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Environmentally benign manufacturing of fine and intermediate chemicals

Wolfgang F. Hoelderich*

Department of Chemical Technology and Heterogeneous Catalysis, University of Technology,
RWTH Aachen, Worringerweg 1, 52074 Aachen, Germany

Abstract

Environmental concerns and regulations are getting more and more severe. A lot of efforts and progress have been accomplished in the environmentally benign and sustainable industrial manufacture of fine and intermediate chemicals in recent years. Solid acid–base catalyzed commercialized processes as well as heterogeneously catalyzed oxidation processes and a dehydrogenation process are reviewed.

The examples for acid catalyzed processes are the BASF-*tert*.-butylamine-process and the Beckmann-rearrangment to form ϵ-caprolactam. For solid base catalyzed processes, the Sumitomo-process for the production of 5-ethylidene-bicyclo [2.2.1] hepta-2-ene and other double bond isomerization processes have been chosen. In addition, short comments are given on side chain alkylation and transesterification reactions. Acid–base bifunctional heterogeneous catalysts are employed for the hydrogenation of aromatic and aliphatic carboxlic acids to the corresponding aldehydes.

In oxidation processes, the oxidation of an unsaturated alcohol to the corresponding aldehyde will be demonstrated on the BASF-citral-process in which a silver catalyst is applied. For the oxidation of alkylaromatic compounds to the corresponding acids, the oxidation of β-picoline to nicotic acid in the presence of V_2O_5/TiO_2-catalyst will be discussed. The oxidation of benzene to phenol using N_2O as oxidant over a MFI-type zeolite is also described. The dehydrogenation of α-limonene to *p*-cymene over Pd/SiO_2 catalyst is selected as an example for the environmentally benign use for a renewable feedstock.

Keywords: Environmental protection; BASF-*tert*.-butylamine-process; Beckmann-rearrangement; Base catalyzed double bond isomerization; BASF-citral-process; Direct oxidation to nicotinic acid; Direct oxidation to phenol; *p*-Cymene production

1. Introduction

Around 95% of all industrial heterogeneous catalysts are used in the production of bulk chemicals and only 3–5% in the synthesis of fine chemicals. In that industrial segment, on the other hand, this low percentage accounts for approximately 20% of the profit. With respect to manufacture fine and intermediate chemicals, the multiplication factor seems to be much higher than in petrochemical or refinery processes. That underlines the economic importance and the need of catalysis not only in petrochemical industry but also in speciality production [1].

The environmental concerns and regulations have been increased very much in the public, political and economical world over the last 15 years, because quality of life is strongly connected to clean environ-

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* Tel.: +49-241-806560; fax: +49-241-8888291.
E-mail address: hoelderich@rwth-aachen.de (W.F. Hoelderich).

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ment. The impulse for developing new, more efficient and more selective catalysts as well as for the development and realization of new process technology is strongly related to environmental protection. In the manufacturing processes of fine chemicals and organic intermediates stoichiometric traditional chemistry or homogeneous acid and base Brønsted and Lewis catalysts are still applied to a great extent in the liquid phase. In case of stoichiometric reaction in particular oxidation reactions unavoidable side product and salt formation cause a lot of problems with the waste disposal. With respect to the homogeneous catalysis no catalyst regeneration is possible, and their application causes unavoidable problems with corrosion of the reactors, tubes, etc. with separation and recycling of the catalysts, with the salt formation due to the neutralization in the working up procedure and with the high costs for waste disposal and polluted water treatment.

In order to avoid such problems, solid acid–base catalysts and oxidation catalysts can contribute tremendeously to environmental protection. Environmental protection has to be seen

- in achieving high selectivity, zero emission, no side product formation. The challenging target is 100% yield. That means we have to be aware of the E-factor [2] and atomic efficiencies [3];
- in replacement of homogeneous Brønsted- and Lewis-acids and bases by heterogeneous systems in order to avoid salt formation, corrosion, wasting catalysts, etc. The challenge is production integrated environmental protection;
- use of cheaper renewable starting materials for the synthesis of fine and intermediate chemicals. Thereby the nature functions as an architect of the desired chemical building units;
- in use of side products of a reaction such as exhaust gases for other reactions to valuable compounds. The challenge is extensive use of starting materials;
- in applying multifunctional catalysis in which chemical conversion consisting of a number of individual reaction steps are brought about in a minimum number of steps, i.e. shorten the reaction procedure in order to avoid loss of starting material in each step and to save capital investment. The challenging target is ‘one-pot’-reaction [4];
- in developing heterogeneous chiral catalysts for stereoselective reactions to avoid toxic or less efficient enantiomers and diastereomers. The targets are the development of stereoselective hydrogenation and stereoselective oxidation catalysts.

In the present review only commercialized processes or processes in the pilot plant scale are selected to demonstrate how heterogeneous catalysts can contribute to a green and sustainable chemistry. Thereby acid–base catalyzed and oxidation processes will be focused on.

2. Solid acid–base catalyzed processes

Solid acid–base catalysts play an extremely important economical and ecological role in chemical and petrochemical industry as well as refinery technology. Recently, K. Tanabe and W.F. Hölderich [5] published a statistical survey of industrial processes using solid acid–base catalysts. They identified and analyzed 127 different processes such as for alkylation, isomerization, amination, cracking, etherification, esterification, condensation reactions, etc. For these processes around 180 different catalyst types such as zeolites, oxides, complex oxides, phosphates, ion-exchange resins are employed. Among them zeolite catalysts represent, with 74 (about 45%), the largest group.

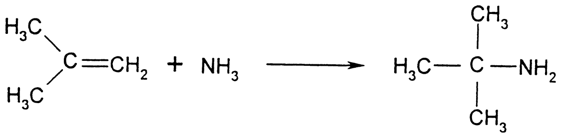
The classification of the types of catalysts into solid acid, solid base, and solid–acid base bifunctional catalysts shows that the number of solid acid catalysts with 103 is the largest group. Even though great progress of petroleum and petrochemical industry for the last 40 years contribute to a high demand of acid heterogeneous zeolite catalyst, it is noteworthy to mention that about 40 processes in the field of fine and intermediate chemicals are catalyzed by such materials. Although the study of solid base catalysts which started much later than that of solid acid catalysts is becoming interesting to chemical industry and is subject of many investigations. Right now around ten base catalyzed processes are on stream. In the case of acid–base bifunctional catalysts 14 industrial processes could be accounted. Even for the reaction, which is regarded to be catalyzed simply by an acid site or a base site, there seems to be a considerably high possibility of bifunctional catalysis by acid–base pair sites, since any kinds of solid acids or solid bases possess more or less base sites or acid sites, respectively.

3. Reactions catalyzed by solid acids

3.1. Direct amination of olefins

A very impressive example for the replacement of a stoichiometric reaction by environmentally benign heterogeneous catalysis is the direct amination of olefins as it is commercialized in the BASF-*tert.*-butylamine-process. Extensive study in the field of direct amination of olefins has been done by Air Products and BASF [6,7]. Among quite a number of heterogeneous catalysts studied, acidic zeolites were found superior to other materials. Thereby the acidity is crucial; on neutral sodium zeolites no amination reaction occurs. Thermodynamics state the amination to be favored by low temperature, high pressure and high ammonia to olefin ratio. However, in the presence of zeolites these facts result in a dilemma as the chemical equilibrium between the H^+- and the NH_4-form of the zeolites has also to be considered. The reaction parameters which favor the amination of the olefins are in contradiction to the formation of the necessary H^+-form of the zeolite. Therefore, the right balance between temperature pressure, ammonia to olefin ratio and acidic strength of the zeolite has to be found. The solution was to run the reaction under supercritical conditions as demonstrated in the BASF-*tert.*-butylamine-process.

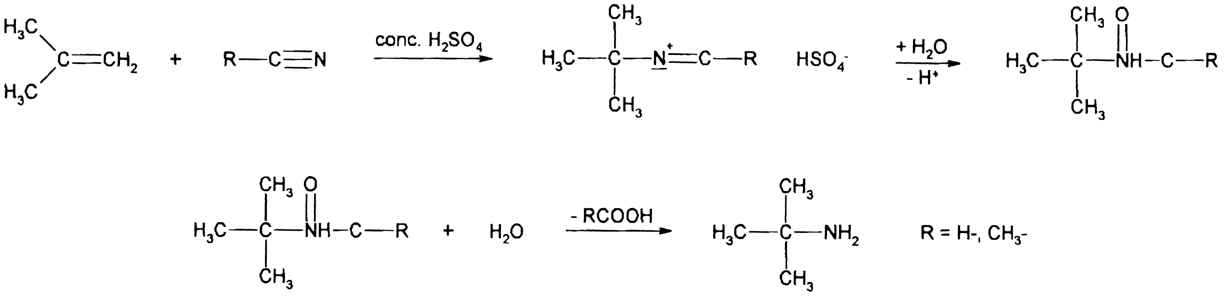
Thereby, isobutene reacts with ammonia according to Eq. (1) over pentasil [7] or beta-zeolites [8] in a fixed bed at around 300°C and around 300 bar, i.e. at supercritical conditions, to give excellent results. The selectivity amounts to around 99% at 12–15% conversion.



(1)

A recyclization of NH_3 and isobutene is necessary. The oligomerization of isobutene is negligible because ammonia is present in excess (molar ratio ammonia/olefin = 1.3–1.5). Furthermore, the dialkylation does not occur due to the transition state shape selectivity. While X and Y zeolites suffer from the disadvantage of rapid deactivation Re-Y, pentasil and beta-zeolites yield commercially acceptable service time.

This one-step procedure for the production of *t*-butylamine evidently provides advantages over the traditional stoichiometric Ritter reaction according to Eq. (2).



(2)

The starting olefin for the Ritter route is the same as for the direct amination. However, in the conventional three-step reaction course the highly toxic HCN is used in the presence of hazardous highly concentrated sulfuric acid. The resulting toxic formamide has to be hydrolyzed in the presence of HCOOH or CH_3COOH. This reaction sequence is inefficient in both raw material usage and by-product formation. Around 4.5 t of raw material has been used to produce

1 t TBA. Approximately 3 t Na_2SO_4 contamination per ton TBA are inevitably formed as by-product.

Therefore, the direct one-step amination is really an environmentally benign and economical process even though high pressure and high temperature as well as the recyclization of starting materials are expensive factors.

3.2. Beckmann-rearrangement

In the synthesis of fine and intermediate chemicals, it seems that sometimes very strong acids as catalysts are not necessary. A weak acid strength is already sufficient to catalyze such reactions in a very efficient and selective way. Recently, we found [9–11] that only extremely weak acidic sites on zeolitic catalysts are needed for the Beckmann-rearrangement. In particular, vicinal silanol groups and silanol nests at the outer surface of zeolites with MFI structure are thought to be the most suitable species for the rearrangement as their appearance is connected to a remarkable increase of conversion, selectivity and lifetime.

As a starting material for the nylon-6 synthesis ϵ-caprolactam is of high industrial importance. Recently, a new route for the production of ϵ-caprolactam and adipic acid was introduced. The first steps of this route are the highly selective partial hydrogenation of benzene to form cyclohexene and the consecutive highly selective hydration in the presence of a special H-ZSM-5 (Asahi-process, 60,000 t per annum since 1990) [5]. In the case of ϵ-caprolactam, after the dehydrogenation of the cyclohexanol to cyclohexanone, the oximation to cyclohexanone oxime is carried out in the presence of ammonia and hydrogen peroxide as oxidant over a Ti-containing MFI-zeolite TS-1 (Enichem-process, 12,000 t per acre demonstration plant) [12].

There are several studies to rearrange the cyclohexanone oxime to ϵ-caprolactam over zeolitic catalysts. Compared with the conventional method, this is an energetically and economically favorable as well as environmentally friendly alternative route, e.g. there is no inevitable formation of ammonium sulfate. However, the heterogeneously catalyzed Beckmann-rearrangement step is going to become commercialized even though some problems such as catalyst lifetime still have to be overcome. Our investigations have been focused on the use of B-MF1 [9–11] zeolite for the Beckmann-rearrangement.

Investigations in the fixed bed showed us that temperatures above 380°C led to major selectivity reduction due to the decomposition of caprolactam and other side effects. Lower temperatures than 280°C enhanced depositions on the catalyst surface and therefore also caused a drop in selectivity. Catalyst lifetime increased along with temperature. It is assumed that coke precursors or deactivating compounds desorb more easily at elevated temperatures. Thus, the reaction was carried out at a reduced pressure below 1 bar to facilitate the desorption of deposits on the catalyst surface. This allows to reduce the temperature to 300°C and to enhance the selectivity (Fig. 1). In combination with ethanol, which turned out in a parameter study to be the most suitable solvent for the gas phase rearrangement, these reaction conditions represent a remarkable improvement [9].

In spite of these significantly increased improvements, the service time of the catalyst could not be prolonged to such an extent that a commercial process can be carried out in the fixed bed reactor. So the next aim of the research was the examination of the deactivation and regeneration process. To gather more information about the type of residuals in and on the catalyst XPS and SIMS experiments were performed [13]. Thereby it was found that the deactivation takes place at the outer surface of the zeolite, i.e. the reaction takes place at the outer surface and not in the interior part of the zeolite. Computer simulations also demonstrated that ϵ-caprolactam does not fit in the channels of pentasil zeolites. The zeolitic channels are most probably blocked by linear oligomers of unsaturated nitriles which can be formed by ring opening reactions. Furthermore, the coke deposit on the outer surface is of aliphatic not aromatic nature.

Another experiment to prove the location where the reaction takes place was to study the rearrangement over catalysts with different crystal sizes [16]. With increasing external surface area, i.e. decreasing diameter the conversion increases significantly. This is an important hint that the external surface area is of relevance for the rearrangement. Decrease of selectivity, however, shows that there must be a considerable amount of molecules entering the pore system and being converted to different by-products. These findings are in agreement with investigations done by Yashima and coworkers [14,15].

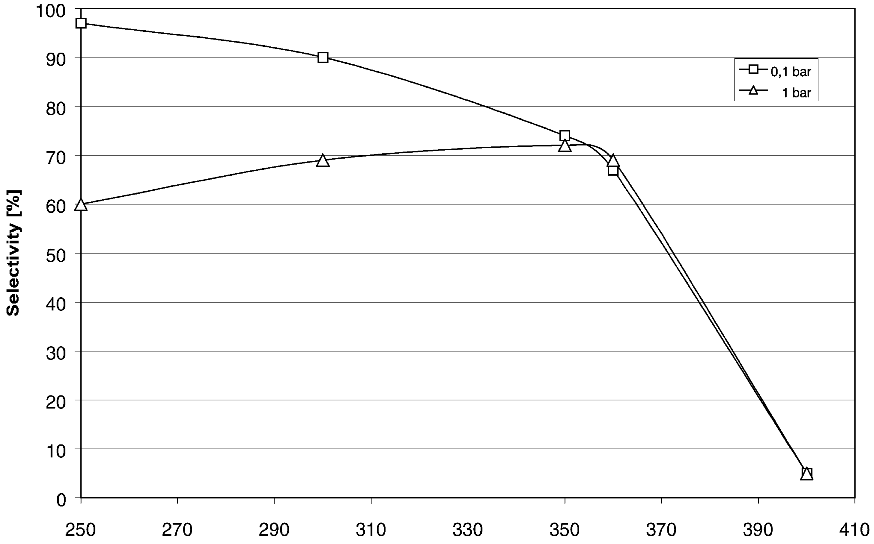


Fig. 1. Influence of pressure and temperature on the selectivity of ϵ-caprolactam.

To analyse the nature of the active sites a variety of zeolitic materials were examined. Treatments with acidic and basic media as well as CVD, deboronation and different steaming procedures were applied. Subsequently, analysis with FT-IR, NMR, NH_3-TPD and pyridine adsorption was performed showing, that the weak acidic vicinal silanols and the so-called silanol nests are the most favorable sites for the vapor phase Beckmann-rearrangement [10,11,16].

Next step in the investigation was the study of the long-term stability of the B-MFI zeolite. The rearrangement of cyclohexanone oxime to ϵ-caprolactam in a fixed bed was investigated. We could demonstrate that the B-MFI catalyst was regenerable in the presence of air at 550°C for 16 h without any problems (Table 1). The results obtained on the 1st day are very similar to the results after the 40th day. Conversion, selectivity and drop in conversion with 6 h time-on-stream (TOS) remained almost the same.

Parallel to the examination of the chemical side of the Beckmann-rearrangement and the investigations concerning the catalyst regenerability much efforts were made to find a suitable reactor system. With the rearrangement, reaction being an exothermal reaction and experiments showing that a short contact time enhances selectivity, the step to a fluidized bed was made [17,18].

The catalysts used for the fluidized bed reactions had a diameter of 80–200 μm. As a results of more than 200 experiments in the fluidized bed and the catalyst in constant use of more than 1 year, it can be stated that this reactor concept is extremely reliable with a very good reproducibility of the experimental results.

Table 1
Reaction: $T = 573.15\,\mathrm{K}$, $p = 0.01\,\mathrm{MPa}$, WHSV $= 0.25\,\mathrm{g_{reactant}}/(\mathrm{g_{catalyst}}\,\mathrm{h})$; solvent: ethanol; carrier: nitrogen; regeneration: $T = 773.15\,\mathrm{K}$, $p = 0.1\,\mathrm{MPa}$; carrier: air

Experiment total time (day)	TOS (h)	Conversion (%)	Selectivity (%)
1	1	95.3	90.7
	6	89.7	93.4
5	1	98.0	86.0
	6	94.4	93.3
10	1	98.5	92.6
	6	95.5	93.6
15	1	96.0	90.0
	6	91.5	92.5
20	1	96.0	91.7
	6	92.0	93.4
30	1	95.4	91.7
	6	90.8	95.6
40	1	95.6	92.7
	6	94.2	94.6

It could be shown that the Beckmann-rearrangement of cyclohexanone oxime to ϵ-caprolactam using a [B]-MFI zeolite in a fluidized bed reactor is a good alternative to the classic process. Yields and selectivities are comparably high by avoiding the production of up to 4 t of ammonium sulfate per ton of product. The catalyst has an industrial applicable lifetime and a good regeneration behavior. But the problem of the deactivation still remains the last target to be solved before the realization as an industrial process could be taken into consideration. A lot of efforts were made at our institute to build a plant with two reactors allowing parallel reaction and regeneration. This was done in several steps. After confirming that the good regeneration behavior in the fluidized bed, the time necessary for a sufficient regeneration had to be evaluated. This was done with a set of thermogravimetrical measurements, which finally yielded a model for the regeneration time based on the activation energy for the regeneration process. Second step was to evaluate the attrition rate of the catalyst in a static fluidized bed. Following this experiments a circulation system for the catalyst interconnecting the two reactors had to be developed and tested. Tests involve the estimation of the attrition rate of this system. Finally, a process control system has to be installed before a long-term experiment can finally prove the industrial applicability [17,18].

4. Reactions catalyzed by solid bases

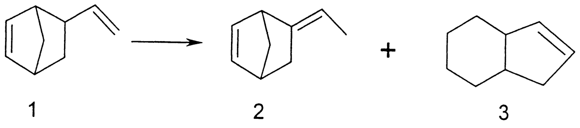
As in the case of conventional acid catalyzed processes in homogeneous liquid phase similar problems exist more or less for the use of typical basic catalysts such as alkali hydroxides or alkali alcoholates. Therefore, there is an ambitious interest for finding and developing new and various solid base catalysts for the organic synthesis of fine and intermediate chemicals. This helps to avoid corrosion and salt formation. A few catalysts are already industrially applied [5].

While alkaline metal oxides as catalysts have not found so much interest in industrial research laboratories, there is an intriguing recent topic of solid super base catalysts, as developed by researches of Sumitomo Chemicals [19]. These catalysts consist of alkali metal hydroxide/alkali metal on γ-alumina according to the general formula $(MOH)_x/M_y/\gamma\text{-}Al_2O_3$, wherein M, x, y are described as

M = Li, Na, K, Rb, Cs,
x = 5–15 wt.% on $\gamma\text{-}Al_2O_3$ and
y = 3–8 wt.% on $\gamma\text{-}Al_2O_3$

They have an extremely high basicity, sometimes higher than $H_0 > 37$. Such super bases do not catalyze cracking reactions, do not deactivate due to strong adsorption of compounds containing basic N or O groups and have a long service time. They are sensitive to moisture and CO_2 and therefore have to be handled carefully. Nevertheless, they are already applied as highly active and effective catalysts for double bond isomerization and side-chain alkylation of alkylbenzenes such as the Sumitomo-process for the production of 5-ethylidene-bicyclo [2.2.1] hepta-2-ene from 5-vinyl-bicyclco [2.2.1] hepta-2-ene via isomerization over the superbase $Na/NaOH/\gamma\text{-}Al_2O_3$ and the Sumitomo-process for the production of *t*-amyl-benzene by side-chain alkylation of cumene with ethylene over $K/KOH/\gamma\text{-}Al_2O_3$ [5].

For example, 5-vinyl-bicyclo [2.2.1] hepta-2-ene (1), is almost completely isomerized even at −30°C over $Na/NaOH/\gamma\text{-}Al_2O_3$ (Eq. (3)) to form 5-ethylidene-bicyclo [2.2.1] hepta-2-ene (2), a compound for vulcanization purposes.



(3)

Compound (1) is thermally unstable and tends to react to tetrahydroindene (3), which can be separated from the desired product (2) only under extreme and very costly conditions. However, at −30°C in the presence of the superbase, the isomer (2) is obtained with extremely high purity, i.e. 99.9% selectivity at 99.7% conversion. Thus, after separation of the catalyst, no additional purification step is necessary. This reaction is carried out by Sumitomo Chemicals in a commercial unit having a capacity of 2000 t per acre being on stream since 1986 [5].

This superbase catalyst $NaOH/Na/\gamma\text{-}Al_2O_3$ can also successfully be employed for the isomerization of safrol (1-allyl-3,4-(methylene-dioxy)-benzene) to *iso*-safrol (3,4-(methylenedioxy-1-propenyl)-benzene) as well as for the isomerization of 2,3-dimethylbutene-1 to 2,3-dimethyl-butene-2, a valuable intermediate for the production of pyrethroids [1]. The side chain alkylation of cumene with ethylene occurs at 40°C over the superbase K/KOH/γ-Al_2O_3 to form *t*-amylbenzene in 99% selectivity. The conversion of cumene is 99%. Also this reaction has found its industrial application in Sumitomo Chemical company [5].

Recently our group used such super base catalysts for transesterification of dimethylterephthalates with ethylene glycol to form bis-hydroxyethylthrephthalate (BHET) with very high selectivity of up to 90% at 100% conversion and 10% of already polymerized product [20]. This is an important reaction step in the production line of polyterephthalates (PET) which is conventionally carried out in the presence of sodium alcoholates.

Right now Sumitomo Chemical seems to be far ahead in the development and commercial use of such solid super bases. New commercial applications can be expected in the not too distant future.

5. Reactions catalyzed by acid–base bifunctional heterogeneous catalysts

Speaking about acid catalyzed reactions, one has to be aware that basic sites are also involved more or less in the reaction mechanism. The cooperation of acid sites with basic counter parts can be extremely effective for specific reactions. Sometimes, such a bifunctional catalyst shows pronounced activity, even if the strength of the acid–base pair sites are much weaker than the acid or basic strength of the isolated solid acid or base.

Aromatic aldehydes belong to the group of fine chemicals being important in the organic chemistry [5]. They are used for the production of pharmaceuticals, agrochemicals and some of them are used directly as flavors and perfumes. Due to their applications these aromatic aldehydes have to be obtained with high selectivity.

There are many synthetic routes to produce aromatic aldehydes, but only the partial oxidation of toluene to benzaldehyde and the halogenation route via benzalchloride are commercially applied. Due to many disadvantages of these processes like low yields or low selectivity and large amounts of by-products as inorganic salts, a new ecologically beneficial and benign synthetic route must be found.

The direct hydrogenation of aromatic carboxylic acids over chrome modified zirconia catalysts was realized as industrial process by the Japanese company, Mitsubishi Chemicals Co. in 1988. Benzaldehyde and its derivatives were produced with a product capacity of 2000 t per year. This vapor phase reaction is carried out in a fixed bed reactor at 300–400°C. At 350°C a selectivity of benzaldehyde of 96% at a conversion of 98% is obtained. It is reported that the high selectivity is due to natural amphoteric surface properties of the zirconia catalyst [5]. Thereby the acid and basic sites are of weak character.

Recently we investigated [21] amphoteric zinkoxides having distinctive surface features for this reaction and we found that the catalytic performance is in particular depending on the acid–base ratio as well as of the BET-surface and pore diameter of the zinkoxide applied (Table 2). ZnO“A” has almost no acid sites and only a few basic sites and those are very weak in comparison to ZnO“B” with more and stronger acid and basic sites. The BET-surface of ZnO“A” is with $17\,m^2\,g^{-1}$ smaller and its pore diameter with >35 nm is larger compared with ZnO“B” with $46\,m^2\,g^{-1}$ and 20 nm.

Table 3 illustrates the catalytic performance of ZnO“A” and ZnO“B” in dependence of the temperature. At 350°C and GHSV $= 800\,h^{-1}$ ZnO“A” yields 96% selectivity at 100% conversion and the space time yield (STY) is $315\,g\,gh^{-1}$. In contrast, using ZnO“B” under the same conditions only 71% selectivity at 100% conversion and STY $= 232\,g\,gh^{-1}$ were found. One can see how deviations in catalysts features influence sensitively the catalytic performance. Thus, the poorer results obtained by T. Yokohama et al. are not so surprising [22].

Recently, Mitsubishi Chemicals was able to transfer this hydrogention technology into the production of linear aldehydes from the corresponding acids [23].

6. Oxidation processes

In addition to acid/base catalysis and hydrogenation reactions oxidation reactions are very important for the chemical and pharmaceutical industry. In the bulk chemical industry for manufacturing, e.g. ethylene

Table 2
Surface properties of ZnO“A” and ZnO“B” for the hydrogenation of benzoic acid to benzaldehyde

Method	Catalyst	
	ZnO“A”	ZnO“B”
XRD	All peaks ZnO High crystallinity	All peaks ZnO High crystallinity
BET	$<17\,m^2\,g^{-1}$ Macropores Pore diameter >35 nm	$<46\,m^2\,g^{-1}$ Macropores Pore diameter >20 nm
Hammett indicators	$9.3 \leq H < 15.0$ No acid sites	$9.3 \leq H < 15.0$ $1.5 \geq H > 0.8$
Titration	0.07 mmol basic sites per gram catalyst	0.08 mmol basic sites 0.07 mmol Acid sites per gram catalyst
Pyridin adsorption + FT-IR spectroscopy	Weakly Lewis acid sites (type I) Hydrogen-bonded pyridine Desorption <50°C	Weakly Lewis acid sites (types I + II) Hydrogen-bonded pyridine Desorption >50°C

oxide (EO), formaldehyde, phthalic anhydride, environmentally unacceptable processes have already been replaced by cleaner catalytic procedures a long time ago, whereas fine and intermediate chemicals are still widely produced via traditional stoichiometric oxidations. Still up to date, organic chemists employ stoichiometric oxidants such as dichromate/sulfuric acid, chromium oxides, permanganates, periodates, osmium oxide or hazardous chlorine causing high salt freights and heavy metal containing dump unable to be recycled, as well as relatively expensive hydroperoxides, alkylperoxides and peroxycarbonic acids. In the case of bulk chemicals heterogeneously catalyzed processes have been developed employing cheap and abundantly available molecular oxygen.

Due to their thermal instability fine chemicals often must be produced in the liquid phase at moderate temperatures. They are generally complex and multifunctional and chemo-, regio- and stereoselectivity play an important role in their synthesis. The reactor systems of choice are batch or semi batchwise operated multipurpose units. Bulk chemicals, mostly consisting of relatively small, thermostable molecules, can be produced in continuously operated fixed bed or fluidized bed reactors in the gas-phase allowing much higher STYs, thus minimizing investment costs.

Table 3
Temperature dependence of the catalytic performance of ZnO“A” and ZnO“B” GHSV $= 800\,h^{-1}$, $(dV/dt)_{H_2} = 10.5\,l\,h^{-1}$, after >10 h TOS

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)	STY
ZnO“A”	380	100	83	272
ZnO“A”	350	100	96	315
ZnO“A”	310	81	96	255
ZnO“B”	350	100	71	232
ZnO“B”	330	96	78	246

The case of fine chemicals and intermediates is especially critical due to the relatively small scale of the production (<500–10,000 t per annum), the complex synthetic routes and the short development time to meet market demands leading to tremendously higher E-factors (25≥100) compared with those for manufacturing bulk chemicals (<1–5) [2]. Still this effect is tolerable from an economic point of view because of the high value added, but it is getting more and more difficult to carry out industrial scale oxidations in such a manner. There is currently a general trend to develop clean and eco-efficient catalytic oxidation processes which minimize the generation of unwanted and harmful by-products (Table 4).

Because of their versatility, their ease of separation, the lack of corrosion problems, the long lifetime and regenerability, solid catalysts for heterogeneously catalyzed direct oxidations in the liquid phase as well as in the gas phase can contribute to solutions of the above-mentioned problems. These catalysts offer a wide variety of different sites for the activation of clean oxidants such as molecular oxygen, hydrogen peroxide and nitrous oxide, in some cases an available off-gas. In the case of intermediate chemicals, the realistic target is extensive use of molecular oxygen in

Table 4
Differences in oxidation reactions of bulk and fine/intermediate chemicals

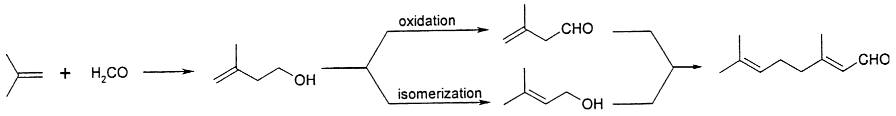
Sustainable and green processes	vs.	Traditional stoichiometric oxidants
Molecular oxygen	vs.	Inorganic/organic peroxides
Small molecules	vs.	Bulkier molecules
Temperature stable	vs.	Temperature sensitive
Higher temperature	vs.	Lower temperature
Fixed bed reactor	vs.	Slurry reactor
Gas phase	vs.	Liquid phase
One purpose unit	vs.	Multipurpose unit
Continuous production	vs.	Batchwise production
Good E-factor	vs.	Bad E-factor

gas phase reactions, allowing cost- and eco-efficient manufacturing as known for the production of bulk chemicals. For fine chemicals and specialities this will rather be the exception due to the reasons outlined above, but in this case the replacement of stoichiometric oxidants by ‘mister clean’ H_2O_2, in liquid phase oxidations, is a cheap and realistic alternative. The heterogeneous catalysts applied thereby can be oxometal or peroxometal species, supported noble metals, heteropolyacids, noble metal pyrochlore oxides, metal containing layered double hydroxides, immobilized complexes (ship-in-the-bottle concept) and last but not least, metal substituted molecular sieves (for an extensive review see e.g. [1]).

6.1. Oxidation of an unsaturated alcohol to the corresponding aldehyde

Gas phase oxidation of ethylene to EO over supported silver catalysts is one of the most prominent examples for the use of noble metals in oxidation catalysis and one of the important industrial scale processes (8–10 × 10^6 t per acre). Ethylene is converted to EO either with air (Scientific Design, UCC) or with mixtures of oxygen and methane (Shell process) in tube bundle reactors at temperatures of 200–300°C with addition of inhibitors, such as 1,2-dichloroethane or vinyl chloride. The yields per pass are approximately 50%. The catalyst is a silver loaded (7–20%) aluminium oxide with a very low specific area ($<2\,m^2\,g^{-1}$) promoted by alkali salts [24]. Thereby the oxygen is activated by silver, other oxidation processes using noble metals such as Pt, Pd, Au, Ir, Ru are also known [1]. In the following we will describe that a ‘similar’ process technology can also be applied for regioselective oxidation of much larger and more temperature sensitive reactive molecules, such as isoprenol [1,25].

Citral is a very valuable intermediate for the production of α- and β-ionone which have importance as fragrances possessing violet smell and are used in perfumes and household cleaners or as building units for carotenoids and vitamin A. It can be isolated from fruits. However, this method makes no sense because the demand is several thousand ton per year. The conventional industrial route uses β-pinene as starting material and chlorine as oxidant. In a five-step procedure β-pinene is converted to citral in low yields and chlorinated side products are also formed. Those drawbacks can be overcome by the new environmentally benign BASF-citral process according to the reaction sequence (Eq. (4)).



(4)

The BASF route (Eq. (4)) starts from cheaply available isobutene and formaldehyde. In this condensation reaction 3-methyl-butene-ol (isoprenol) is formed. A part of that is isomerized by shifting the double bond, the other part is oxidized to the corresponding aldehyde. Afterwards a cope-rearrangement of those compounds takes place to form citral with more than 95% overall yield. The regioselective oxidation of isoprenol to isoprenal is a remarkable environmentally benign process step. Patent literature reports that alcohols can readily be converted to the corresponding aldehydes over supported and massive metallic copper, silver and gold catalysts and alloys thereof [25]. The best results have been obtained with coated inert shapes, e.g. silica spheres where metallic silver (>10 wt.%) has been applied by flame spraying. In a continuous flow fixed bed reactor at 300–600°C and an extremely short residence time of about 0.001 s, undiluted isoprenol is oxidized in the presence of pure oxygen surprisingly almost without deep oxidation. The trick thereby is the use of a short fixed bed reactor temperature controlled by a salt melt in order to run the reaction more or less isothermal and with an ultra short residence time [26]. These facts and an efficient quench allow the production of several thousand ton per annum of citral with extremely high selectivity, even though oxygen is used as oxidant at high temperatures in a gas phase reaction.

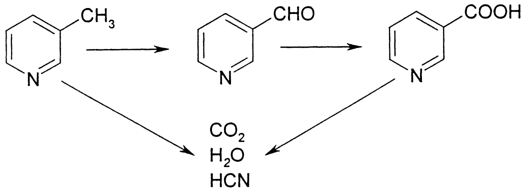
Another approach to carry out oxidation reactions of sensitive compounds such as isoprenol to isoprenal could be the use of honeycomb structured carrier doped or impregnated with noble metals [26]. In such cases also very short residence times can be achieved due to the almost complete lack of pressure drop. But such a new technology has to be developed in such a way as to overcome the difficulties which may occur in the catalyst preparation, in the adjustment of isothermy, etc.

In conclusion, this example demonstrates clearly how even a sensitive chemical such as isoprenol can be oxidized in very high yields, and how catalyst development, process conditions and reactor design have to meet each other. 'Just' by changing the construction of a conventional multitubular reaction system and the modification of a silver catalyst, the oxidation of an intermediate chemical can be carried out similar to the production of a bulk chemical in an environmentally benign and sustainable way.

6.2. Oxidation of alkyl aromatic compounds

Nicotinic acid is an important intermediate for pharmaceuticals and serves as a provitamin in food additives for animal feeding. It is produced via the Lonza-process or the Degussa-process. The Lonza-process is the oxidation of 2-methyl-5-ethylpyridine by using nitric acid [27]. This process suffers from the separation of nicotinic acid, a high amount of harmful salts due to the neutralization of nitric acid, and NO_x-formation as well as the loss of valuable framework carbon in form of CO_2. A two-step reaction is the Degussa-process: hydrolysis of β-cyanopyridine [28] produced by the ammonoxidation of β-picoline. The disadvantages are the high investment costs (two reactors, distillation) and the still improvable yield.

Selective vapor phase oxidation of β-picoline catalyzed by vanadium titanium oxide catalysts has been described in [29]. The side products of this reaction are pyridine-3-carbaldehyde as reaction intermediate and CO_2, CO and HCN as thermodynamically stable products. According to our experiments [30] deep oxidation mainly takes place via oxidation of the substrate and the desired product, whereas pyridine-3-carbaldehyde proved to be remarkably stable. Blank tests in the empty tube with β-picoline/H_2O and nicotinic acid/H_2O mixtures showed conversions of up to 40% with 100% selectivity to CO_x and HCN, especially in the presence of high excesses of water. Pyridine-3-carbaldehyde was stable in the empty tube and converted to the corresponding acid in the presence of the catalyst. From these observations we developed the simplified reaction scheme (Eq. (5)).



(5)

The precise control of residence time will be crucial for this reaction in order to avoid the consecutive oxidation of nicotinic acid. The selectivity towards nicotinic acid could be tremendously improved by appropriate process design, thereby avoiding the parallel reaction. It is very important that the procedure is carried out by separate feeding of β-picoline and water as well as the mixing of both components just at the catalyst bed and a rapid quenching of the product stream after leaving the catalyst bed [30]. Concerning the catalyst development we used a series of TiO_2-carriers of the anatase modification with different BET-surfaces, impregnating them with adequate amounts of vanadia (Table 5).

The catalytic performance of those catalysts depicted in Fig. 2 clearly shows that the increase of original TiO_2-carrier surface enhances activity and selectivity of the catalyst at identical reaction conditions. First, due to the higher surface area of the carrier material, a higher amount of vanadia could be impregnated upon them. Nevertheless, it has to be considered that other parameters of these catalysts were also changed. Furthermore, the V_2O_5 and therewith the

Table 5
V/Ti-oxide catalysts with various BET-surface of the carriers

Catalyst	TiO_2-carrier	BET-surface carrier ($m^2 g^{-1}$)	V_2O_5-content (wt.%)	BET-surface catalyst ($m^2 g^{-1}$)
A	TiO_2-P25	50	2.3	25
B	Anatase B	130	17	65
C	Anatase C	265	19	40

active sites can be much better dispersed on the larger surface of the catalyst carrier. This higher dispersion should be maintained, even though the BET surface of the final catalysts is drastically reduced (Table 5).

Regarding the differing chemical composition of the TiO_2-materials the way they were produced has to be considered. The TiO_2-P25 material has been produced by burning $TiCl_4$, yielding an anatase material with a slight amount of rutile formation. In contrast, the TiO_2 materials Anatase B and Anatase C were synthesized by the sulfate process, yielding a higher surface area and Brønsted acid sites due to sulfate residue, which was the subject of further investigations. TiO_2 materials with a BET surface of around 270 $m^2 g^{-1}$ and sulfate contents of 0.5 wt.% (Anatase C) and 1.5 wt.% (Anatase C*) have been impregnated with 20 wt.% V_2O_5. The BET surface of the catalysts was in both cases around 40 $m^2 g^{-1}$.

Fig. 3 clearly demonstrates that the total sulfate content has not such a strong influence on conversion and selectivity as the actual surface area of the TiO_2-carrier does. It can be observed that the reaction temperature, where the maximum yield is obtained, is shifted with a higher sulfate content from 275 to approximately 255°C, i.e. the higher the sulfate content the better the activity.

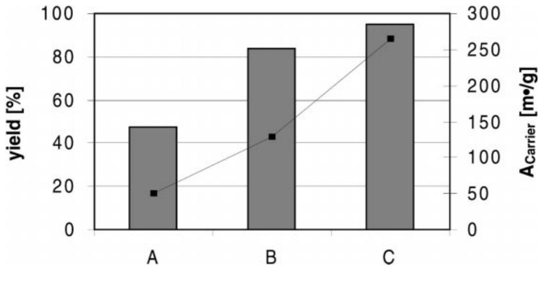


Fig. 2. Relation between variation of BET-surface of the carrier and the yield of nicotinic acid. Reaction conditions: $T = 265–275°C$, WHSV $= 0.04\,g\,(g_{Kat}\,h^{-1})$, $O_2/H_2O/\beta$-Pic = 35/55–70/1 (molar).

In conclusion, our experiments present a clear statement: it is necessary that β-picoline and water have to be added separately to the catalyst bed in order to avoid the parallel reaction to the deep oxidation products. That can be managed by appropriate reactor design. The main parameter which improves the performance is the original surface area of the TiO_2-carrier. This might happen in combination with the sulfate content. Thereby the Brønsted acid centers promote the activation of oxygen resulting in lowering the optimum of the reaction temperature. Therefore, it is possible to improve the yield of nicotinic acid to values up to 98% [30].

6.3. Oxidation of benzene

Since 1983 there has been a lot of research going on the hydroxylation of benzene with N_2O to phenol. Yields of up to 27% and a selectivity of 98% were achieved using the catalyst with the highest amount of Al. Therefore, Brønsted acid sites have been believed as species affecting the reaction [31,32]. By contrast, Panov et al. [33,34] found a correlation between the amount of iron in the ZSM-5 zeolite and the conversion of benzene with N_2O to phenol. They tested H-[Al]ZSM-5 zeolites with iron as impurity and H-[Fe]ZSM-5 zeolites. Due to the same molecular activation energy for each tested catalyst they postulated that only one species is catalytic active for the direct hydroxylation of benzene with N_2O to phenol, namely iron.

Solutia, formerly Monsanto, has taken over the patent rights of Panov et al. from the Boreskow Institute. They designed an integrated phenol-adipic acid production plant which is supposed to go on stream in 2000. The background is that in the Monsanto's adipic acid production at Pensacola, Florida with a capacity of 600 million pounds per year also 200 million pounds of environmentally unacceptable dinitrogenoxide is inevitably produced. Using this

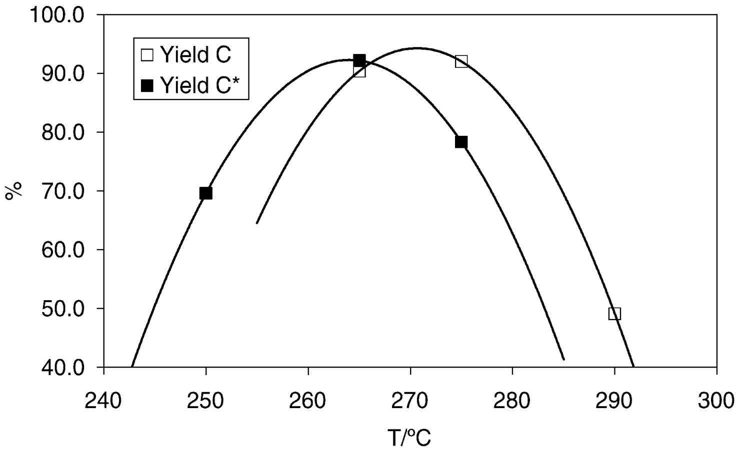


Fig. 3. Temperature dependence of catalyst C (0.5 wt.% SO_4) and C* (1.5 wt.% SO_4), WHSV = 0.04–0.05 g (g_{Kat} h^{-1}), $O_2/H_2O/\beta$-Pic = 35/55/1 (molar).

amount of N_2O around 400 million pounds of phenol per year could be manufactured by the direct hydroxylation of benzene. The phenol will be hydrogenated to cyclohexanol and recycled to the adipic acid plant [34]. That means that the efficiency in the use of all starting materials including nitric acid is extremely high. The exhaust gas has not to be destroyed, e.g. by $DeNO_x$ technology in catalytical decomposition. It can be used as a valuable starting material. Thus, an adipic acid plant working via the nitric acid oxidation of cyclohexanol/cyclohexanone can be operated in an environmentally benign manner.

We had the idea [35,36] to create coordinatively unsaturated extra-framework alumina as center for Lewis acidity. Therefore, at 550°C (10°C min^{-1}) HAl-ZSM-5 (SiO_2) Al_2O_3 = 28) was steamed at a water partial pressure of 300 mbar with a varying steaming time. Estimates for Al distribution (framework to non-framework Al) were obtained with MAS-NMR spectroscopy.

To find a dependency of the ratio of Lewis to Brønsted acidity and the duration of steaming, the samples were loaded with pyridine and subsequently analyzed by IR spectroscopy. The peaks representing Brønsted and Lewis acidity were evaluated quantitavely under the conditions determined by Khabtou et al. [37].

Fig. 4 illustrates that there is a strong increase of the Lewis/Brønsted ratio after 3 h of steaming and a maximal value after 4–5 h of steaming time. The ratio decreases only slightly with a long time of treatment. This maximal value agrees with the results from IR and ^{27}Al NMR spectroscopy. After a 3-h period of steaming almost no further extra-framework aluminium is created.

These steamed H-[Al]ZSM-5 were used as catalysts for the conversion of benzene and N_2O to phenol. Fig. 5 presents the results of conversion and selectivity. It displays that a longer time of calcination (15 h instead of 5 h) does not increase the catalyst activity; the conversion of benzene does not increase

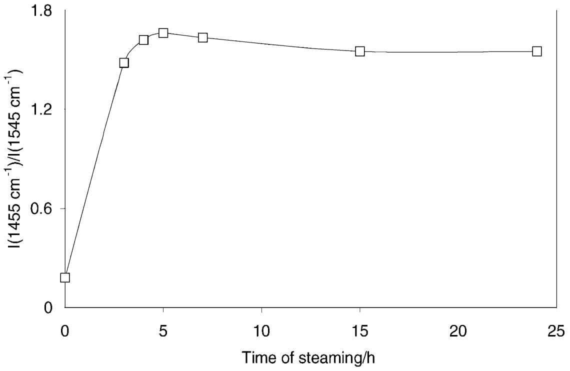


Fig. 4. The ratio of the band intensities representing pyridine adsorbed at Lewis acid sites and pyridine adsorbed at Brønsted acid sites, respectively, as a function of steaming time (steamed 550°C, 30% H_2O).

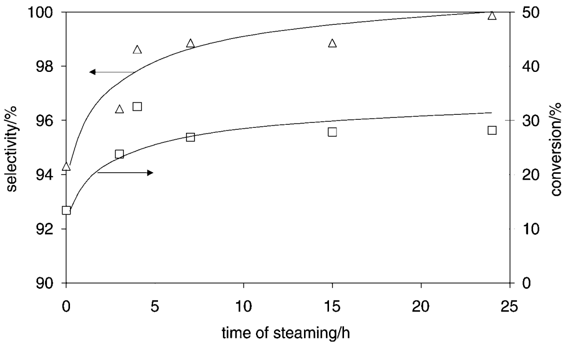


Fig. 5. Conversion (□) and selectivity (Δ) to phenol obtained with hydrothermally treated samples.

significantly. Only the selectivity towards phenol is enhanced from 91 to 96%. There is a significant influence on the conversion and selectivity towards phenol by hydrothermal treatment. The maximum conversion is 30% with a selectivity of about 99% after 5 h of steaming (Fig. 5).

It is noteworthy that there is a correlation of the ratio of Lewis/Brønsted acidity (Fig. 4) and the conversion of benzene (Fig. 5). The maximum for the ratio of Lewis/Brønsted acidity and the conversion of benzene is achieved after 4 and 5 h of steaming, respectively. This implies that the maximum conversion of benzene depends on the maximum amount of Lewis acid sites created by extra-framework aluminium. The latter is achieved when the apparent stagnation of dealumination occurs and a further steaming leads only to agglomeration of the extra-framework aluminium.

Extra-framework Al in dealuminated H-[Al]ZSM-5 zeolites is also active and can be successfully applied. That means for this oxidation reaction using N_2O as oxidant Lewis acid sites are important and necessary. Concerning a possible reaction mechanism we believe that catalytically active centers of the steamed material are the Lewis acids. The stronger the Lewis acid sites the easier the decomposition of N_2O molecule. After that decomposition the resulting oxygen remains as very active surface oxygen on Lewis acidic coordinatively unsaturated aluminium or iron species in the framework or extra-framework. Subsequent hydrogen abstraction is followed by benzene hydroxylation to phenol. This is certainly also true in the case of Ga ZSM-5 zeolite catalyst which have been also applied for the direct hydroxylation of benzene with N_2O [38].

7. Renewable feedstock

The annual total consumption of organic raw materials in Germany is about 19 million ton; 75% are based on crude oil and natural gas, 15% on coal as well as 10% on renewable feedstock. These 10%, however, means 22% of the value of all chemicals produced in the German chemical industry. Considering such figures for the use of renewable as raw materials one has to realize that there is a big margin between the production costs and the sale prices resulting in high profit. Therefore and also due to the environmental constrains there is a strong interest in Germany to broaden the base for renewable feedstock in the organic synthesis of fine and intermediate chemicals. As an example, the conversion of mixtures of terpenes to *p*-cymene is presented here.

The selective conversion of mixtures of terpenes to one important intermediate in chemical industry,

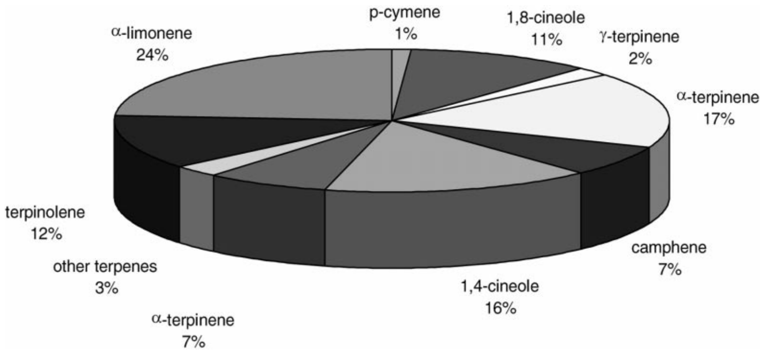


Fig. 6. Composition of the dipentenes sylvapine DP-738.

Table 6
Catalyst composition with silica (SiO_2) as carrier material

Catalyst	Acid strength H_0 (pKA)	Acid strength $^{(*)}$ TPD ($10^{-4}\, n_{NH_3}\, g^{-1}$)	Pd-content (wt.%)	Pore size (wt.%)	BET-area ($m^2\, g^{-1}$)
A	3.3	1.18	0.5	115	120–160
B	4.8	0.12	0.5	80	200
C	6.0	0.65	0.5	170	200

p-cymene, is of a high commercial interest. Mixed terpenes are renewable feedstocks widely and cheaply available as by-products from the orange and lemon juice production as well as from pulp and paper industry [39]. The valuable *p*-cymene can be used, e.g. in the fragrance industry (non-nitrated musks) and as intermediate for the production *p*-cresol [40]. This procedure would allow the direct synthesis of *p*-cresol without *m*- or *o*-isomers, thereby avoiding costly distillation. *p*-Cymene is also of high interest for the formation of polymers, e.g. synthetic fibers. Thus, the aim is to develop an environmental benign and heterogeneously catalyzed process in the gas phase.

The examined starting material was dipentene provided by Arizona Chemical, Florida, USA. This vendor offers a large product spectrum of several dipentenes. For the present study dipentene Sylvapine DP-738. Its composition is given in Fig. 6.

Pd-catalysts on SiO_2-carriers (Table 6: catalysts A, B, C). The activation of these catalysts occurred by reduction of the metal in the startup period. In the startup period the temperature was raised from room temperature up to reaction temperature with a $5\,K\,min^{-1}$ ramp. A change of the atmosphere from pure nitrogen to pure hydrogen was performed at 100°C.

The conversion of dipentene was studied in an integral fixed bed reactor at atmospheric pressure and temperatures between 200 and 400°C. The investigation of the catalytic behavior over various Pd-modified silica catalysts (A, B and C) with the reaction conditions $p = 1\,bar$, $WHSV = 3\,h^{-1}$, $1.5\,Nl\,h^{-1}$ H_2, but different reaction temperatures delivers interesting results. The conversion of dipentene Sylvapine DP-738 to *p*-cymene over catalyst A was examined at three different temperatures ($\theta = 200$, 300, 400°C). The conversion over catalyst B at $\theta = 200$ and 300°C was also investigated as well as the behavior in case of catalyst C at 300°C. The worst results are at $\theta = 200$°C (catalysts A and B, about 40% selectivity to *p*-cymene). Catalyst A produces the best results both at 300 and 400°C (90% selectivity), thus 300°C is favored. In the case of catalysts B and C ($\theta = 300$°C) the selectivity to *p*-cymene reaches 70–80%.

The silica based catalysts are superior over the zeolitic based ones [41,42]. Thereby, the presented data clearly show that the silica based catalysts result in a higher space–time yield. The lifetime behavior of the most promising catalyst A has been studied in the conversion of DP-738 for 120 h time on stream (TRS). Selectivity (90%) to *p*-cymene in the product mixture was obtained. The catalyst showed no deactivation for more than 100 h.

Encouraged by the promising results a scale-up of the process (reactor length 700 mm and external dia-

Table 7
Conversion of α-limonene in a fixed bed reactor (external temperature regulation)

Temperature (°C)	300	275	250	225	200
Catalyst	A	A	A	A	A
Composition	0.5% PD/SiO_2	0.5% PD/SiO_2	0.5% PD/SiO_2	0.5% PD/SiO_2	0.5% PD/SiO_2
Charge (g)	10	10	10	10	10
Carrier gas	H_2	H_2	H_2	H_2	H_2
Volume-flow	7.0	7.0	7.0	7.0	7.0
WHSV	2.5	2.5	2.5	2.5	2.5
TOS	6	6	6	6	6
Conversion (GC-%)	100	100	100	100	100
Selectivity (GC-%)	95.7	90.9	83.3	79.4	68.5

meter 30 mm) was performed with α-limonene as starting material. The observed selectivities were nearly as well as expected [41–42]. Table 7 gives an overview of the results carried out in this fixed bed reactor at various temperatures with an external temperature regulation. The cited temperatures describe the temperature of the catalyst bed at the beginning of the reaction (TOS = 0 h).

Using Sylvapine DP-738, as starting material, the results show that pure silica impregnated with Pd (0.5 wt.%) yields over 90% *p*-cymene without deactivation of the catalyst over a total TOS of 120 h. In conclusion, Pd is the active catalyst, but an effect of the support material is evident. Although the support is not the main factor in the catalytic conversion of mixtures of terpenes to *p*-cymene, an amorphous support provides higher yields than crystalline zeolitic carriers. Again, reneweable feedstocks can be used in an envrionmentally benign way for the production of valuable intermediates or fine chemicals.

8. Conclusion

New environmentally benign processes for the production of fine and intermediate chemicals are already realized and some others have a good chance for commercialization. All of them have a lot of advantages compared with the traditional production lines due to the ecological and economical point of view. The awareness, the needs and targets for the future according to my opinion are the following.

- Atomic efficiency, E-factor, 100% yield or selectivity, i.e. replacement of environmentally unacceptable processes.
- Development of catalyzed processes in fine and intermediate chemistry, no stoichoimetric chemistry anymore.
- Further and stronger replacement of homogeneous Lewis and Brønsted acids and bases by heterogeneous catalysis, e.g. acylation of aromatic compounds.
- More developments in base catalysis.
- More developments in acid–base bifunctional catalysis, i.e. using the synergetic effects.
- Reproducibility of catalyst preparation in particular for the synthesis of fine and intermediate chemicals.
- New oxidation processes using environmentally benign oxidants, e.g. avoiding inorganic and organic peroxides, no chlorine.
- Development of redox catalysts with acidic or basic properties.
- Activation of oxygen by hydogen, i.e. in situ H_2O_2.
- Development of multifunctional catalysis, i.e. combining several individual reaction steps in one step.
- Development of direct synthesis routes saving energy and starting material, i.e. 'one-pot'-reactions, e.g. direct amination or oxidation of aromatic compounds.
- Catalyst design in combination with reactor design and process technology.
- Extensive use of by-products in other syntheses.
- Use of regenerable and biodegradable resources.
- Direct C–H activation, i.e. using natural gas and alkanes, e.g. CH_3OH from CH_4, CH_3COOH from CH_4 and CO_2, CH_3COOH from C_2H_6, CH_2=CHCN from C_3H_8.
- Anti-Markownikow, addition of water and ammonia to olefins to synthesize primary alcohols and amines.
- Development of true chiral heterogeneous catalysts, i.e. immobilization of chiral homogeneous catalysts is not a real solution.
- Development of heterogeneous catalysts for the treatment of polluted water (wet air oxidation) and contaminated soil.

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