our case follows the ASF product distribution.

Although there are deviations from this distribution for some catalysts, there is a general agreement in literature that FT synthesis follows more or less this ASF product distribution. The methodology is mainly divided into a kinetic approach and a thermodynamic approach. The ASF distribution model was developed in the early years of FT-synthesis and it assumes a constant probability of chain growth.¹⁹ The ASF distribution is only valid in the presence of a constant probability of chain growth. The reaction is then a one-by-one addition of monomers to a growing chain. In the ASF model, the parameter α represents the probability of chain growth. Typical values are between 0.7 and 0.9

Reported in Fig. 7 is the molar and weight percentage product distribution for the Pt/GDE_{com} and Pt_{nano}/GDE electrodes. Results for the Pt_{nano}-C/GDE electrode were not reported for clarity, but were not very different in terms of general trend from those shown in Fig. 7. The expected product distribution in terms of molar and weight percentage for the ASF model and a probability of chain growth of 0.85 were also reported in Fig. 7 for comparison. It is evident that the experimental results largely deviate from that expected by the ASF model.

Lox and Froment²⁰ present a model for an iron catalyst, often used as a reference in the literature. The model allows predicting the product distribution as a function of the H₂/CO ratio in the feed. However, this model also predicts results which largely deviate from the product distribution we observed (Fig. 7). This suggests that the reaction mechanism in our case is different from the FT mechanism and involves at least in part the possible reaction between a surface intermediate with the intermediate formed by readsorption of the hydrocarbons in the gas phase.

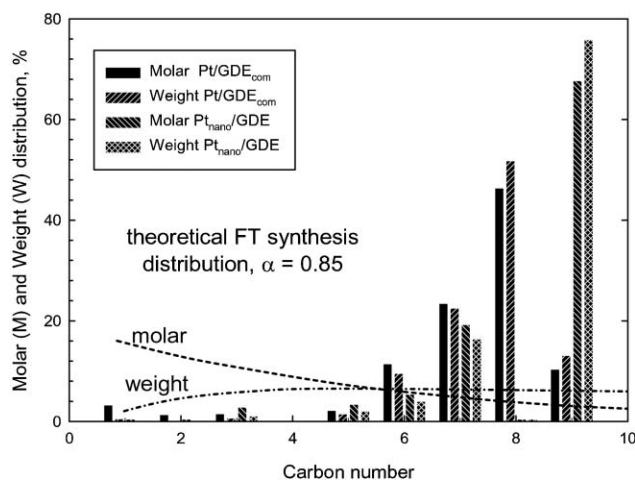


Fig. 7 Molar and weight distribution/% in the CO₂ electrocatalytic reduction using Pt/GDE_{com} and Pt_{nano}/GDE as the working electrode. Semi-half continuous cell.

Song *et al.*²¹ presented a kinetic model which considers the dependence of the product distribution on the reaction temperature. Lowering the temperature the production of heavier hydrocarbons increases, and for production of heavier products, the reaction temperature is of crucial importance. As the FT reaction is strongly exothermic, typically, it is necessary to cool the reactor enough to enable production of long hydrocarbons. The reaction needs a certain amount of energy to start and maintain the reaction. There is a lower limit of temperature around 180 °C. The low temperature operation (LTFT) operates at temperatures ranging from 180 °C to 240 °C.

In the electrocatalytic conversion, this lower temperature limit is not necessary, because electrons are available and therefore the reaction may proceed at room temperature and pressure. However, it is reasonable that in these conditions, the surface reaction-chain growth is much slower and thus desorption, readsorption and consecutive transformation of the lower molecular weight hydrocarbons can occur. On the other hand, this mechanism offers the potential possibility of bypassing the limits in the product distribution given by the FT reaction mechanism and thus potentially to tailor the product distribution to the most interesting one for commercial uses.

Conclusions

The results presented here show for the first time the possibility of electrocatalytically converting CO₂ to hydrocarbons with carbon chains >C₅ and with a product distributions which do not follow the ASF distribution model typical for FT synthesis. This result opens a new perspective in the gas-to-liquid conversion—for example, using a similar approach to convert methane to liquid hydrocarbons without passing through syn gas, and in the conversion of CO₂ back to fuels. In fact, in contrast with all the previous observations, easily storable liquid hydrocarbons could be produced, a significant step forward.

This result derives from two main differences with respect to previous results on the electrochemical reduction of CO₂: the use of gas phase instead of liquid phase, and the use of working electrodes based on nanostructured carbon instead of the metallic planar-type. Present data do not allow estimating the faradaic efficiency of the process, because room temperature operations determine the fact that a large part of the heavier reaction products remains adsorbed on the electrode preventing their exact quantification, as discussed above. This is a current limit, which may be solved in future both operating at higher temperatures and possibly using a modulation in the potential applied to the cell. Operations at higher reaction temperature are limited from the use of proton-conductive membranes, which are typically stable at temperatures below about 100 °C.

The electrocatalyst is designed to be one side of a photoelectrocatalytic (PEC) device (Fig. 1) which ultimately will allow using solar energy and water to convert CO₂ back to fuels. This is a long-term goal. It will require both the further development of efficient electrocatalysts for the reduction of CO₂ in order to improve productivity, and for integration in

the PEC device. It is also necessary to improve/develop the photocatalyst. However, several studies are on going on the development of improved photocatalysts for water splitting. They may be potentially used in the PEC device, even if there are further constraints such as the need of a specific nanoarchitecture, which will allow a fast diffusion through Nafion[®] membrane of the protons produced in the reaction and a fast collection of photogenerated electrons as well.

In terms of cost, it is expected that the components and materials to construct the cells will largely benefit from the reduction of costs due to the expected large increase in the use of PEM fuel cells. It was observed above that a PEC device shows several analogies in terms of general characteristics and components to PEM fuel cells.

Therefore, although a long research would be necessary before a possible application, the recent results open the possibility to develop a new PEC device able to convert back CO₂ to fuels.

An interesting, although niche application, which may be anticipated, is related to space missions. In Mars missions, the need to use Martian resources to produce Earth-return propellant and life support consumables is a crucial goal.²² The PEC device could be used on Mars to convert atmospheric CO₂ and water (present in the atmosphere and soils on Mars) to hydrocarbons for a range of applications—as propellants, for the manufacture of foodstuffs for life support, and plastics for the fabrication of structures and spare parts for Martian bases. On the photo-catalyst side of the PEC reactor, O₂ will be produced which is also extremely valuable on Mars.

We may conclude that converting CO₂ back to fuel (using solar energy) is not a dream, but a challenge,²³ which still requires long-term research to develop the application side. Present data represent a contribution in this direction which demonstrates that, using metal nanoparticles on carbon-based working electrodes, it is possible to reduce CO₂ to high carbon-chain hydrocarbons (>C₅) at room temperature and atmospheric pressure in a continuous flow cell having the working electrode directly in contact with the CO₂ in the gas phase.

The performance and product distribution depend on the nature of the electrocatalyst and the reaction conditions. It is also shown that product distribution is different from that expected from Anderson–Schultz–Flory distribution for Fischer–Tropsch synthesis.

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Effect of co-solvents on production of biodiesel *via* transesterification in supercritical methanol†

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Previous studies on the transesterification of vegetable oil in supercritical methanol in a batch reactor resulted in a non-saponified product with high methyl esters content and high glycerol purity. For the continuous reactor, the high viscosity of vegetable oil might result in problems in the flow system. This study selected THF and hexane as co-solvents to reduce the viscosity of the vegetable oil. The effect of co-solvents was investigated in both 250 mL and 5.5 mL batch reactors by 2-replicate 2^3 factorial design at temperatures from 290–350 °C, a molar ratio of methanol to vegetable oil from 12–42 and a molar ratio of co-solvent to vegetable oil from 0–5. The reaction time was fixed at 10 min. The products from the employed and unemploy co-solvent process were analyzed by GC-MS to confirm that the reaction among the vegetable oil, methanol and co-solvent was non-existent. However, some thermal cracking was observed in a 250 mL reactor at 350 °C and 30 min reaction time. The amount of co-solvents had no significant effect on methyl esters content and also did not allow the reaction to be completed under milder conditions. Thus, it was concluded that both THF and hexane were appropriate co-solvents to reduce the viscosity of vegetable oil for the continuous production of biodiesel in supercritical methanol.

Introduction

Biodiesel, an alternative diesel fuel, refers to the lower alkyl esters of the long chain fatty acids which are synthesized by transesterification (also called alcoholysis) of vegetable oils with lower alcohols. The conventional methods for biodiesel production use a basic or acidic catalyst. With an acid catalyst, a reaction time of 1–45 hours is necessary for the formation of the respective esters, and with a basic catalyst it is somewhat faster, depending on the temperature and molar ratio of methanol to vegetable oil. Unfortunately it still poses some separation and purification problems.¹ A more recent method involves the non-catalytic transesterification of vegetable oil in supercritical methanol.^{2–9} Saka *et al.*^{3,4} found that the reactions of rapeseed oil were complete within 240 s at 350 °C, 19 MPa and a molar ratio of methanol to vegetable oil of 42 in a 5 mL batch reactor. While Demirbas⁵ found that the reaction of cotton seed oil, hazelnut kernel oil, safflower seed and sunflower seed oil were completed at a molar ratio of methanol to vegetable oil of 41, 250 °C, and a 300 s reaction time in a 100 mL batch reactor. Madras *et al.*⁶ found that the reaction of sunflower seed oil was completed at a molar ratio of methanol to vegetable oil of 40, 400 °C, and an 1800 s reaction time in a 250 mL batch reactor.

Recently, the reactivity of various alcohols in a transesterification reaction under supercritical conditions was studied at 300 °C reaction temperature.⁷ It was found that the alcohol

reactivity relates to their critical properties, and methanol has the highest reactivity. Furthermore, the effects of water and free fatty acid on biodiesel production in supercritical methanol, compared with those of biodiesel prepared by acidic and basic catalyzed methods, were investigated.⁸ The presence of water and free fatty acid did not have a significant effect on the yield in the supercritical process. Moreover, transesterification in supercritical methanol employing propane and CO₂ as co-solvents was developed.^{9,10} Their studies indicate that the addition of co-solvent allows the reaction to be completed under milder conditions due to the lower critical properties of the reaction mixture. Recently, biodiesel production in a lab-scale plug flow reactor was developed by us.¹¹ Vegetable oils (palm kernel and coconut oils) and methanol were fed into a 247 mL reactor by HPLC pumps at approximately 10 g min^{−1} maximum flow rate. The optimal conditions of this flow reactor were: molar ratio of methanol to vegetable oil, 42; 350 °C; and, 400 s reaction time. The results of the lab-scale reactor were thus used for the reactor scale-up design.

In running the scale-up reactor at higher flow rates, the viscosity of vegetable oil posed some problems, such as fluctuation of system pressure and lower flow rate output. The first viscosity reduction method was attempted by heating the vegetable oil to around 70–80 °C. By doing this, the viscosity of the vegetable oil and the fluctuation of system pressure were reduced, but flow rate output was still low. In the second method, the vegetable oil was mixed with a liquid co-solvent. For simplification, this study selected tetrahydrofuran (THF) and hexane as co-solvents.

THF improves the solubility of methanol in vegetable oil and forms a single-phase mixture. A single high-pressure pump could be used to feed the vegetable oil–THF–methanol mixture into the reactor. Hexane, on the other hand, which is the

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Table 1 Physical properties of PKO sample and diesel fuels

Properties	High speed diesel	Low speed diesel	Palm kernel oil
Kinematic viscosity at 40 °C/cSt	4.1	6.3	30.8
Gravity/°API	33.2	26.1	24.6
Cetane index	54	46	35
Flash point/°C	75	78	218
Heating value/MJ kg ⁻¹	43.1	42.1	34.6
Acid value/mg KOH g ⁻¹ oil	—	—	11.3
Saponification value/mg KOH g ⁻¹ oil	—	—	198.6
Iodine value/g I ₂ per 100 g oil	—	—	12.8

conventional solvent in the vegetable oil extraction process, could be another good solvent for vegetable oil for the continuous production of biodiesel in supercritical methanol. Moreover, as their boiling points are close to that of methanol (65 °C, 66 °C and 69 °C for methanol, THF and n-hexane, respectively) both co-solvent and methanol could be recovered simultaneously at the end of reaction and recycled.

Experimental

Materials

Crude palm kernel oil (PKO) was supplied by Chumporn Palm Oil Industry, PCL. Its analysis, together with diesel analysis, is presented in Tables 1 and 2. The sample was warmed and filtered prior to use. Commercial grade methanol, hexane (mixture of C₆ isomers containing more than 65% n-hexane) and tetrahydrofuran (THF) were used with no further purification. All standard methyl esters for gas chromatograph calibration and methyl undecanoate (internal standard) were supplied by Fluka. Analytical grade carbon disulfide (CS₂), which was used as a dilution solvent for the gas chromatography, was supplied by Merck.

Experimental design

The 2-replicated 2³ factorial design with 4 central runs was employed in this study, requiring 20 experiments for each reactor and each co-solvent.¹² The factors were temperature (290–350 °C), molar ratio of methanol to vegetable oil (12–42) and molar ratio of co-solvent to vegetable oil (0–5) and the resulting response was methyl esters content. Tables 3 and 4 show the factors, levels and experimental result employing the THF and hexane process in a 250 mL reactor, respectively. The result in Table 4, combined with zero moles of co-solvent

Table 2 Fatty acid profile in PKO sample

Name	Composition (%wt)	Molecular weight	
		Fatty acid	Pseudo-triglyceride
Caprylic acid	2.99	144	470
Capric acid	3.06	172	554
Lauric acid	49.51	200	638
Myristic acid	17.91	228	722
Palmitic acid	8.64	256	806
Stearic acid	4.19	284	890
Oleic acid	11.64	282	884
Linoleic acid	2.07	280	878
Average molecular weight			704

Table 3 Experimental data from employed THF process in 250 mL reactor for 10 min with crude PKO as reactant

Run order	Temperature/°C	Molar ratio of THF to oil	Molar ratio of MeOH to oil	Methyl esters content (%wt)	Pressure/MPa
1	350	0.0	12.1	79.7	17.9
2	290	5.6	41.3	72.6	17.5
3	350	4.8	39.9	86.5	19.3
4	290	5.0	41.9	73.2	17.4
5	350	0.0	41.3	84.9	19.0
6	290	0.0	42.2	63.7	16.6
7	320	2.4	24.0	79.6	19.0
8	350	5.0	12.2	79.6	19.8
9	320	2.5	23.9	80.4	17.8
10	350	4.9	41.9	79.3	19.4
11	350	0.0	12.1	80.9	19.8
12	320	2.6	24.1	79.7	19.1
13	350	0.0	42.1	85.1	19.6
14	290	5.1	11.9	45.0	16.3
15	350	5.1	12.1	82.5	21.6
16	290	0.0	12.1	43.7	15.6
17	290	0.0	11.2	47.6	16.2
18	290	5.1	12.3	47.3	15.9
19	320	2.5	24.1	78.6	18.0
20	290	0.0	42.1	62.3	16.9

in oil (unemployed co-solvent process, run order 13–20) from Table 3, was used to minimize the number of experiments.

To eliminate the effect of pressure, the amount of reactants and co-solvent was adjusted to a specified pressure (19.0 MPa) by using the Redlich–Kwong equation of state and the Lorentz–Berthelot-type mixing rule.¹³ Unfortunately, the calculated pressure was not exactly equal to the observed pressure. In some experiments, where there was a large difference between the calculated and observed pressure, the amounts of reactant and co-solvent were readjusted by trial and error. The observed pressures for each experiment are shown in Tables 3 and 4.

As for the 5.5 mL reactor, the experimental design was similar to that for the 250 mL reactor. The amounts of reactants were also adjusted for a pressure of 19.0 MPa.

Table 4 Experimental data from employed hexane process in 250 mL reactor for 10 min with crude PKO as reactant

Run order	Temperature/°C	Molar ratio of hexane to oil	Molar ratio of MeOH to oil	Methyl esters content (%wt)	Pressure/MPa
1	290	4.7	41.3	62.4	19.6
2	350	4.6	40.9	87.6	18.7
3	290	5.1	12.4	46.2	19.2
4	290	4.8	42.6	65.2	20.0
5	350	5.0	12.4	79.8	18.6
6	320	2.5	24.2	77.8	19.2
7	290	4.9	12.2	48.5	20.0
8	320	2.6	24.3	78.2	18.6
9	350	5.0	43.4	88.1	17.7
10	320	2.5	24.2	76.5	18.2
11	320	2.4	24.1	76.6	19.6
12	350	5.2	12.4	85.9	19.0
13	290	0.0	12.1	43.7	15.6
14	290	0.0	11.1	47.6	16.2
15	350	0.0	12.1	80.9	19.8
16	350	0.0	12.1	79.7	17.9
17	290	0.0	42.2	63.7	16.6
18	290	0.0	42.1	62.3	16.9
19	350	0.0	42.1	85.1	19.6
20	350	0.0	41.3	84.9	19.0

Table 5 Experimental data from employed THF process in 5.5 mL reactor for 10 min with refined PKO as reactant

Run order	Temperature/ °C	Molar ratio of THF to oil	Molar ratio of MeOH to oil	Methyl esters content (%wt)
1	350	0.0	44.5	99.3
2	320	3.7	24.3	83.2
3	350	5.2	12.0	83.3
4	320	2.1	20.2	81.3
5	290	0.0	12.0	53.6
6	350	5.0	43.0	97.5
7	350	0.0	12.0	81.1
8	350	0.0	40.8	99.4
9	290	8.3	20.1	56.5
10	290	4.8	40.7	78.3
11	290	5.0	12.0	54.2
12	320	2.3	21.7	82.5
13	350	5.1	41.9	98.7
14	350	5.3	12.2	84.6
15	290	0.0	41.9	78.2
16	320	2.5	22.9	84.6
17	350	0.0	12.0	82.6
18	290	0.0	41.8	76.8
19	290	5.2	42.4	77.5
20	290	0.0	12.0	57.0

Tables 5 and 6 show the factors, levels and experimental result for the employed THF and hexane process in 5.5 mL reactor, respectively.

Experimental setup

First, the effect of co-solvents was studied in a 250 mL batch reactor (Parr Instrument Company, Model 4842), equipped with a mechanical stirrer and internal cooling. The reactor was heated with an external electrical heater. The maximum pressure and temperature values of the equipment were 50 MPa and 500 °C, respectively. The temperature of the reactor was measured with a j-type thermocouple and controlled at ± 5 °C for a set time. The pressure of the reactor was measured with a pressure gauge and transducer.

Table 6 Experimental data from employed hexane process in 5.5 mL reactor for 10 min with refined PKO as reactant

Run order	Temperature/ °C	Molar ratio of hexane to oil	Molar ratio of MeOH to oil	Methyl esters content (%wt)
1	320	2.6	23.9	80.5
2	290	5.4	42.0	79.5
3	320	2.5	23.9	81.2
4	290	5.4	12.0	52.2
5	350	5.1	11.9	76.0
6	290	5.0	11.9	54.4
7	350	6.8	43.5	97.1
8	320	2.6	23.7	80.2
9	290	5.0	41.1	80.1
10	320	2.5	23.0	80.2
11	350	4.9	37.9	86.7
12	350	5.0	12.2	78.1
13	290	0.0	12.0	57.0
14	290	0.0	12.0	53.6
15	290	0.0	41.8	76.8
16	290	0.0	41.9	78.2
17	350	0.0	12.0	81.1
18	350	0.0	12.0	82.6
19	350	0.0	44.5	99.4
20	350	0.0	40.8	99.3

As the highest methyl esters content obtained from the 250 mL reactor was slightly lower than expected, the effect of co-solvent was studied in the 5.5 mL batch tube reactor, the dimensions of which were 0.375 mm od, 0.124 mm thickness and 200 mm length. The reactor was heated by immersion in a fluidized sand bath. The temperature was measured by a k-type thermocouple.

Experimental procedure

(a) 250 mL reactor. The reaction vessel was charged with a given amount of vegetable oil, methanol and co-solvent and was then heated to the desired temperature. The reaction time and stirring speed were fixed at 10 min and 500 rpm, respectively, for every experiment. At the end of the reaction, the reactor was quenched in an ice–water bath to approximately room temperature and pressure. The content in the reaction vessel was weighed and put in a rotary evaporator to remove the solvent phase (co-solvent and methanol). The oil phase was left to settle for at least 8 hours in a separating funnel to ensure complete separation. Two liquid phases were obtained: ester (top layer), and crude glycerol (bottom layer). The ester layer was then analyzed for methyl esters content.

(b) 5.5 mL reactor. The reaction vessel was charged with a given amount of reactant and co-solvent, immersed in a fluidized sand bath at the designed temperature and was shaken manually from time to time to ensure uniform mixing. The reaction time was held constant at 10 min. At the end of the reaction, the reactor was then quenched in an ice–water bath to stop the reaction. The solvent phase was then evaporated by warming in a water bath at 80 °C for 2 hours. Glycerol was separated by centrifuging at 4000 rpm for 10 min. The ester (top layer) phase was then analyzed for methyl esters content.

Methyl esters analyses

For the methyl esters content measurement, a gas chromatograph (Varian Model CP-3800), equipped with a capillary column coated with polydimethylsiloxane (30 m $\times$ 0.25 mm $\times$ 0.25 μ m, DB-1, J&W Scientific) and an FID detector, was used with helium as the carrier gas. The ester product and the known amount of internal standard was diluted with CS₂ before injection and standardized by the internal standard method. The temperature of the injection port and detector were 250 °C and 280 °C, respectively. The column oven was held at 110 °C for 2 min and then raised to 260 °C at 15 °C min⁻¹. The final temperature was held constant for 10 min.

The methyl esters content was calculated from their content in the biodiesel product as analyzed by GC. The content (or purity) was defined as a ratio of the weight of methyl esters, as obtained from GC, to the total weight of the biodiesel product.

For the GC-MS analysis, a Shimadzu Model GCMS-QP2010 gas chromatograph coupled with a mass spectrometer and equipped with a capillary column coated with polydimethylsiloxane (30 m $\times$ 0.25 mm $\times$ 0.25 μ m, DB-1ms, J&W Scientific) was used with helium as the carrier gas. The sample was diluted in CS₂ before injection. The injection port, ion

Table 7 Critical properties of methanol, THF, n-hexane and PKO sample

Critical properties	Methanol	THF	n-Hexane	PKO	Unit
T_c	512.6	540.2	507.6	926.1	K
P_c	7.91	5.12	3.06	0.59	MPa
V_c	0.118	0.224	0.373	2.476	L mol ⁻¹

source and interface temperature were 250, 200 and 230 °C, respectively. The molecular weight scan range was 50–800 m/z and 3 min of solvent cut time. The column was held at 90 °C for 5 min and then raised to 260 °C at 20 °C min⁻¹. The final temperature was held constant for 10 min.

Results and discussion

Physical characteristics of PKO sample versus diesel fuel

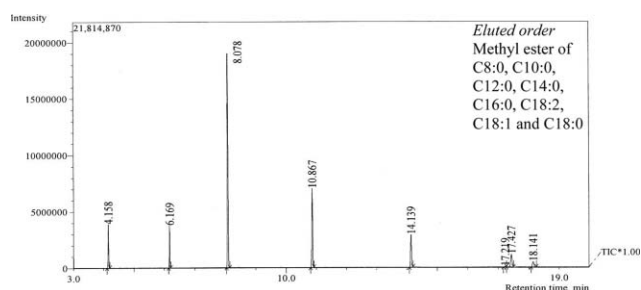
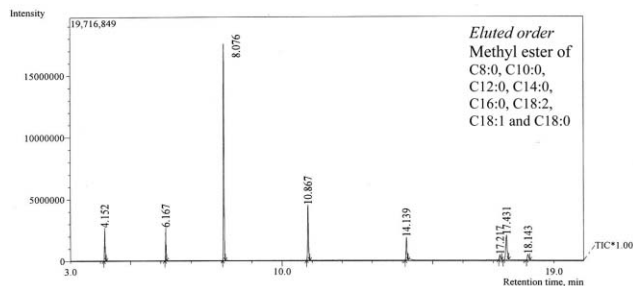
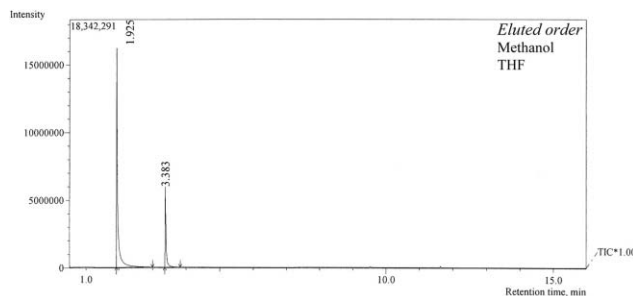
From Table 1, it is clear that the PKO had a lower heating value and much higher viscosity than those of diesel fuels. This indicates troublesome atomization and poor engine performance if these oils are to be used as neat fuels. Furthermore, this PKO had higher acid value, which implies that biodiesel with lower methyl esters content would result if this PKO was used as the reactant in alkaline catalytic transesterification.⁸

From Table 2, the PKO sample contained lauric acid as the major fatty acid, which is consistent with the literature.¹⁴ The chemical formula of PKO was represented by a pseudo-triglyceride, which consists of 3 molecules of fatty acid and a molecule of glycerol. The average molecular weight was calculated by the pseudo-triglyceride molecular weight and corresponding fatty acid composition and was found to be 704. The critical properties of the sample, as estimated by the GC method,^{15,16} are given in Table 7. Additional details of these calculations can be found in our previous work.¹¹

Reaction between vegetable oil, methanol and co-solvents

To ensure that the reaction between co-solvent and other reactants did not occur, the GC-MS chromatograms of mixed methyl esters standard and biodiesel products, obtained from the THF used at 350 °C, a molar ratio of methanol to vegetable oil of 42 and 5 mole of THF in vegetable oil at 10 min reaction time, were obtained as illustrated in Figs. 1 and 2.

Comparing Fig. 1 with Fig. 2, it can be seen that the biodiesel composition from the employed THF process was

**Fig. 1** GC-MS chromatogram of mixed methyl esters standard.**Fig. 2** GC-MS chromatogram of biodiesel from employed THF process in 250 mL reactor for 10 min with crude PKO as reactant.**Fig. 3** GC-MS chromatogram of THF phase in 250 mL reactor for 10 min with crude PKO as reactant.

basically the same as the mixed fatty acid methyl esters standard. On the other hand, from the THF and hexane chromatograms in Figs. 3 and 4, one can deduce that THF and hexane peaks did not show up in Fig. 2. Therefore, it is concluded that there was no co-solvent interference in the transesterification reaction.

The critical properties of the PKO sample, methanol, n-hexane and THF were the parameters in the Redlich–Kwong equation of state and the Lorentz–Berthelot-type mixing rules employed to calculate the amount of methanol, co-solvent and vegetable oil for a specified pressure.

Effect of co-solvent on methyl esters content in biodiesel production in a 250 mL reactor

The experimental order (Table 3 and run order 1–12 in Table 4) was done randomly. For run order 13–20 in Table 4, *i.e.* the unemployed co-solvent process, the experimental data were obtained from Table 3. All experimental data were analyzed

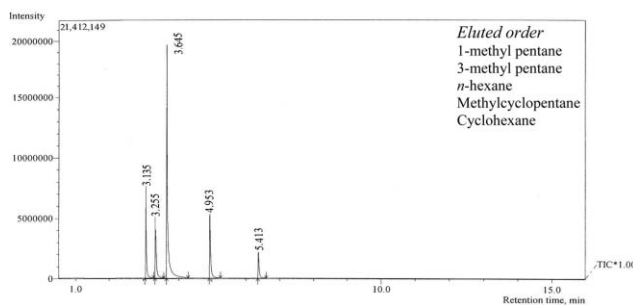
**Fig. 4** GC-MS chromatogram of hexane phase in 250 mL reactor for 10 min with crude PKO as reactant.

Table 8 Analysis of variance from employed THF process in 250 mL reactor for 10 min with crude PKO as reactant

Source	Sum of squares	Degree of freedom	Mean square	F value	Probability > F
<i>A</i> (Temperature)	2583.77	1	2583.77	69.47	<0.0001
<i>B</i> (THF to oil)	18.28	1	18.28	0.49	0.4966
<i>C</i> (MeOH to oil)	538.21	1	538.21	14.47	0.0025
<i>AB</i>	31.45	1	31.45	0.85	0.3759
<i>AC</i>	338.75	1	338.75	9.11	0.0107
<i>BC</i>	10.41	1	10.41	0.28	0.6065
<i>ABC</i>	39.51	1	39.51	1.06	0.3230
Residual	446.29	12	37.19		
Total	4043.78	19			

Table 9 Analysis of variance from employed hexane process in 250 mL reactor for 10 min with crude PKO as reactant

Source	Sum of squares	Degree of freedom	Mean square	F value	Probability > F
<i>A</i> (Temperature)	3374.01	1	3374.01	142.32	<0.0001
<i>B</i> (Hexane to oil)	15.18	1	15.18	0.64	0.4391
<i>C</i> (MeOH to oil)	421.18	1	421.18	17.77	0.0012
<i>AB</i>	2.16	1	2.16	0.09	0.7679
<i>AC</i>	141.41	1	141.41	5.96	0.0310
<i>BC</i>	4.31E-03	1	4.32 E-03	1.8 E-04	0.9895
<i>ABC</i>	0.08	1	0.08	3.4 E-03	0.9539
Residual	284.49	12	23.71		
Total	4249.48	19			

by the factorial design procedure¹³ to obtain the analysis of variance tables (ANOVA), which are shown in Tables 8 and 9.

From Tables 8 and 9, the molar ratio of co-solvent to vegetable oil (factor *B*) and its interaction (factors *AB*, *BC* and *ABC*) had no significant effect on methyl esters content, as noticed from the probability of *F* value less than 0.05, at the confidence level of 95%. Thus, it was concluded that the addition of a co-solvent in this process did not show either negative or positive effect on methyl esters content.

The regression models in terms of coded units of employed THF and hexane process then can be correlated as shown in equations 1 and 2, respectively. Temperature (*A*) and the molar ratio of methanol to vegetable oil (*C*) has positive effects on methyl esters content, and the temperature effect has a higher magnitude than the molar ratio of methanol to vegetable oil effect by approximately two orders. The interaction term (*AC*) indicated the complete regression model might be second order, which is consistent with our previous finding.¹¹

$$\%ME = 71.88 + 12.67A + 5.90C - 4.67AC \quad (1)$$

$$\%ME = 71.21 + 14.53A + 5.12C - 2.99AC \quad (2)$$

where %ME is methyl esters content in biodiesel product (%wt), and *A* is temperature in terms of coded unit, derived by the equation:

$$A = \frac{\text{Temperature} (^{\circ}\text{C}) - 320}{30} \quad (3)$$

C is the molar ratio of methanol to vegetable oil in terms of coded unit, derived by the equation:

$$C = \frac{\text{MeOH(mole)} - 27}{15} \quad (4)$$

and *AC* is the product of *A* and *C*.

Effect of reaction time on methyl esters content

From Tables 3 and 4, the highest methyl esters content obtained was found to be not over 88%, which is lower than the 95% reported in the latest literature of experiments employing co-solvents.^{9,10} According to relevant literature, the conditions were: reaction temperature 350–400 °C; molar ratio of methanol to vegetable oil 40–42; reaction time 2.4–40 min; and, reactor volume 5–250 mL.^{3–6,9,10} To confirm that the reaction reached equilibrium in this work, we ran another set of experiments for 5–60 min and the result is illustrated in Fig. 5.

From Fig. 5, maximum methyl esters content was reached after 30 min reaction time and a methyl esters content of $92.0 \pm 1\%$ was observed. Because of the slightly lower methyl esters content, we further established two possible hypotheses and verified them as follows.

Effect of temperature gradient between reactor wall and bulk fluid

In the 250 mL reactor, the reaction vessel employed was heated externally and the contents in the vessel were mixed by a

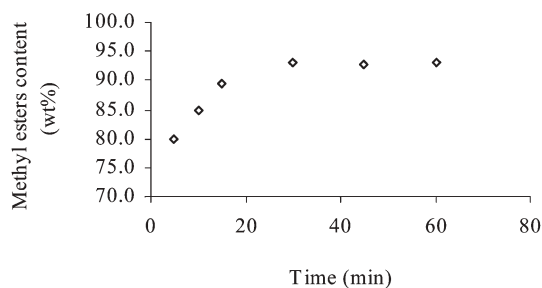


Fig. 5 Changes in methyl esters content of unemployed co-solvent process as a function of reaction time in 250 mL reactor with crude PKO at 350 °C and 42 molar ratio of methanol to vegetable oil.

stirrer. As the temperature near the wall of the vessel is somewhat higher than in the center, it may cause an *in situ* thermal cracking reaction, resulting in slightly lower methyl esters content. To verify this hypothesis, the experiments were performed at high temperature, *i.e.* 350 and 400 °C, in both 5.5 and 250 mL reactors at 30 min reaction time, and the biodiesel samples were analyzed. The chromatograms obtained were then compared with that obtained from the conventional method at 60 °C, 30 min reaction time, 1% NaOH, and 6 moles of methanol in vegetable oil.

From Fig. 6, sample (a), it was assumed that no thermal cracking occurred. In the chromatogram of this sample, no noise was detected, as in sample (b). Therefore, it was concluded that thermal cracking did not take place in the 5.5 mL reactor at 350 °C. Sample (c) had higher noise than samples (a) and (b). The retention times of the noises in both sample (c) and (d) were nearly the same, so these noises were probably the same compounds derived from the thermal cracking reaction at temperature over 350 °C. However, the results from GC-MS (Fig. 2) did not show this noise, probably because that sample was run at 10 min reaction time.

According to the methyl esters content obtained from the 5.5 mL reactor, it is assumed that there was no temperature gradient between the reactor wall and the bulk fluid, at 350 °C, a molar ratio of methanol to vegetable oil of 42, a molar ratio

Table 10 Experimental data from 5.5 mL reactor for 10 min with crude PKO as reactant, temperature controlled by fluidized sand bath

Process	Temperature/ °C	Molar ratio of co-solvent to oil	Molar ratio of methanol to oil	Methyl esters content (%wt)
Unemployed	350	0.0	42.0	95.5
co-solvent	350	0.0	42.1	96.3
THF	350	5.1	41.1	94.7
	350	6.8	45.1	93.8
Hexane	350	5.2	40.3	93.9
	350	5.8	42.3	94.5

of co-solvent to vegetable oil of 0–5, and 10 min reaction time. The experimental data are illustrated in Table 10. The methyl esters content of the biodiesel products was slightly higher than those obtained from the 250 mL reactor under the same conditions (see Tables 3 and 4). Therefore, the assumption that thermal cracking occurred in the 250 mL reactor might be plausible. However, the methyl esters content was still slightly lower than the literature value, especially for the co-solvent process employed. Therefore, we established a second hypothesis, which is discussed in next section.

Effect of contaminants in crude palm oil

The crude palm oil contained 95–98% of triglyceride and 2–5% complex minor compounds such as wax ester, hydrocarbons, pigments and alcoholic compounds.¹⁷ Thus, the slightly lower methyl esters content obtained from crude PKO compared with that from refined PKO was probably due to the percentage of triglyceride. This hypothesis was verified in the 5.5 mL reactor, to ensure thermal cracking did not take place, by using refined PKO (cooking oil shelf product) as the reactant. The effect of co-solvent by using the experimental design as mentioned earlier was also investigated. The experimental data, as shown in Tables 5 and 6, were treated by the factorial design procedure and the ANOVA tables, as shown in Tables 11 and 12, respectively.

From Tables 5 and 6, the maximum methyl esters content was 99.4%. It was clear that the maximum methyl esters content from refined PKO was higher than that from crude PKO, which was 96.3% (Table 10).

From Tables 11 and 12, it is clear that the co-solvents did not affect the methyl esters content. Also, the interaction term between temperature and molar ratio of methanol to vegetable oil (Factor *AC*) had no significant effect. The regression model in terms of coded units for a 5.5 mL reactor for the employed THF and hexane process are given in eqns 5 and 6, respectively;

$$\%ME = 79.79 + 12.32A + 9.08C \quad (5)$$

$$\%ME = 78.24 + 10.51A + 10.11C \quad (6)$$

where %ME is methyl esters content in biodiesel product (%wt), *A* is temperature in terms of coded unit, derived by eqn (3) and *C* is molar ratio of methanol to vegetable oil in terms of coded unit, derived by eqn (4).

For the 5.5 mL reactor, the regression model indicated that the effect of temperature and molar ratio of methanol to

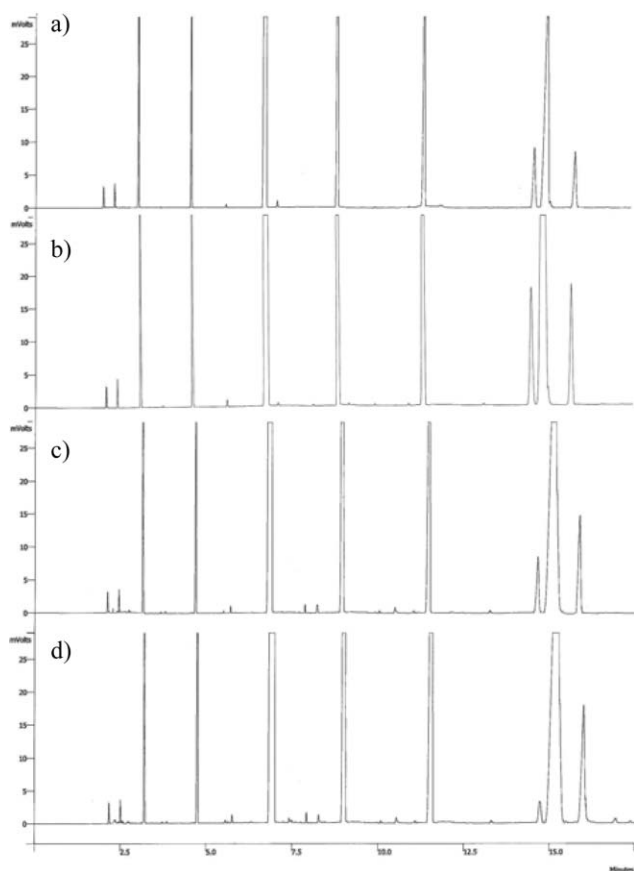


Fig. 6 Comparison of GC chromatogram of biodiesel product from crude PKO at various temperatures, indicating some noises observed in (c) and (d). (a) Conventional method (60 °C), (b) 350 °C in 5.5 mL reactor, (c) 400 °C in 5.5 mL reactor and (d) 350 °C in 250 mL reactor.

Table 11 Analysis of variance from employed THF process in 5.5 mL reactor for 10 min with refined PKO as reactant

Source	Sum of squares	Degree of freedom	Mean square	F value	Probability > F
A (Temperature)	2400.84	1	2400.84	138.81	<0.0001
B (THF to oil)	2.00	1	2.00	0.12	0.7399
C (MeOH to oil)	1340.93	1	1340.93	77.53	<0.0001
AB	6.11	1	6.11	0.35	0.5634
AC	58.91	1	58.91	3.41	0.0898
BC	0.02	1	0.02	0.00	0.9756
ABC	8.39	1	8.39	0.49	0.4994
Residual	207.55	12	17.30		
Total	3950.57	19			

Table 12 Analysis of variance from employed hexane process in 5.5 mL reactor for 10 min with refined PKO as reactant

Source	Sum of squares	Degree of freedom	Mean square	F value	Probability > F
A (Temperature)	1783.85	1	1783.85	136.94	<0.0001
B (Hexane to oil)	22.61	1	22.61	1.74	0.2123
C (MeOH to oil)	1640.57	1	1640.57	125.94	<0.0001
AB	27.62	1	27.62	2.12	0.171
AC	53.23	1	53.23	4.09	0.0661
BC	9.30	1	9.30	0.71	0.4146
ABC	2.88	1	2.88	0.22	0.6466
Residual	156.31	12	13.03		
Total	3673.21	19			

vegetable oil had a similar magnitude and also had a positive effect. Furthermore, the overall mean (the first term on the right hand side) was higher than the regression model of the 250 mL reactor. This indicates that the methyl esters content in the biodiesel product, which is obtained from the same temperature and molar ratio of methanol to vegetable oil in the 5.5 mL reactor, is always higher than that obtained from the 250 mL reactor.

Conclusions

The effects of co-solvents (THF and hexane) on the production of biodiesel from PKO in supercritical methanol were successfully investigated. This system achieves equilibrium after 30 min reaction time in a 250 mL reactor and in less than 10 min in a 5.5 mL reactor. The reaction of co-solvent with other reactants (vegetable oil and methanol) did not occur at supercritical conditions. The addition of co-solvents in this process did not show either negative or positive effects on the methyl esters content. The methyl esters content from crude PKO was slightly lower than that of refined PKO, plausibly because of the lower triglyceride content.

Acknowledgements

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Effect of synthesis parameters on the catalytic activity of Co–ZrO₂ for bio-ethanol steam reforming†

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The effects of synthesis parameters on the activity of Co–ZrO₂ catalysts in bio-ethanol steam reforming (BESR) were investigated. The supported catalysts were prepared by incipient wetness impregnation (IWI) and characterized through N₂ physisorption, H₂ chemisorption, X-ray diffraction, X-ray photoelectron spectroscopy, temperature programmed calcination, temperature programmed reduction, temperature programmed oxidation, thermogravimetric analysis, ethanol pulse chemisorption, and temperature programmed reaction techniques. The synthesis parameters examined include calcination temperature, reduction temperature, and reduction time. The catalyst evolution at different stages of the synthesis process was investigated. The ethanol adsorption and temperature programmed reaction experiments indicated a strong correlation between the catalytic activity and metallic cobalt surface area for the 10 wt% Co–ZrO₂ catalyst.

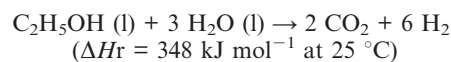
1. Introduction

As the world population increases and larger and larger areas of the globe become industrially developed, the energy demands of the world will continue to rise. Increased energy requirements, on the other hand, create some of the most serious environmental pollution problems that face the world. These problems include VOC, NO_x and SO₂ emissions, acid rain, ground level ozone formation, smog, particulate matter, and increased green house gases. It has now been widely accepted that global warming is directly linked to increased green house gases, especially CO₂, in the atmosphere. Although many fields of chemistry, such as catalysis, have provided many significant solutions to pollution problems in the form of emission control (*e.g.*, three way catalysts, SCR), cleaner fuels (*e.g.*, HDS, HDN) and increased combustion efficiencies (*e.g.*, catalytic combustion), much more is needed to mitigate the negative impact of energy consumption on the environment. Recently, much attention has been given to hydrogen as a clean fuel. Whether it is combusted directly or whether it is used as a fuel for fuel cells, hydrogen has the promise of being the cleanest energy carrier since it only produces water when it is burned. Especially when it is used with fuel cells, hydrogen has the potential to provide electricity at much higher efficiencies compared to combustion processes, since fuel cells are not limited by Carnot efficiencies.

There exist several routes for hydrogen production from fossil fuels. Steam reforming of lower organic compounds such as methane and propane is an effective method of manufacturing hydrogen. However, for hydrogen to fulfil its potential as a clean energy carrier, it is necessary to produce it from

renewable sources, such as plant matter. Hydrogen production from renewable sources can indirectly harness the energy from the sun and minimize the CO₂ emissions, since CO₂ emitted from reforming plant matter can be recycled in a closed carbon loop through the photosynthesis process. A promising route for hydrogen production involves the steam reforming of bio-ethanol. Ethanol can be produced renewably from fermentation of biomass including starch, sugar, and cellulosic and lignocellulosic materials. Also, ethanol has no impurities such as sulfur, which is found in some fossil fuels and can poison the catalysts in downstream processes. Moreover, ethanol has the characteristics of non-toxicity, easy transportability, and when steam reformed, a high theoretical hydrogen yield (6 moles of H₂ per mole of C₂H₅OH). Hydrogen production from bio-ethanol through steam reforming also has the potential to resolve many of the issues involved in hydrogen storage and hydrogen delivery infrastructure, and lends itself very well to a distributed hydrogen production strategy. All these considerations render bio-ethanol an economically and environmentally attractive energy starting material for H₂ production. Currently there is no commercial catalyst for bio-ethanol reforming, mainly due to the relatively higher cost compared with methane steam reforming. In addition, many fundamental questions in catalytic reforming of ethanol still remain, such as the nature of active sites, the network of competing reactions and catalyst deactivation.

Ethanol reforming is an endothermic reaction.



Although the reaction looks simple enough, in reality, depending on the reaction conditions and catalysts used, the product distribution can be governed by a very complex network of reactions, including hydrogenation, dehydrogenation, hydration, methanation, reverse water–gas shift reaction, Boudouard reaction, and coking. There have been several

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studies in the literature on ethanol steam reforming catalysts. Catalysts utilized are mainly Ni, Cu and supported noble metals, such as Rh, Pd and Pt.¹ Although supported noble metal catalysts have been shown to have significant activity in 500–600 °C range and high space velocities,^{2–5} the high cost of these metals limits their application. As a less expensive alternative, cobalt-based catalysts have been reported to have superior ethanol steam reforming performance due to their high activity for C–C bond cleavage at temperatures as low as 350–400 °C.^{6–8} At these temperatures, researchers have reported good selectivity to CO₂ and H₂, with CH₄ being the only by-product.

While Co catalysts are reported to have activity for ethanol steam reforming, the catalyst preparation methods and the pretreatment conditions used for these catalysts are known to have great influence on the nature of cobalt and cobalt oxide species formed on the surface, thus determining the catalytic properties. Synthesis of highly dispersed Co catalysts requires the initial formation of fine CoO or Co₃O₄ crystallites, as indicated by Tsubaki's work.⁹ They used different solvents including water, dehydrated ethanol and cyclohexanol to dissolve Co precursors and found that depending on the solvent, the interaction of Co particles and support during precipitation and calcination varied significantly, resulting in different particle sizes, distributions and reaction performance. Llorca *et al.*⁷ did similar work on a ZnO-supported Co system by impregnation of nitrate and carbonyl cobalt precursors. They use Co₂(CO)₈ as a precursor to produce a highly stable and selective catalyst for CO-free hydrogen production at low reaction temperature (623 K). Ho and Su¹⁰ impregnated Co precursor into the silica support by using two solvents, ethanol and water. Smaller Co₃O₄ crystallites and more Co–SiO₂ interaction species were obtained when catalysts were prepared with ethanol instead of an aqueous solution. They attributed it to the presence of a surface ethoxy group which might hinder the aggregation of Co₃O₄ during its formation from the thermal decomposition of cobalt nitrate. This leads to differences in surface cobalt dispersion and catalyst reducibility, and thus reaction activity. Kaddouri and Mazzochia¹¹ synthesized Co supported on SiO₂ and Al₂O₃ by three preparation methods, incipient wetness, sol-gel and a combination of the two methods. The hydrogen selectivity and product distribution were found to be dependent on the preparation procedure and on the nature of the support used. Ruckenstein and Wang¹² investigated effects of preparation method and heat treatment conditions on steam reforming Co–MgO catalysts. The extent of solid solution formation was found to increase as the calcination temperature and calcination time increased. From TPR studies, degree of reduction increased with increasing calcination temperature up to 600 °C and then decreased with further increase in calcination temperature.

Goodwin *et al.*¹³ studied the effect of calcination and reduction temperatures on the activity of a Ru-promoted Co–Al₂O₃ catalyst for CO hydrogenation reaction. The calcination temperature was found to have a pronounced effect on the overall activity of the catalyst but the reduction temperature had only a negligible effect. Higher calcination temperatures caused a decrease in the number of surface active

sites and the reducibility of the catalyst decreased as well. Enache *et al.*¹⁴ examined several thermal treatment protocols for zirconia- and alumina-supported cobalt catalysts. It was found that the direct reduction of nitrate precursor lead to weaker metal support interactions than in the case of calcined catalysts and increases the quantity of metallic cobalt. Calcination atmosphere also had an effect on the crystallinity of Co₃O₄ formed, which is directly related with catalyst reducibility.

The nature of active sites in Co-based catalysts has also been examined by several researchers. Borgmann *et al.*¹⁵ characterized cobalt catalysts supported on different oxides. Through X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), Co was observed as Co₃O₄ phase after calcination in Co–SiO₂ and CoO phase in Co–TiO₂ and Co–Al₂O₃ samples. Co₃O₄ in the sample can go through a two-step reduction: first to CoO and then to metallic Co. Ticianelli's work^{16,17} identified Co metallic sites as the active phase for steam reforming of ethanol. By using temperature programmed reduction (TPR) and TEM, Freni *et al.*¹⁸ came to the conclusion that the metallic Co constitutes the active sites, but these sites could be reoxidized and cause deactivation for reforming reaction. By combination of XRD, Raman and TEM, Llorca *et al.*⁷ studied the Co phase in Co–ZnO catalysts. If there was no pre-reduction, the post-reaction catalysts only exhibited CoO. If the catalysts were pre-reduced, however, CoO and metallic Co were seen to coexist. By magnetic studies, Llorca *et al.*¹⁹ calculated the amount of metallic Co after reaction and after reduction. They concluded that both CoO and Co may be involved in the ethanol reforming reaction. Crystallite size of Co was found to affect ethanol adsorption on the Co–Al₂O₃ system and have a strong effect on ethanol reforming activity and selectivity.²⁰

In an earlier publication, we have reported the effect of different supports on the activity of Co-based catalysts in ethanol steam reforming.²¹ In this study, we report the effect of synthesis parameters on the BESR activity of ZrO₂-supported cobalt catalysts prepared by incipient wetness impregnation method. Effects of calcination temperature, reduction temperature, and reduction time were examined systematically. Characterization was performed using BET surface area measurement, H₂ chemisorption, TPR, temperature programmed oxidation (TPO), XRD, XPS, temperature programmed calcination (TPC), thermogravimetric analysis (TGA), ethanol pulse chemisorption, and temperature programmed reaction (TPRxn) techniques. It was found that under different treatments, physical and chemical properties of the catalyst vary significantly, affecting the catalytic performance in ethanol steam reforming.

2. Experimental

2.1. Catalysts preparation

Supported cobalt catalysts with 10 wt% metal loading were prepared in air by incipient wetness impregnation from cobalt (II) nitrate hexahydrate (Aldrich 99.999%) aqueous solution. The support used was ZrO₂ (Saint Gobain) with a surface area and pore volume of 55 m² g^{−1} and 0.21 cm³ g^{−1}, respectively. The support pellets were ground and then sifted to obtain a

100–150 mesh particle size. The sifted support was then calcined for 3 h in air at 500 °C prior to impregnation. After repeating the impregnation and drying steps (at 95 °C) as many times as determined by the pore volume of the ZrO₂ support, the resulting samples were divided into seven aliquots. Each of them was calcined at a different temperature for 3 h in the air and stored for use.

2.2. Catalysts characterization and activity tests

The surface areas of the prepared samples were measured using nitrogen adsorption at 77 K (Micromeritics ASAP 2010).

The volumetric measurement of H₂ chemisorption was conducted using a Micromeritics ASAP 2010 chemisorption system. Prior to adsorption measurements, calcined samples were reduced *in-situ* under 5% H₂-He at the desired reduction temperature for various times, followed by evacuation to 1.33–0.67 KPa and cooling down to 100 °C to maximize activated chemisorption while minimizing H₂ spillover.²² The adsorption isotherms were measured at equilibrium pressures between 6.67–66.7 KPa. The first adsorption isotherm was established by measuring the amount of H₂ adsorbed as a function of pressure. After completing the first adsorption isotherm, the system was evacuated for 1 h at 1.33–0.67 KPa. Then a second adsorption isotherm was obtained. The amount of probe molecule chemisorbed was calculated by taking the difference between the two isothermal adsorption amounts. Metallic surface area was determined by assuming a one-to-one stoichiometry between Co and atomic hydrogen and a cross-sectional area of 0.0662 nm² for a Co atom.

XRD profiles were collected from 20° to 90° at a step width of 0.0144° using a Bruker D8 Advance X-Ray Diffractometer equipped with a CuK α source. *In-situ* XRD was also performed during calcination and reduction processes under air and 5% H₂-N₂, respectively, using a linear heating rate of 10 °C min⁻¹ and holding at different preset temperatures for a given time for stabilizing and data collection.

XPS analysis was performed using an AXIS His, 165 Spectrometer manufactured by Kratos Analytical with a monochromatized Al X-ray source. A voltage of 2.3 V was chosen to balance the charging. A stainless steel holder was employed to support catalysts. The survey scan was performed to identify all the elements within the sample, followed by regional scans for Co 2p, C 1s, O 1s, Zr 3d orbitals in order to achieve the high resolution for elements of interest.

The calcination process was investigated through a TPC technique. The sample was sandwiched within two layers of quartz wool in a stainless steel reactor which was placed in the center of a temperature programmable furnace. A constant air flow rate was maintained over the sample throughout the process and the reactor outlet stream was monitored by a Cirrus Mass Spectrometer (MKS Instruments, 1–300 amu).

H₂ TPR experiments were performed using a laboratory flow system equipped with a thermal conductivity detector. Samples of 100 mg were subjected to an oxidative cleaning step at the samples' calcination temperature in air, followed by cooling to room temperature under helium. TPR experiments were subsequently performed under 5% H₂-N₂ (30 ml min⁻¹) with a heating rate of 10 °C min⁻¹.

The TPR–TPO–TPR was performed using an Autochem-2920 (Micromeritics). The sample was first reduced under 10% H₂-Ar with a heating rate of 10 °C min⁻¹. After cooling down under helium, the sample was subsequently oxidized under 10% O₂-He with the same heating rate followed by the second TPR running under the same condition as the first one.

TGA experiments were performed using a TG-DSC 111 (SETARAM). Samples were first pretreated under helium (30 ml min⁻¹) at 400 °C for 30 min and then cooled down to the room temperature under helium. The mass signal was subsequently recorded during the temperature programmed increase with a ramp rate of 5 °C min⁻¹ under 5% H₂-N₂ (30 ml min⁻¹).

The ethanol pulse chemisorption experiments were performed using an AutochemII 2920 at room temperature to measure the ethanol uptake capability of the catalysts prepared under various conditions. The sample loop was calibrated by injections of a known volume of argon through the analyzer septum using a syringe. The ambient temperature and pressure corrections were incorporated for each measurement. The effluent from the sample was monitored by a Cirrus mass spectrometer by following the *m/z* ions of 2, 16, 18, 8, 31, 43, 44, 58, 59, and 60.

TPR_{rxn} experiments were performed using a Cirrus MS (MKS Instruments, 1–300 amu) to monitor reactor outlet composition. The H₂ signal was corrected using H₂-He flow of known concentration before each reaction for catalytic activity comparison. The samples of 100 mg were pre-reduced (5% H₂-He at 30 ml min⁻¹) at pre-designated temperatures and cooled to room temperature under helium. The feed for the TPR_{rxn} experiments was provided by saturating helium streams with water and ethanol in a double-bubbler arrangement to provide an ethanol : water molar ratio of 1 : 10. The total flow rate was set at 60 ml min⁻¹. After stabilization of water and ethanol signals, the temperature was ramped at 10 °C min⁻¹ while the product signals were monitored by a mass spectrometer.

3. Results and discussion

3.1. BET

The surface areas of the samples calcined at different temperatures were measured using the BET technique. The results are shown in Fig. 1. As expected, the surface area

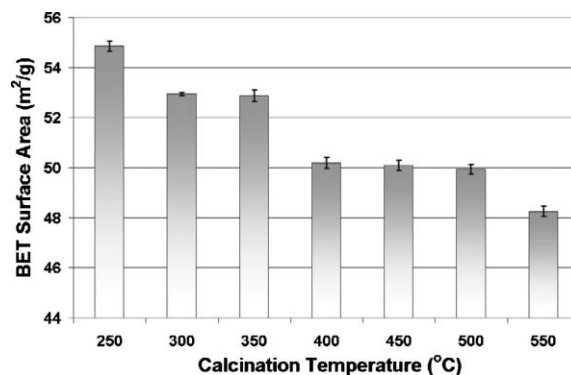


Fig. 1 BET surface areas of 10 wt% Co-ZrO₂ calcined at different temperatures.

decreases from $55 \text{ m}^2 \text{ g}^{-1}$ to $48 \text{ m}^2 \text{ g}^{-1}$ as the calcination temperature increases from 250° to 550°C . There are three distinct steps in the surface area decrease, between 250 and 300°C , between 350 and 400°C , and between 500 and 550°C . The first step may signal the decomposition of the nitrate left behind from the synthesis. The second step may be due to the onset of crystallization of the Co oxide species. The final decrease observed at higher temperatures may be due to sintering and/or strong interaction between the support and the metal. The changes in the overall surface area are expected to affect the reducibility of the catalysts as well as their metallic surface areas, as will be discussed in the next sections.

3.2. H_2 chemisorption

Using a constant reduction temperature of 350°C ($5\% \text{ H}_2$ for 2 h), the metallic surface areas of the samples calcined at different temperatures were measured. The results are shown in Fig. 2 (cobalt dispersion data are incorporated). A gradual increase in Co surface area was observed up to 400°C followed by a sharper decline at higher calcination temperatures. This indicates that 400°C is the optimum calcination temperature that will allow for the highest metallic surface area. The sintering of the cobalt oxide particles or the metal-support complex formation may suppress the reducibility of the sample, which results in a decrease of cobalt dispersion at higher calcination temperatures.

To examine the effect of reduction temperature on the cobalt dispersion of the $10 \text{ wt}\%$ Co catalysts, several batches of the catalyst calcined at 400°C but reduced at different temperatures ($5\% \text{ H}_2$ for 2 h) were used in hydrogen chemisorption experiments. The results, which are given in Fig. 3 (cobalt dispersion data are incorporated), indicate that the highest metallic surface area is obtained at 350°C , after which a decline is observed. The sintering of the reduced metal cobalt particles could contribute to the decline of the cobalt dispersion at higher reduction temperatures.

The effect of reduction time was also examined by using samples calcined at 400°C . The reduction temperature was kept constant at 350°C while the duration of reduction was varied. The results are presented in Fig. 4 (cobalt dispersion data are incorporated). The metallic surface area was seen to increase up to 2 h and then steadily declined with the

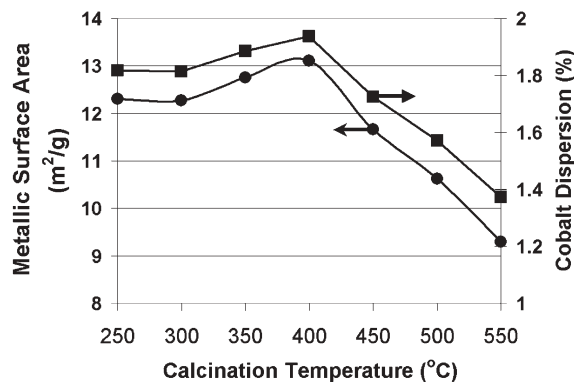


Fig. 2 Metallic surface areas of $10 \text{ wt}\%$ Co– ZrO_2 calcined at different temperatures after reduction treatment at 350°C for 2 h.

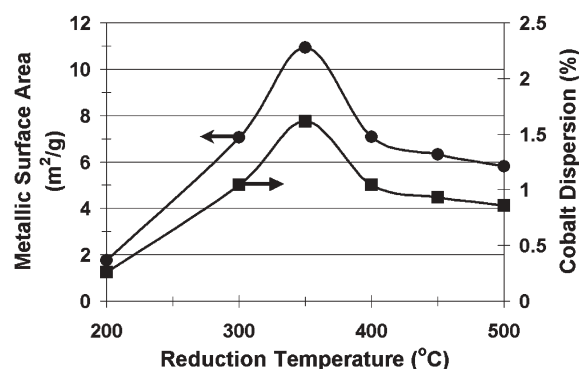


Fig. 3 Metallic surface areas of $10 \text{ wt}\%$ Co– ZrO_2 calcined at 400°C and reduced at different temperatures for 2 h.

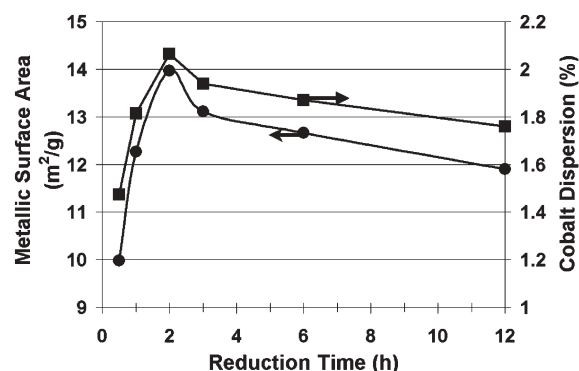


Fig. 4 Metallic surface areas of $10 \text{ wt}\%$ Co– ZrO_2 calcined at 400°C and reduced at 350°C for different lengths of time.

increasing reduction time. The maximum in the metallic surface area is likely due to competing effects of increased extent of reduction and increased agglomeration of the metal with increasing reduction time.

3.3. XRD

In order to identify the crystalline phases present in the cobalt catalysts after calcination and after reduction, XRD experiments were performed. The X-ray diffraction pattern of a catalyst calcined at 400°C is presented in Fig. 5. The diffraction line at 36.96° can be identified as the (311) crystal plane reflection from the cubic Co_3O_4 phase. The other diffraction lines in Fig. 5 can be assigned to the monoclinic ZrO_2 crystal phase. The intensity of the Co_3O_4 pattern is very weak, implying that Co_3O_4 is well dispersed on ZrO_2 surface and not highly crystalline. There are no other phases detected.

The calcination process of the catalyst precursor was investigated using *in-situ* XRD technique. As shown in Fig. 6, the monoclinic ZrO_2 support is visible at each temperature. However, there is no crystalline phase associated with Co in the catalyst precursor until a calcination temperature of 250°C is reached. The diffraction line that corresponds to cubic Co_3O_4 increases with increasing calcination temperature. Above a calcination temperature of 400°C , the area of the Co_3O_4 peak does not change. The sharpening of the Co_3O_4 peak at higher temperatures implies the sintering of the Co_3O_4 particles.

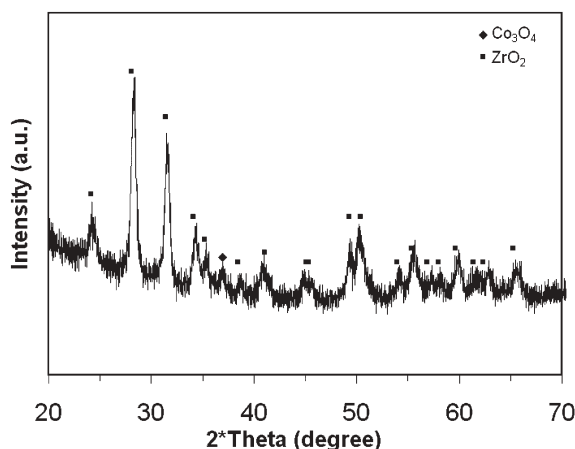


Fig. 5 The XRD pattern of 10 wt% Co-ZrO₂ after calcination at 400 °C for 3 h.

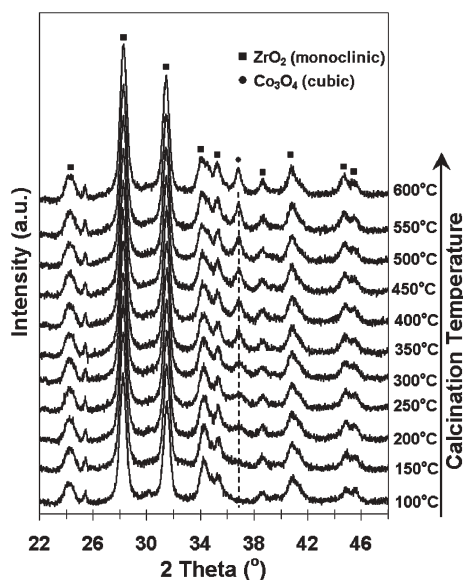


Fig. 6 *In-situ* XRD patterns of 10 wt% Co-ZrO₂ during calcination in air.

The evolution of the crystalline phases during the reduction process is also shown through the *in-situ* XRD patterns acquired during reduction (Fig. 7). The disappearance of the Co₃O₄ phase along with the appearance of the CoO phase coincides at a reduction temperature of 350 °C. The diffraction line that corresponds to the CoO phase disappears above 450 °C and a metallic Co phase appears at 525 °C.

3.4. XPS

The Co 2p regions of the XPS spectra of the 10% Co-ZrO₂ calcined at different temperatures are shown in Fig. 8. At lower calcination temperatures there are very weak and broad features at about 6 eV higher binding energy from the main peaks, which may be due to shake-up lines, suggesting the presence of some Co²⁺ species on the surface. This may be due to nitrate species left behind from the impregnation step or to a CoO phase. At higher calcination temperatures (>400 °C), this

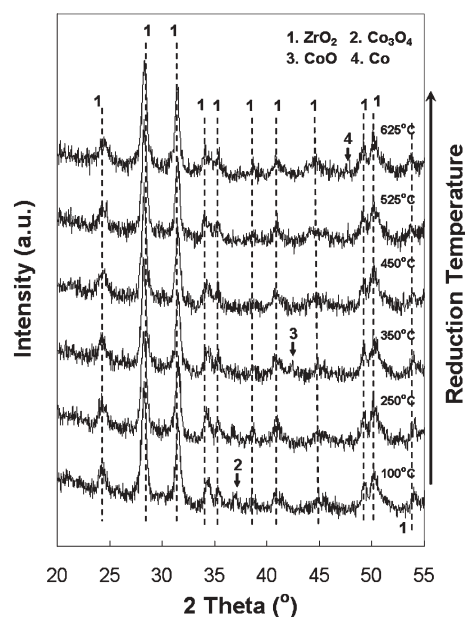


Fig. 7 *In-situ* XRD patterns of 10 wt% Co-ZrO₂ during reduction under 5% H₂-N₂. Catalysts were calcined at 400 °C for 3 h.

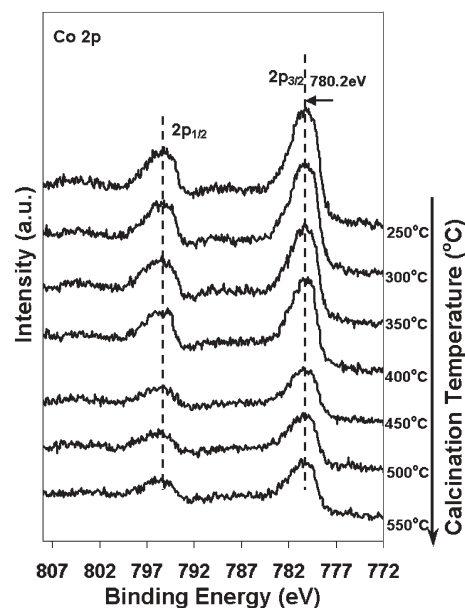


Fig. 8 XPS spectra of 10 wt% Co-ZrO₂ calcined at different temperatures for 3 h.

feature disappears, indicating that a significant amount of cobalt was in the Co³⁺ oxidation state, consistent with Co₃O₄ in which 2/3 of the cobalt is in the Co³⁺ oxidation state. The absence of clear shake-up peaks on these samples containing 10% Co is not surprising, since even the shake-up peaks observed from bulk Co₃O₄ were relatively weak.^{23–25} Calcination at higher temperatures (>450 °C) leads to a decrease in intensity. From this observation, it appears that the cobalt oxide particles begin to sinter with the increasing calcination temperature above 450 °C, resulting in a decrease in Co surface concentration.

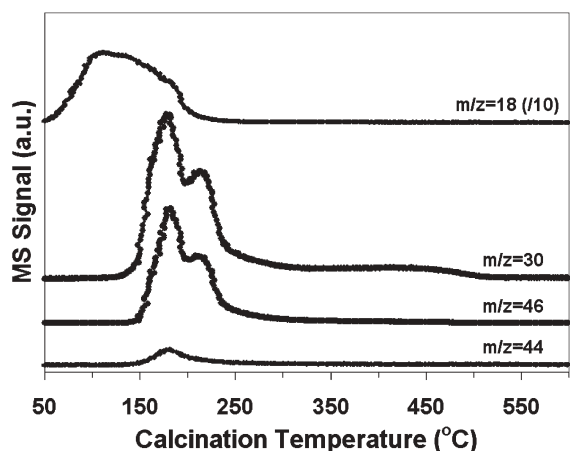


Fig. 9 Evolution of different species during the calcination process for 10 wt% Co-ZrO₂.

3.5. TPC

The evolution of the catalyst during the calcination process was also examined by calcining the sample in an air stream using a linear temperature program, while monitoring the gas phase effluents by an on-line mass spectrometer. The products eluting from the sample during the calcination process are shown in Fig. 9. As expected, the water and NO_x (determined by $m/z = 30$ and 46 ion fragments) result from the decomposition of the cobalt precursor, Co(NO₃)₂·6H₂O. The $m/z = 30$ signal could be due to fragmentation of NO₂, however formation of NO cannot be ruled out. The elution of NO_x up to temperatures well above 300 °C supports our earlier assertion that part of the Co may still be in a nitrate matrix when calcined below 400 °C, as seen through the XPS results. The water signal may also have a contribution from adsorbed H₂O. The CO₂ signal is also due to the CO₂ adsorption from the atmosphere during sample handling.

3.6. TPR

The TPR profiles of the samples calcined at different temperatures are shown in Fig. 10(a). The first small peak at lower calcination temperature comes from residual nitrate from the catalyst preparation, since, as seen in Fig. 9, the cobalt precursor is not completely decomposed until 400 °C. The first major feature is due to Co₃O₄ → Co²⁺ reduction and the second main feature results from the Co²⁺ → Co reduction step. The identification of the reduction steps was verified by measuring the hydrogen consumption through CuO reduction calibration. When the H₂ consumption quantified in the first peak is compared to the amount of H₂ needed for the Co₃O₄ + H₂ → 3CoO + H₂O reduction step, the relative error is found to be around 10%. When a similar comparison is carried out between the H₂ consumed in the second step and H₂ needed for the CoO + H₂ → Co + H₂O reduction, the relative error is about 5%. The TPR results agree very well with the *in-situ* XRD data, which showed the disappearance of Co₃O₄ and the formation of CoO around 350 °C and the formation of metallic Co above 450 °C under a linear temperature program.

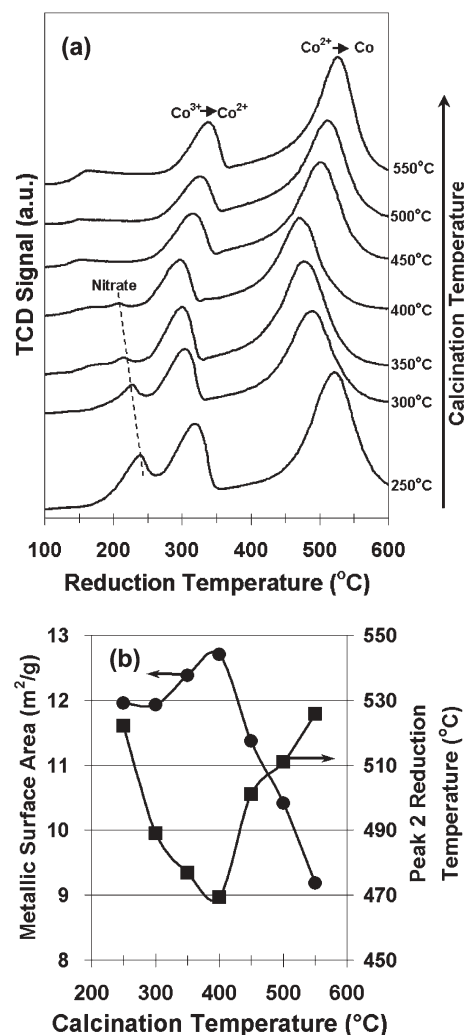


Fig. 10 (a) H₂ TPR profiles of 10 wt% Co-ZrO₂ calcined at different temperatures for 3 h, and (b) correlation of reducibility with H₂ chemisorption results.

Fig. 10(b) shows the variation of the second reduction peak temperature with calcination temperature. It is seen that the temperature for this second reduction step goes through a minimum with increasing calcination temperature. When the metallic surface area measured from H₂ chemisorption experiments is plotted on the same graph, the two curves show a mirror image of one another. Initial increase of reducibility may be due to structural changes in the cobalt phase as the nitrate phase decomposes and the Co₃O₄ phase is formed. Much higher calcination temperatures, on the other hand, lead to the sintering of the cobalt oxide particle, which contributes to the final decrease of the reducibility. The sample calcined at 400 °C has the minimum reduction temperature and should thereby be the easiest to reduce. The H₂ chemisorption results indicate that this sample has also the maximum metallic surface area. The calcination temperature of 400 °C is also the lowest at which residual nitrate from the preparation is not present in the calcined sample. Based on these results, 400 °C is chosen as an optimum calcination temperature for these catalysts.

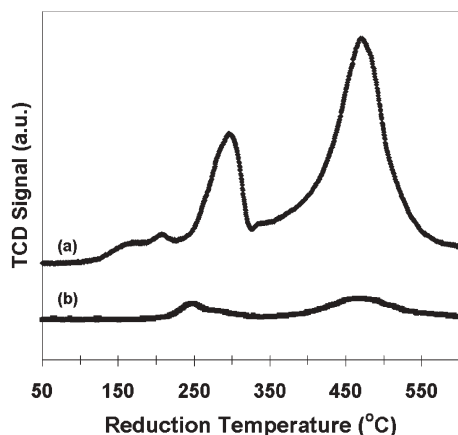


Fig. 11 H_2 TPR profiles of 10 wt% Co- ZrO_2 calcined at 400 °C for 3 h: (a) without pre-reduction treatment, (b) with pre-reduction treatment at 350 °C for 2 h.

One of the questions that come to mind is whether a reduction temperature of 350 °C is sufficient to obtain metallic Co sites, since the bulk reduction to metallic Co takes place at a much higher temperature under a linear temperature ramp. To answer this question, a TPR experiment similar to the one described above was performed over a catalyst sample that was calcined at 400 °C and reduced at 350 °C for 2 h. The resulting TPR profile is shown in Fig. 11. The TPR profile from a calcined sample is also included for comparison. Very low hydrogen consumption seen over this pre-reduced sample (manifested as a flat TPR profile) indicates that the pre-reduction treatment at 350 °C is sufficient to reduce most, if not all of the cobalt to metallic Co. Although under a linear temperature program, the reduction is not complete until much higher temperatures are reached, if the temperature is held for a longer time, the reduction process will proceed until the cobalt oxide is fully transformed into metallic cobalt even at lower temperatures.

3.7. TPR–TPO–TPR

The TPR–TPO–TPR experiment was performed on 10% Co- ZrO_2 calcined at 400 °C, the results of which are shown in Fig. 12. The sample, which went through an initial TPR

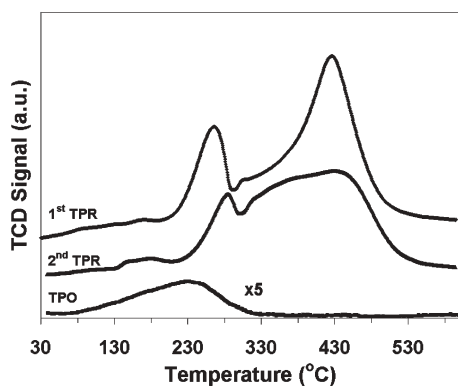


Fig. 12 TPR–TPO–TPR profiles of 10 wt% Co- ZrO_2 calcined at 400 °C for 3 h.

process was oxidized under a similar temperature profile and then the TPR was repeated. Unlike the H_2 signal, the O_2 consumption signal is very weak since TCD has much less sensitivity for O_2 . Therefore, the O_2 consumption signal in Fig. 12 has been multiplied by 5 for better observation. As can be seen from Fig. 12, two reduction peaks are still observed after the oxidation of cobalt, which indicates that during the TPO step, the metal cobalt has been fully oxidized into Co_3O_4 rather than to CoO . However, a higher starting point of the reduction and broader second peak indicate that the sample is harder to reduce. Moreover, after integration, the area under the second TPR curve is seen to be smaller than that of the first H_2 consumption curve, which indicates that part of the sample has been sintered during the first TPR step at higher reduction temperatures. This amount of sample could not be oxidized, and consequently, could not be reduced again. Interaction of cobalt with the support at higher reduction temperatures to form some metal-support complex is also a possibility.

3.8. TGA

The reduction process of the sample is also investigated through the TGA technique. As shown in Fig. 13, three mass losses in the TG signal and corresponding peaks in DTG curve (first derivative of the TG signal) are readily apparent. The first small peak comes from residual nitrate decomposition from the catalyst preparation. The first reduction peak is due to $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ and the second reduction peak comes from $\text{Co}^{2+} \rightarrow \text{Co}$, which are calculated from the mass change. The results are consistent with the H_2 TPR profile in Fig. 11(a).

3.9. Ethanol pulse chemisorption

Because the catalytic performance of these materials may be directly linked to their ethanol adsorption capacity, pulsed chemisorption experiments were performed over catalysts that were exposed to different pretreatment parameters. The results from one such series of experiments are presented in Fig. 14. In these experiments, samples calcined at 400 °C were pre-reduced at 350 °C for different time periods, then ethanol vapor was pulsed over the sample at room temperature and each pulse was sent to the TCD detector. In the same Figure, the relationship between metallic Co surface area and reduction time determined by H_2 chemisorption is also presented. It is interesting to note that the reduction time that gives the

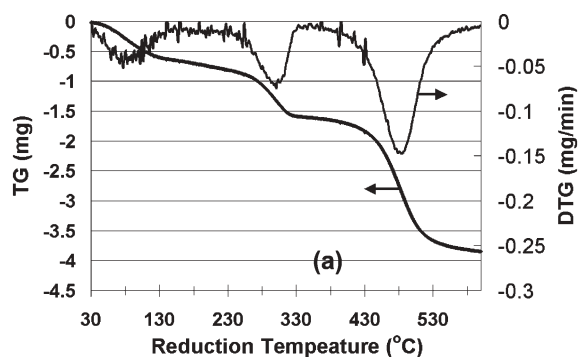


Fig. 13 TGA curves during reduction over 10 wt% Co- ZrO_2 calcined at 400 °C for 3 h.

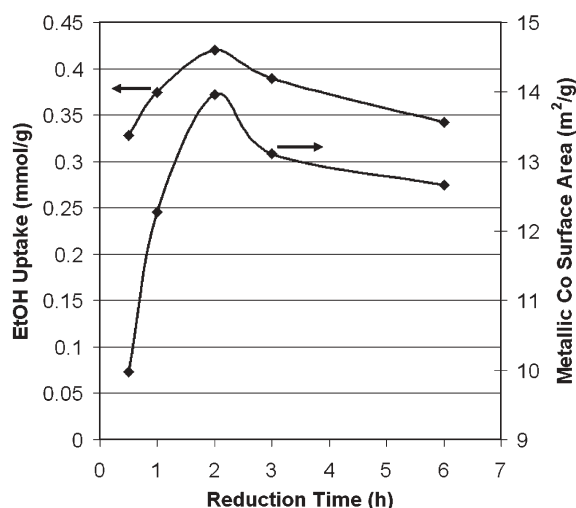


Fig. 14 Variation of ethanol chemisorption capacity with the length of reduction time for 10 wt% Co–ZrO₂ calcined at 400 °C and reduced at 350 °C. Variation of metallic Co surface area with reduction time is included for comparison.

highest ethanol uptake coincides with the reduction time that gives the highest metallic Co surface area. The similarity of the trends in these two measurements strongly suggests that the metallic Co centers constitute the active sites for ethanol adsorption in BESR.

3.10. TPRxn

The TPRxn experiments were performed for samples calcined at 400 °C and reduced at different temperatures for 2 h. The maximum in the hydrogen signal in each run has been plotted as a function of reduction temperature (shown in Fig. 15). The variation of metallic Co surface area with the reduction temperature is also plotted in the same Figure for comparison. As can be seen from Fig. 15, the TPRxn results are in agreement with the chemisorption results, showing similar overall trends, especially for reduction temperatures above 200 °C. The reduction temperature which leads to the maximum H₂ formation is also the reduction temperature which gives the highest metallic surface area. The observation

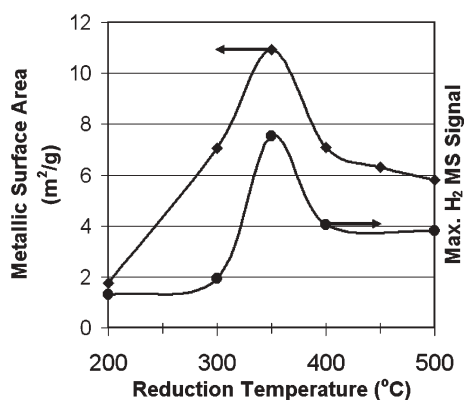


Fig. 15 Variation of H₂ yield with reduction temperature for 10 wt% Co–ZrO₂ calcined at 400 °C. Variation of metallic Co surface area with reduction temperature is included for comparison.

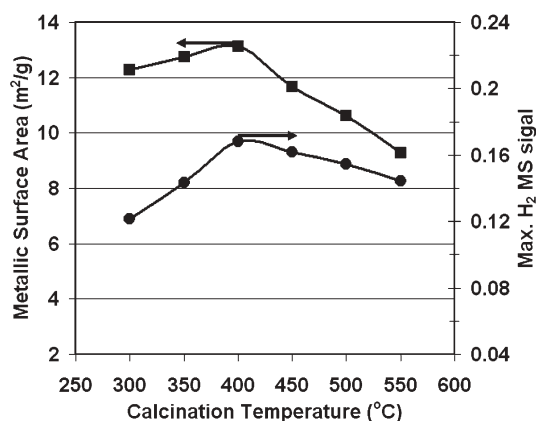


Fig. 16 Variation of H₂ yield with calcination temperature for 10 wt% Co–ZrO₂ reduced at 350 °C for 2 h. Variation of metallic Co surface area with calcination temperature is included for comparison.

that the trend does not continue for the lowest reduction temperature can be explained by the fact that when the catalyst is mostly in an oxide phase there may be other reactions, besides the steam reforming of ethanol, that dominate the reaction network and these reactions may take place on active sites other than the metallic Co sites.

A similar comparison was made by performing TPRxn experiments over catalysts calcined at different temperatures, but reduced at 350 °C for 2 h. The maximum in H₂ signal is plotted against calcination temperature as seen in Fig. 16. The variation of metallic Co surface area with calcination temperature is also plotted in the same Figure for comparison. Again, there appears to be a close correlation between the H₂ yield and the metallic Co surface area. The dependence of both ethanol adsorption capacity and H₂ yield on the metallic Co surface area strongly suggests that metallic Co centers are the active sites in BESR reaction.

It should be noted that in Fig. 15 and Fig. 16 although the general trends are similar, there may not be an exact correlation at each temperature point. As described in the introduction section, many side reactions which could affect the H₂ yield might take place at different temperature regions besides the BESR reaction, such as ethanol dehydration or dehydrogenation at lower temperature and reverse water–gas shift at higher temperature. Therefore, the accurate correlation of the BESR activity with the metallic Co sites might be difficult, due to the complex networks of reactions governing the H₂ production.

4. Conclusions

Investigation of the evolution of the Co–ZrO₂ catalysts through different stages of the synthesis process showed that catalyst precursors start out with Co existing primarily in a nitrate phase and transforming into a Co₃O₄ phase in the fully-calcined state. The reduction proceeds in two distinct steps as in Co₃O₄ → CoO and CoO → Co. There is an optimum in each of the synthesis parameters, which gives the highest metallic Co surface area. The maximum in metallic Co area is often determined by a series of competing processes, such as transformation from a nitrate to an oxide phase and onset of

crystallinity *versus* reaction with the support at higher calcination temperatures, reduction to metallic state *versus* sintering at higher reduction temperatures. The maximum in metallic Co area was seen to coincide with the maxima in both ethanol adsorption capacity and H₂ yield in the BESR reaction, suggesting a strong correlation between metallic Co sites and BESR activity. The steady-state reaction studies, which will be presented in the next article of this series, provide further evidence that metallic Co centers may be the active sites for the bio-ethanol steam reforming reaction.

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A nanoporous polymeric sorbent for deep removal of H₂S from gas mixtures for hydrogen purification†

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A nanoporous composite sorbent (PEI/SBA-15) was developed by the wet impregnation loading of a linear polyethyleneimine (PEI) on a mesoporous molecular sieve SBA-15, which was prepared by hydrothermal synthesis. The sorbent was characterized by XRD at low angles, N₂ physisorption, scanning electron microscopy (SEM) and FT-IR. The sorption performance of the sorbent for removing H₂S from H₂-containing gas mixtures was evaluated in a flow system. The characterization results showed that after PEI loading, PEI was dispersed inside the meso-channels of SBA-15 with almost no change of the SBA-15 structure, and the interaction of amine groups in PEI with the functional groups on the SBA-15 surface may anchor PEI on the inner surface of SBA-15. The effects of the inlet H₂S concentration and co-existing moisture on the sorption performance were examined. With increasing inlet H₂S concentration, both the breakthrough capacity and the saturation capacity increased. The sorption of H₂S on the PEI/SBA-15 sorbent can be expressed by the Langmuir adsorption isotherm. A higher sorption capacity was observed in the presence of moisture, indicating that moisture has a promoting effect on the sorption removal of H₂S from gas streams on the PEI/SBA-15 sorbent. However, the desorption rate of the sorbed H₂S was also reduced in the presence of moisture. The sorption/desorption cycles showed that the PEI/SBA-15 sorbent had a good regenerability and stable sorption performance.

Introduction

Purification is an important task in the processing of various industrial gas streams such as natural gas, synthesis gas and hydrogen gas. Related to gas purification is the development of the integrated gasification combined cycles (IGCCs), which is one of the most promising technologies for advanced power generation from coal. In IGCC technology, it is important to remove pollutants, such as hydrogen sulfide, from coal-derived gas. Hydrogen sulfide is not only harmful to human health and corrosive to pipelines in a wide number of industrial installations, but also poisons the gas turbine, and the fuel-processing catalysts and anode catalysts in fuel cell system.^{1,2} Thus significant attention has been focused on the development of various materials and methods to remove hydrogen sulfide for IGCC and/or for fuel cell applications.

Currently, wet processes using basic organic amine solvents are commercially used worldwide for removing hydrogen sulfide from gas streams. The major drawbacks include high energy consumption, low adsorption/desorption rate and amine loss in regeneration. Many metal oxides (Zn, Ca, Cu, Mn, Mo, W) have been studied to develop regenerable

sorbents at high temperature (>300 °C).^{3–8} Recently, various metal oxides, such as Ag, Cu, Ni, Zn, Ti, Fe oxide and their mixtures, have been used as sorbents for removing hydrogen sulfide from gas streams at low temperatures (<100 °C).^{9–16} However, the regeneration of these spent sorbents needs still to be conducted at high temperature (>500 °C).

A new concept called ‘molecular basket’ has been developed more recently in our laboratory for the design of a high-capacity and highly selective CO₂ sorbent.^{17–20} In the ‘molecular basket’ sorbent, a polymer with a high density of desired amine groups, such as polyethyleneimine (PEI), was packed into the channels of a mesoporous molecular sieve such as MCM-41. Since H₂S is also an acid gas like CO₂, it is expected that the sorbent may be able to remove H₂S besides CO₂ through an acid–base interaction. In a previous study in our laboratory, Xu *et al.* reported that the H₂S concentration could be decreased to less than 40 ppbv using a PEI/MCM-41 sorbent at 90 °C.²¹ Huang *et al.* reported that an amine-grafted MCM-48 sorbent was able to capture CO₂ and H₂S.²² Our approaches in computational chemistry also showed that the amine group can interact with H₂S, although it is weaker than that with CO₂.^{23,24} In addition, it was reported that moisture has a promoting effect on the sorption of CO₂ by the MCM-41-supported PEI sorbents,²⁵ while the H₂S adsorption was barely affected by the presence of water on the amine-grafted MCM-48 sorbent based on the temperature programmed desorption (TPD) results,²² although there was no direct evidence to support it. On the other hand, moisture has been reported to show a positive effect on H₂S removal over activated carbon adsorbents.^{26–28} Whether and how moisture

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affects the sorption performance of the supported-PEI sorbent remains to be clarified.

In a previous work, we have studied the effect of different sorption conditions, and different mesoporous molecular sieves as a support on the H₂S sorption performance of the supported-PEI sorbent.²⁹ In the present study, the effect of PEI loading on the structure and the sorption performance, the adsorption isotherm of the PEI/SBA-15 sorbent for H₂S removal, the effect of moisture co-existence and the stability of the PEI/SBA-15 with moisture are further examined and discussed.

Experimental

Preparation of the sorbents

Mesoporous molecular sieve SBA-15 was hydrothermally synthesized according to the method in the literature.^{29–31} Typically, a homogeneous mixture, which was composed of triblock copolymer Pluronic P123 (EO₂₀PO₇₀EO₂₀, MW = 5800, Aldrich) and tetraethyl orthosilicate (TEOS) in hydrochloric acid, was stirred at 40 °C for 20 h and further treated at 100 °C for 24 h. After the synthesis, the resultant solid was recovered by filtration, washed, dried at 100 °C overnight and finally calcined at 550 °C for 6 h to remove the template.

The SBA-15-supported PEI sorbents were prepared by a wet impregnation method. In a typical preparation, 4.0 g of PEI (linear PEI with a MW of 423 from Aldrich) was dissolved in 32 g of methanol under stirring, and then 4.0 g calcined SBA-15 was added to the above solution and further stirred at room temperature for 8 h. The slurry was then dried with continuous stirring at room temperature. Before sorption, the sorbent was pretreated at 100 °C with nitrogen (99.999%) at 50 mL min^{−1} flow overnight.

Characterization of the sorbents

The SBA-15-supported PEI sorbent was characterized by XRD, N₂ physisorption, SEM and FT-IR. XRD was performed with a Rigaku Geigerflex X-ray diffractometer with Cu K α radiation (λ = 0.154 nm) at low angle range (2θ = 0.6–7°). N₂ physisorption was carried out at liquid-N₂ temperature with a Micromeritics ASPS 2010 analyzer to examine the porosity and surface area of each sample. The sample was pretreated at 75 °C in a high vacuum for 48 h before N₂ adsorption. The scanning electron microscopy (SEM) images were obtained on a Hitachi S-3500N instrument operating at 5 kV. A Nicolet NEXUS 470 FT-IR spectrometer (Thermo Electron Corp.) was used to obtain the IR spectra in our laboratory on the SBA-15 and PEI/SBA-15 samples. The resolution was 4 cm^{−1} and KBr was used as background.

H₂S sorption measurement

A fixed-bed flow system was assembled in our laboratory, which was coupled with an on-line H₂S analyzer (ANTEK 9000NS) (Fig. 1). The sorption tube was made of Pyrex glass with outer diameter of 12.5 mm and inner diameter of 11.5 mm. The sorbent bed was at the center of the tube and the residual place in the tube was filled with inert glass beads. Before sorption, the sorbent bed was heated to 100 °C in nitrogen at a

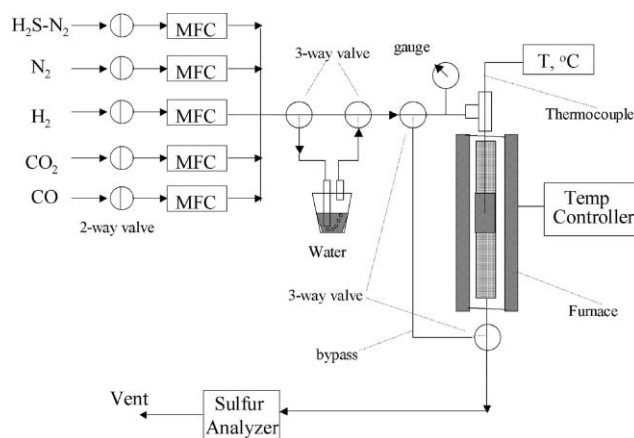


Fig. 1 Schematic of the fixed-bed flow system for H₂S adsorption measurements. (MFC = mass flow controller.)

flow rate of 50 mL min^{−1} and held overnight to ensure that it was 'clean' prior to any experiment. When the bed was cooled to the sorption temperature, a model gas that contained a ppmv level of H₂S and 20 vol% of H₂ in N₂ was introduced into the sorption bed. The model gas was prepared by blending ultra-high pure (UHP) nitrogen (99.999%) and 1.00 vol% H₂S gas in UHP nitrogen (both purchased from GT&S Inc.). All the sorption tests were conducted at room temperature and atmospheric pressure unless otherwise described. When the outlet H₂S concentration reached the initial feed concentration, *i.e.* the sorbent was saturated by H₂S, the gas line was switched to UHP nitrogen at a flow rate of 100 mL min^{−1}, and the sorbent bed temperature was increased to 75 °C and held at this temperature to perform the desorption. The H₂S concentration in the effluent gas was detected by the on-line sulfur analyzer. Moisture was added into the model gas by passing the model gas through water to mimic the moisture in the gas streams, as shown in Fig. 1. The detailed calculation method for the breakthrough capacity and saturation capacity were described in the previous paper.²⁹ The limitation of the sulfur analyzer was *ca.* 2 ppmv.

Results and discussion

Characterization

Fig. 2 shows the X-ray powder diffraction patterns of calcined SBA-15 and 50 wt% PEI/SBA-15 samples. The characteristic (100), (110) and (200) peaks were clearly observed at 2θ = 0.89, 1.52 and 1.76° in the diffraction of SBA-15, indicating the synthesized SBA-15 had a typical hexagonal structure. These peaks were still observed in the diffraction pattern of 50 wt% PEI/SBA-15, although the intensities of these peaks declined significantly. No peak shift was found. These constant patterns implied that the structure of SBA-15 remained unchanged after PEI loading. The decrease of diffraction intensity suggested that PEI was filled into the meso-channels of SBA-15.^{18,29}

The nitrogen adsorption–desorption isotherms at 77 K for SBA-15 and 50 wt% PEI/SBA-15 samples are shown in Fig. 3. The N₂ adsorption isotherm of the calcined SBA-15 was a typical reversible type IV adsorption isotherm which is the

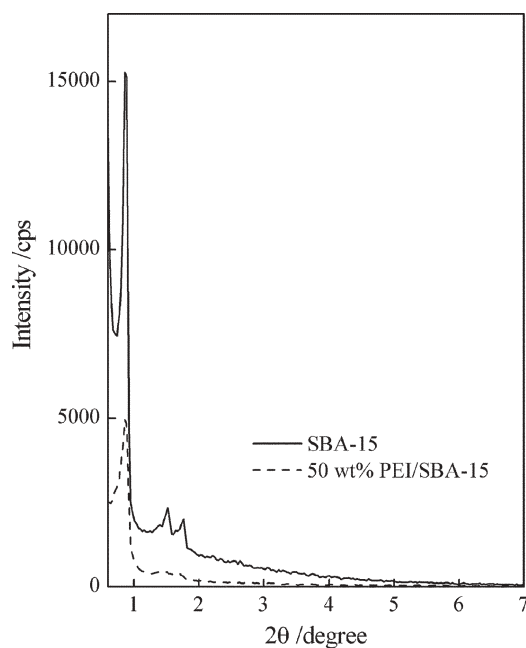


Fig. 2 X-Ray diffraction patterns of SBA-15 and 50 wt% PEI/SBA-15.

characteristic of a mesoporous molecular sieve. After PEI loading, the S-shaped adsorption isotherm was still observed. A BET surface area of $950 \text{ m}^2 \text{ g}^{-1}$ and a mesopore volume of $1.31 \text{ cm}^3 \text{ g}^{-1}$ were observed for calcined SBA-15. After PEI loading, a significant decrease in surface area and mesopore volume were observed, which were $80 \text{ m}^2 \text{ g}^{-1}$ and $0.20 \text{ cm}^3 \text{ g}^{-1}$, respectively, for the 50 wt% PEI/SBA-15 sample. In addition, the pore size decreased from 6.59 to 6.06 nm (Fig. 3), which could be attributed to the formation of an organic layer within the mesopores. The N_2 physisorption results also indicated

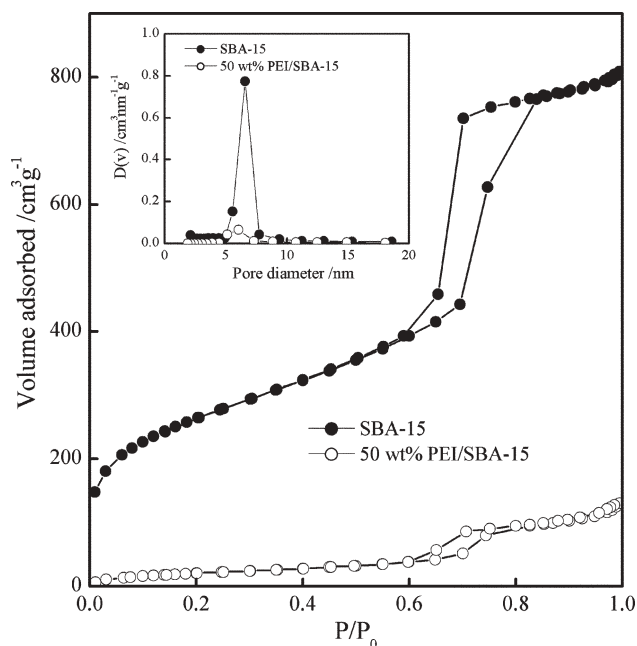


Fig. 3 N_2 adsorption-desorption isotherms of SBA-15 and 50 wt% PEI/SBA-15 samples at 77 K.

that PEI was dispersed into the mesopores of SBA-15 and that the structure of SBA-15 was preserved after PEI loading.

The SEM microphotographs of SBA-15 before and after the PEI loading are shown in Fig. 4. The remarkable feature in these two photos is the long-range, self-organized morphology and uniformly-sized particles. The size of most particles in the SBA-15 support was below $1 \mu\text{m}$ [Fig. 4(a)] with an ordered arrangement. After PEI loading, the particle size of SBA-15 was almost same as that of SBA-15, indicating that the appearance of the SBA-15 particles was maintained mostly after loading, and that PEI was dispersed into the mesopore channels of the SBA-15. However, compared with SBA-15, some particles in 50 wt% PEI/SBA-15 were stuck together [Fig. 4(b)], which implies that a small part of the PEI may coat the outer surface of the particles and/or fill in the gaps between the small particles.

The FT-IR spectra of calcined SBA-15 and 50 wt% PEI/SBA-15 are shown in Fig. 5. Two sharp absorption bands at 3747 and 1652 cm^{-1} , and a broad band at around 3500 cm^{-1} presenting in the IR spectra of the calcined SBA-15 were assigned to single Si-OH and hydrogen-bonded Si-OH groups, respectively.³² The band of single Si-OH groups almost completely disappeared after PEI loading, indicating that loaded PEI interacted with the -OH groups and dispersed inside the mesopores of SBA-15. The doublets at 3375 and 3315 cm^{-1} could be assigned to the amine N-H stretching vibrations, while the bands at 2973 and 2854 cm^{-1} were due to

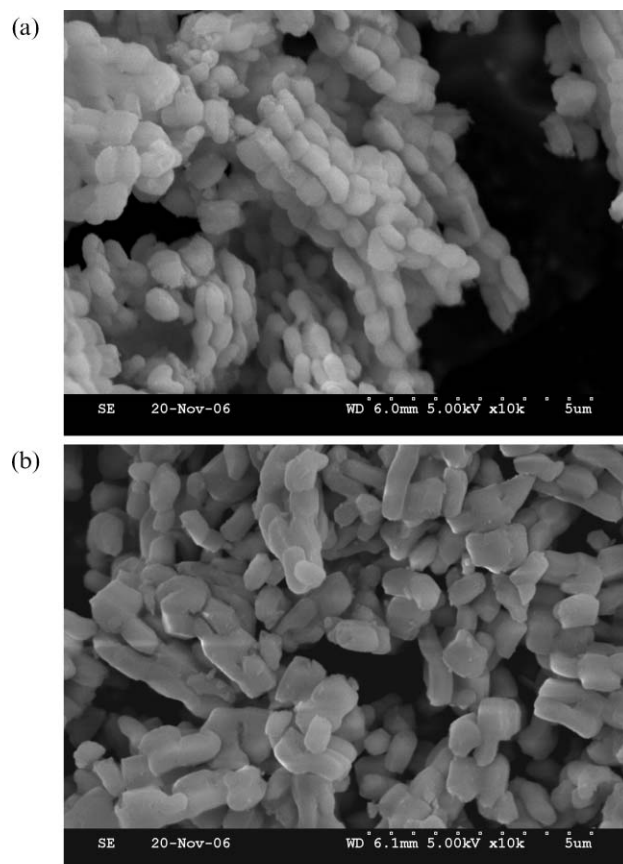


Fig. 4 SEM images of (a) SBA-15 and (b) 50 wt% PEI/SBA-15.

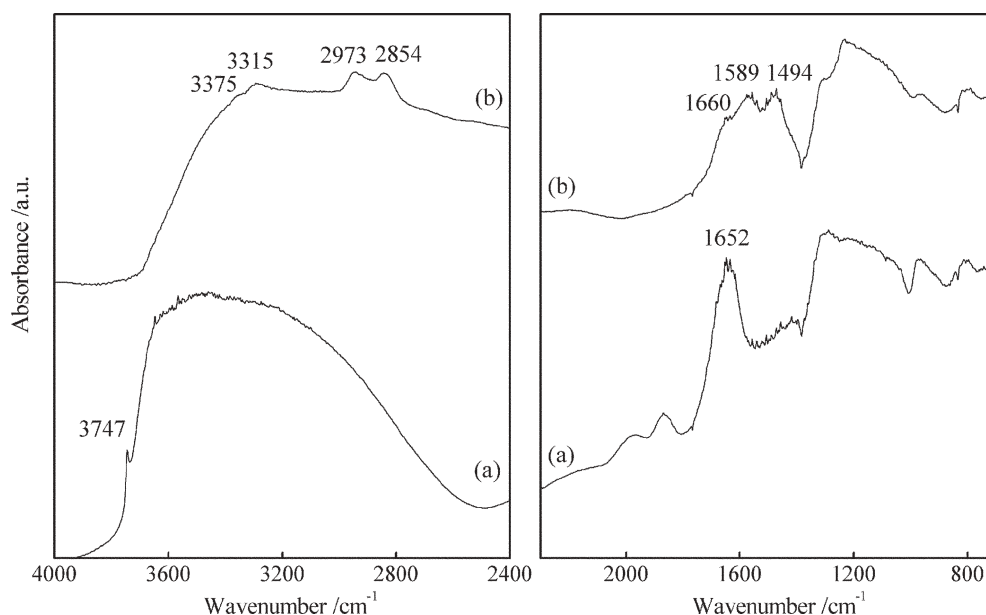


Fig. 5 FT-IR spectra of (a) SBA-15 and (b) 50 wt% PEI/SBA-15.

the CH₂ stretching modes of the PEI chain.^{33,34} A broad band at 2700–3800 cm⁻¹ was attributed to the –NH₂ stretching vibration. The absorbance of the C–N stretching vibration is normally observed around 1000–1200 cm⁻¹.³⁴ However, the peak is unresolved because of the absorbance of the Si–O–Si stretch in the same range.³⁵ In the spectrum of PEI/SBA-15, the bands at 1589 and 1494 cm⁻¹ were attributed to asymmetric and symmetric bending of the primary amines (–NH₂), respectively, while that emerging at 1660 cm⁻¹ was assigned to the bending of secondary amines [–N(R)H] in PEI.³⁶ The values of these peaks reflect a little shift from the normal positions, indicating that there was an interaction between PEI and the internal surface of SBA-15.

H₂S sorption performance

Effect of initial H₂S concentration. The prepared sorbent was evaluated for H₂S removal at ambient conditions (22 °C and atmospheric pressure). The breakthrough curves of H₂S sorption over SBA-15 at 4000 ppmv of H₂S and 50 wt% PEI/SBA-15 at different inlet H₂S concentrations *versus* sorption time are shown in Fig. 6, and the corresponding breakthrough capacity and saturation capacity are listed in Table 1. SBA-15 alone showed very poor H₂S adsorption performance. The breakthrough and saturation capacity of SBA-15 were less than 0.1 mmol g-A⁻¹. However, after PEI loading, both the breakthrough capacity and saturation capacity increased dramatically. The improvement of the sorbent by loading PEI can be considered as the contribution of the amine groups in PEI, which have a high affinity with H₂S on the basis of the acid–base interaction. Obviously, the inlet H₂S concentration had an effect on the sorption capacity, as shown in Fig. 6. A higher saturation sorption capacity (2.38 mmol g-A⁻¹) was obtained at higher inlet H₂S concentration (6000 ppmv), compared with the relatively lower H₂S inlet concentrations (2.06 mmol g-A⁻¹ at 4000 ppmv and

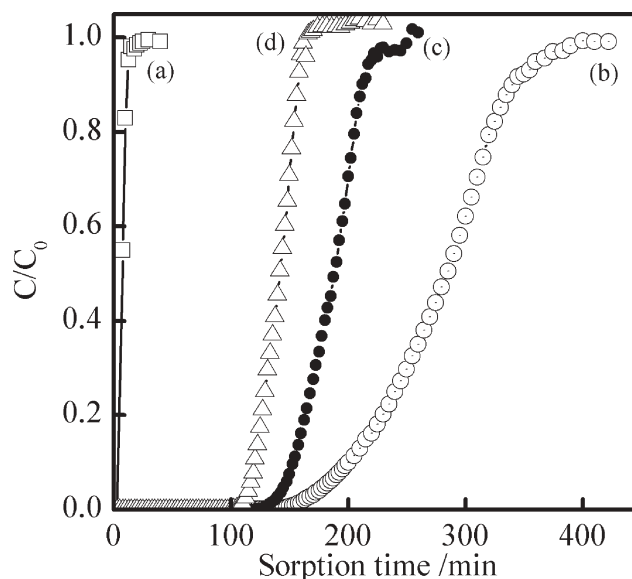


Fig. 6 H₂S breakthrough curves *versus* sorption time over (a) SBA-15 at 4000 ppmv (□) of H₂S, and over 50 wt% PEI/SBA-15 at (b) 2000 (○); (c) 4000 (●), and (d) 6000 ppmv (△) of H₂S, respectively. Conditions: weight of sorbent, 1.0 g; T, 22 °C; feed-gas flow rate, 60 mL min⁻¹.

Table 1 Breakthrough and saturation capacity of SBA-15 at 4000 ppmv H₂S and 50 wt% PEI/SBA-15 at different H₂S concentrations

	Cap(BT)/ mmol g-A ⁻¹	Cap(S)/ mmol g-A ⁻¹	LUB ^a / cm
SBA-15 at 4000 ppmv	0.017	0.034	—
50 wt% PEI/SBA-15 at 2000 ppmv	0.68	1.50	2.7
50 wt% PEI/SBA-15 at 4000 ppmv	1.18	2.06	2.1
50 wt% PEI/SBA-15 at 6000 ppmv	1.48	2.38	1.9

^a LUB, the length of unused bed. Conditions: weight of sorbent, 1.0 g; T, 22 °C; feed gas flow rate, 60 mL min⁻¹. Gas composition, H₂S with 20% H₂ in N₂.

1.50 mmol g-A⁻¹ at 2000 ppmv, respectively, see Table 1). It is because there is a sorption equilibration.

The breakthrough capacity also increased with the increase of the inlet H₂S concentration. The breakthrough capacity of 1.48 mmol g-A⁻¹ was obtained at 6000 ppmv H₂S concentration, while it was 1.18 mmol g-A⁻¹ at 4000 ppmv and 0.68 mmol g-A⁻¹ at 2000 ppmv (Table 1). Generally, in the process of a fixed-bed sorption, there are three different zones existing in the sorbent bed, *i.e.* the equilibrium zone, mass-transfer zone and unused zone.³⁷ Since the saturation sorption of H₂S usually increases with increasing concentration of H₂S in gas phase, the sorption capacity in the equilibrium zone at higher concentration was higher than that at the lower concentration, which contributes greatly to the higher breakthrough capacity. The concentration wave front also moved faster than that at lower concentration, which indicates that the height of the mass-transfer zone is smaller and the length of the unused bed becomes less. As shown in Fig. 6, the breakthrough curve at 6000 ppmv (curve d) was much steeper than that at 2000 ppmv (curve b), suggesting that the transfer zone is much shorter at high inlet concentration. The length of the unused bed (LUB) can be calculated by using the following equations:³⁷

$$\text{LUB} = \frac{t_s - t_b}{t_s} L \quad (1)$$

$$t_s = \int_0^{t_e} \left(1 - \frac{C}{C_0}\right) dt \quad (2)$$

where t_b is the time to breakthrough and L is the length of the adsorbent bed, which is *ca.* 5.0 cm here. And t_s is the sorption time for reaching to the half of the equilibrium concentration, which can be determined from eqn (2), where t_e is the time for saturation, C is the outlet concentration and C_0 is the inlet concentration. As shown in Table 1, the LUB was 2.7, 2.1 and 1.9 cm at 2000, 4000 and 6000 ppmv, respectively. With increasing the inlet H₂S concentration, the LUB decreased and

the usage of the sorbent became more effective at higher concentration, which resulted in the increase of the breakthrough capacity.

It should be noted that the outlet sulfur concentration increased rapidly after breakthrough, as shown in Fig. 6. It indicates that the effect of mass transfer on the sorption performance is not significant in the present case. Our previous studies also showed that the sorption capacity decreased slightly with the increase of the particle size of the sorbent and the space velocity,^{20,29} which implies that there may be only a minor internal and external mass-transfer effect on the sorption performance of the 50 wt% PEI/SBA-15 sorbent under the present experimental conditions.

H₂S adsorption isotherm. The adsorption isotherms of H₂S on the 50 wt% PEI/SBA-15 sorbent at different temperatures are plotted in Fig. 7(A). It is clear that the adsorption capacity increased with increasing equilibrium concentration of H₂S, as described above. However, such a relationship was non-linear. As is well known, assuming that the adsorption obeys the Langmuir adsorption isotherm, the following relationship should exist:

$$q = \frac{Kq_m C_e}{1 + KC_e} \quad (3)$$

where C_e and q are the concentration of H₂S in the gas stream and the saturation capacity at equilibrium, respectively,³⁷ K is the adsorption equilibrium constant and q_m is the maximum adsorption saturation capacity of the sorbent. If this is the case, a plot of $1/q$ versus $1/C_e$ will result in a straight line, as in eqn (4) given below:

$$\frac{1}{q} = \frac{1}{Kq_m C_e} + \frac{1}{q_m} \quad (4)$$

The plots of $1/q$ versus $1/C_e$ for 50 wt% PEI/SBA-15 are shown in Fig. 7(B). A good linear relationship between $1/q$ and

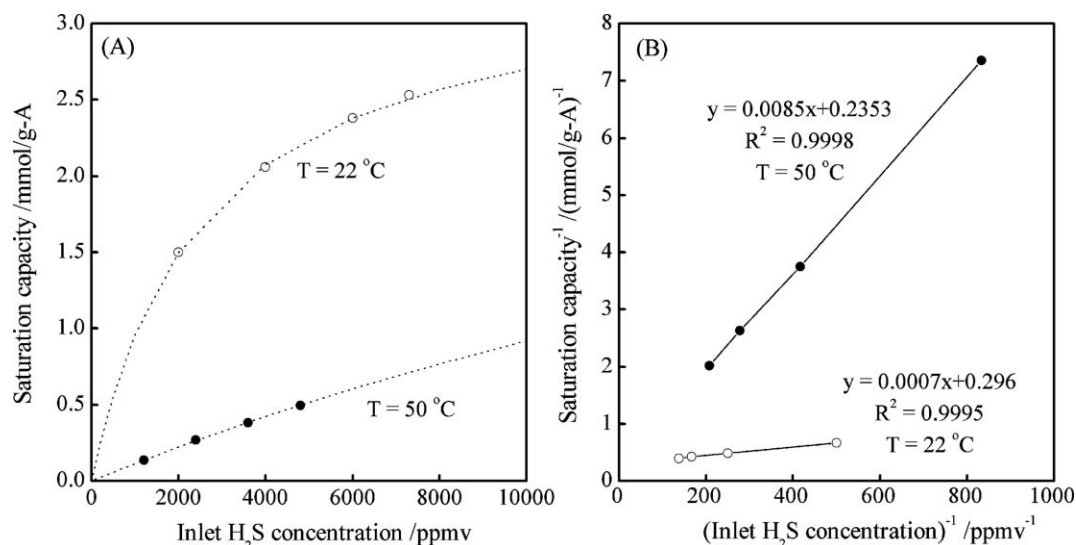


Fig. 7 (A) Adsorption isotherms of and (B) plots of $1/q$ versus $1/C_e$ for 50 wt% PEI/SBA-15 at 22 and 50 °C. The dotted lines are fitted to Langmuir isotherms. Conditions: weight of sorbent, 0.2034 g; feed gas flow rate, 60 mL min⁻¹.

$1/C_e$ was obtained with R^2 values of 0.9995 and 0.9998 at 22 and 50 °C, respectively. The q_m and K values estimated by linear regression were 3.38 mmol g-A⁻¹ and 422.9 at 22 °C and 4.25 mmol g-A⁻¹ and 27.7 at 50 °C, respectively. Although a higher q_m could be obtained at a higher adsorption temperature, the adsorption equilibrium constant at high temperature (27.7) was much lower than that at low temperature (422.9), indicating that the sorption strength at high temperature was much weaker than that at low temperature. In addition, the adsorption heat on the 50 wt% PEI/SBA-15 sorbent could be estimated based on the van't Hoff equation:

$$\ln K = \frac{-\Delta H_s}{RT} + \ln K_0 \quad (5)$$

where, ΔH_s is the heat of adsorption and R is the gas constant. Thus, the adsorption heat of H₂S sorption on the SBA-15-supported PEI was *ca.* 77 kJ mol⁻¹. It should be mentioned that the sorption of H₂S on the supported polymer sorbent is not a simple chemisorption process on the surface of the sorbent. It might be involved in the adsorption of H₂S on the polymer surface and the absorption of H₂S in the polymer phase, which will be discussed further in our other paper.

Effect of moisture on the sorption performance. The influence of moisture on the sorption removal of H₂S from a simulated gas stream was investigated at 22 °C and atmospheric pressure. Fig. 8 compares the H₂S breakthrough and desorption curves for the simulated dry and moist gas streams with *ca.* 3% moisture, which is the saturation moisture concentration at room temperature. For the dry gas, H₂S broke through very early. In the presence of moisture, the 'molecular basket' sorbent still effectively sorbed H₂S. At the beginning of the sorption, H₂S was completely sorbed by the sorbent and the

H₂S concentration was below the detection limit of the sulfur analyzer, *i.e.* <2 ppmv. After 15 min of sorption, H₂S was detected in the effluent gas. Compared with the sorption of H₂S from the dry gas under the same conditions, the H₂S breakthrough time increased when a gas with moisture was used. In the meantime, the H₂S saturation time also increased significantly [Fig. 8(A)]. Without moisture in the gas with 7300 ppmv of H₂S, the breakthrough capacity and the saturation capacity were 0.17 and 2.53 mmol g-A⁻¹, respectively. When moisture was added, the breakthrough capacity and the saturation capacity were enhanced to 1.41 and 9.57 mmol g-A⁻¹, which were 8 × and 4 × higher than those of the dry gas, respectively. The results indicated that moisture had a promoting effect on the sorption of H₂S by the SBA-15-supported PEI sorbent. The same positive effect of moisture was reported on the sorption of CO₂ by 50 wt% PEI/MCM-41 sorbent²⁵ and H₂S removal from moist air (80% humidity) at low temperature by some activated carbon adsorbents.^{26–28}

There are some possible reasons that may cause the increase of H₂S sorption capacity in the presence of water. One is that H₂S may be absorbed by water that is adsorbed by the sorbent and therefore the H₂S sorption capacity increases. The other is that the chemical interaction between H₂S and PEI may be changed in the presence of water. PEI is a polymer with numerous amine groups. In the dry conditions, the main reactions between the amine and H₂S are shown as follows:



These have been confirmed by the computational studies.²⁴ This limits the sorption capacity to 1 mol of H₂S for every

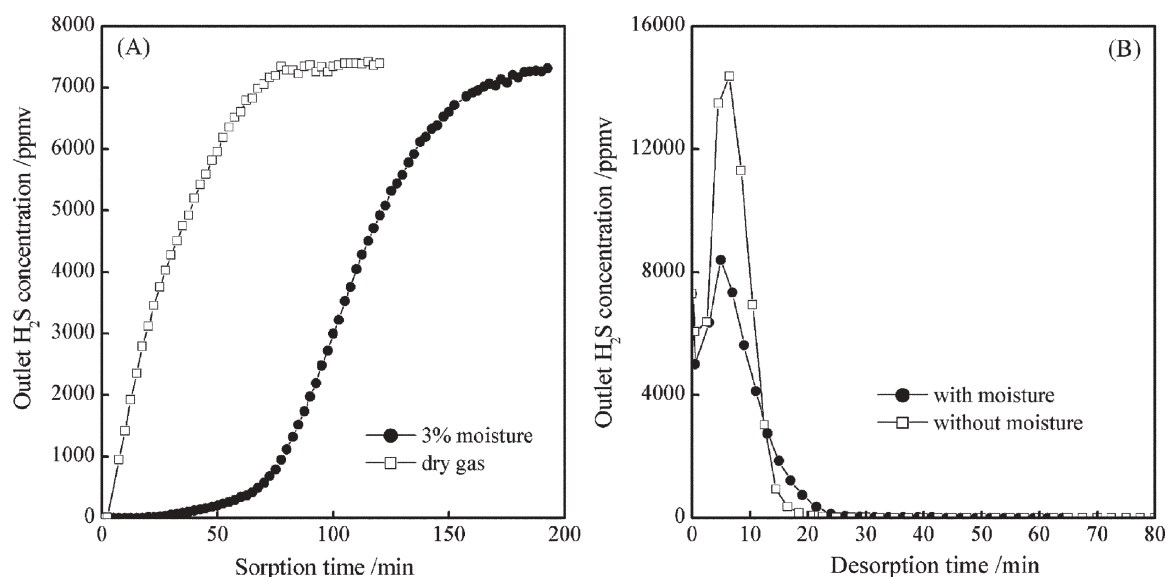
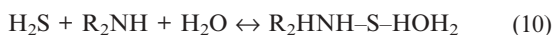


Fig. 8 Comparison of (A) H₂S breakthrough curves, and (B) desorption curves for simulated dry/moist gas over the 50 wt% PEI/SBA-15 sorbent. Conditions: (A) sorption: weight of sorbent, 0.2034 g, T , 22 °C; feed gas flow rate, 60 mL min⁻¹; gas composition, 7300 ppmv of H₂S with 20% H₂ in N₂; (B) desorption: T , 75 °C; purge gas, N₂; flow rate, 100 mL min⁻¹.

2 mol of amine groups. In the presence of water, the amine group itself might directly react with H_2S and H_2O , as shown in the following:



Thus, in this case, 1 mol of amine group can sorb 1 mol of H_2S . Actually, the saturation capacity in the presence of water was $9.57 \text{ mmol-H}_2\text{S g-A}^{-1}$, which corresponds an H_2S : amine group ratio of 0.83, suggesting that each H_2S molecule may react with each single amine group. The third possible reason is that PEI may react with water and become more flexible. In this case, more affinity sites may be exposed to the H_2S and the diffusion in the PEI bulk may become much easier, thus resulting in the increase of the H_2S sorption capacity.

It is worth noticing that the desorption of the sorbed H_2S in the presence of water was more difficult than that without moisture, as shown in Fig. 8(B). The desorbed amount of H_2S was only $1.81 \text{ mmol g-A}^{-1}$ after sorption in the presence of moisture, which was lower than that without moisture ($2.49 \text{ mmol g-A}^{-1}$), although the saturation capacity with moisture was *ca.* $4\times$ higher than that without moisture. It is consistent with the results reported by Huang *et al.* that the amount of H_2S desorbed was only slightly decreased when water vapor was present in the gas using the TPD method.²² Compared with the desorption percentage, only 19% of sorbed H_2S was desorbed from the sorbent within 80 min of pure N_2 purging, whereas it was 98% for the case without moisture. However, after being purged with pure N_2 at 100°C overnight, the majority of the sorption capacity could be recovered (see Fig. 9). Besides the desorption capacity, the desorption rate also became lower after sorption in the presence of moisture in comparison with the desorption after sorption with dry H_2S gas. The results indicate that there is a strong interaction between water and PEI, between water and H_2S , or both contributing to the increase of the sorption capacity and the decrease of desorption capacity and desorption rate in the presence of moisture.

Regenerability of the sorbent. Considering the practical applications, the sorbent should not only possess a high sorption capacity, but should also show good regenerability and stable performance for thousands of sorption/desorption cycles. The sorption/desorption cycles in the presence of moisture were carried out and the results are shown in Fig. 9. After saturation, the desorption was conducted at 100°C with pure N_2 purging at 100 mL min^{-1} overnight. Our previous work showed that the H_2S sorption capacity hardly changed under simulated dry gas. However, in the presence of water, the sorption capacity decreased with increasing cycle numbers. As shown in Fig. 9, the saturation capacity decreased from $9.57 \text{ mmol g-A}^{-1}$ for the first cycle to $8.33 \text{ mmol g-A}^{-1}$ for the second cycle and $7.85 \text{ mmol g-A}^{-1}$ for the third cycle, since the desorption of H_2S became difficult in the presence of water as discussed above. Although the sorption capacity

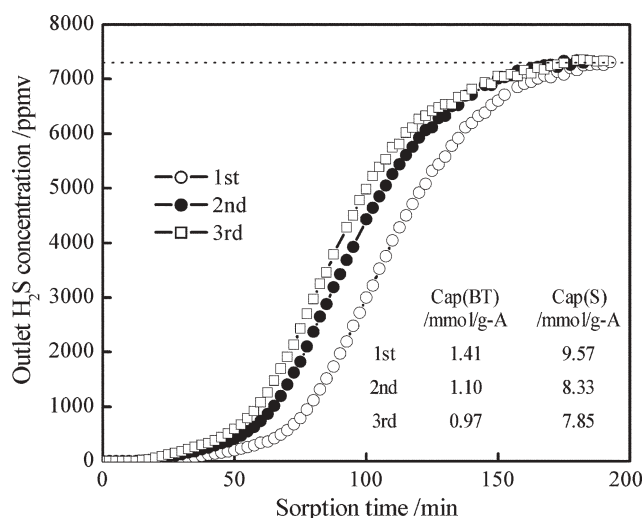


Fig. 9 H_2S breakthrough curves versus cycle number. Conditions: sorbent, 50 wt% PEI/SBA-15; weight of sorbent, 0.2034 g; T , 22°C ; feed gas flow rate, 60 mL min^{-1} ; gas composition, 7300 ppmv of H_2S with 20% H_2 and 3% moisture in N_2 . Desorption at 100°C overnight with 100 mL min^{-1} of N_2 purging.

decreased, about 82% of the saturation capacity can be recovered, which was still much larger than that in the absence of moisture in the sorption process. The decrease of the sorption capacity became smaller with increased cycle numbers. The results implied that the sorbent still had good regenerability and stable sorption performance in the presence of water, suggesting that the novel SBA-15-supported PEI sorbent is promising for practical applications. Such sorbents may be promising for post-reforming desulfurization for fuel cell applications with or without pre-reforming adsorption desulfurization.^{38,39}

Conclusions

A SBA-15-supported PEI sorbent was prepared by a wet impregnation method. The characterization by XRD, BET, SEM and FT-IR showed that after PEI loading, the structure of SBA-15 was preserved and that the PEI was dispersed inside the meso-channels of SBA-15 and that the amine groups interacted with the surface groups of SBA-15, which anchored PEI on the inner surface of the SBA-15.

With increasing inlet H_2S concentration, both the breakthrough capacity and the saturation capacity increased. The sorption of H_2S on the SBA-15-supported PEI sorbent can be expressed by the Langmuir adsorption isotherm, although the process is not a simple chemisorption on the surface. Moisture had a promoting effect on the sorption removal of H_2S from gas streams by the PEI/SBA-15 sorbent. However, a negative effect of the presence of moisture in the sorption on the desorption of H_2S was also observed. The results of the sorption/desorption cycles in the presence of moisture in the sorption step indicated that the PEI/SBA-15 sorbent had good regenerability and stable sorption performance. More investigations are necessary for understanding the detailed sorption mechanism of H_2S on the supported polymer sorbent.

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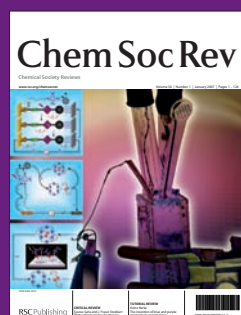
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