Catalysis Today 144 (2009) 318–323

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalytic activation of CO_2: Use of secondary CO_2 for the production of synthesis gas and for methanol synthesis over copper-based zirconia-containing catalysts

R. Raudaskoski [*], E. Turpeinen, R. Lenkkeri, E. Pongrácz, R.L. Keiski

Department of Process and Environmental Engineering, Mass and Heat Transfer Process Laboratory, P.O. Box 4300, FI-90014 University of Oulu, Finland

ARTICLE INFO

Article history:
Available online 20 January 2009

Keywords:
Carbon dioxide
Methanol
Secondary gas
Sustainable production
Synthesis gas

ABSTRACT

Consumption of fossil fuel resources throughout the industrial era has resulted in an enormous increase in carbon dioxide concentration in the atmosphere. Developed countries have committed to reducing the atmospheric load of greenhouse gases and ratified the Kyoto Protocol. Chemical utilization of carbon dioxide captured from large scale stationary sources is one possible pathway to decrease the rate of emissions. Catalysis plays a crucial role in these carbon dioxide utilization reactions. In this paper, the production of synthesis gas from carbon dioxide-containing secondary gases and carbon dioxide hydrogenation to methanol over copper-based zirconia-containing catalysts have been investigated. Pathways of carbon dioxide utilization are outlined, research done on carbon dioxide hydrogenation over copper-based zirconia-containing catalysts is reviewed, and the challenges of these reactions are reported. It is argued that direct utilization of secondary carbon dioxide from industrial sources can be a significant step toward developing sustainable industrial practices and a critical part in sustainable energy strategies.

1. Introduction

For two centuries, human beings have been transferring carbon from the lithosphere to the atmosphere. Presently, the world's coal-, oil- and natural gas industries dig and pump up about seven billion tons of carbon a year. Over the past 30 years, as the world production of goods and services grew at 3% a year, carbon emissions rose half as fast [1]. As a consequence, the concentration of carbon dioxide (CO_2) in the atmosphere has reached approximately 380 ppm, while during the preindustrial period it was only about 250 ppm [2,3]. The long-term environmental consequences of this trend are yet uncertain and have been a subject of much academic and public debate.

The tightening legislation due to the Kyoto Protocol to the United Nations Framework Convention on Climate Change, which was introduced in December 1997 and entered into force in February 2005, requires cutting the emissions of six key greenhouse gases (GHG), which are CO_2, methane (CH_4), dinitrogen oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulfur hexafluoride (SF_6). By the years 2008–2012, the developed countries ratifying the Kyoto Protocol should reduce their GHG emissions by a collective average of 5% below their 1990 levels. The member states of the European Union (EU) have undertaken to reduce their emission by 8%. [4] The targets are distributed among the EU member states; in Finland the GHG emissions should be stabilized to the 1990 level [5].

Reducing GHG emissions is a long-term and multi-faceted task. Finland's strategy includes promoting energy end-use efficiency, supporting the use of renewable energy resources, as well as endorsing sustainable transportation and waste management. In addition to these, recovery of CO_2 from flue gases and its direct or indirect utilization can also contribute to reducing CO_2 accumulation to the atmosphere (e.g. [2,6–8]). The utilization of CO_2 as a feedstock for producing chemicals is appealing not only because it can contribute to mitigation of GHG emissions, but also because it is an interesting challenge in exploring new concepts and new opportunities for catalysis and industrial chemistry [9]. In addition, virgin resources can be saved when secondary CO_2 is used as a raw material to replace them [6]. Remarkable also are the cheap price and non-toxicity of CO_2, and the potential to discover entirely new materials and novel routes to existing chemical intermediates and products, which are more efficient and economical than current methods, provides strong motivations to use CO_2 as a feedstock whenever possible [7].

The target of our research is to use secondary CO_2 as a raw material for valuable chemicals and products inside industrial facilities of CO_2 intensive sectors such as oil refineries, power plants, chemical, pulp and paper and metallurgical industries. The purpose of this article is to highlight the potential of catalysis in CO_2 utilization and to illustrate, in particular, synthesis gas

---

[*] Corresponding author. Tel.: +358 8 553 2362; fax: +358 8 553 2369.
E-mail address: riitta.raudaskoski@oulu.fi (R. Raudaskoski).

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.11.026

production from CO_2-containing gases and to review the use of copper-based zirconia-containing catalysts in CO_2 hydrogenation reaction to methanol. We will also argue that chemical utilization of CO_2 satisfies the principles of sustainable production, as apart from contributing to the reduction of the atmospheric load of CO_2, it also makes economic sense, and provides a safer route to some high-value and high-volume chemical intermediates.

2. From waste to resource—CO_2 utilization routes

In Finland, the major contributor to GHG emissions is CO_2 from energy generation, most of it coming from public electricity and heat production. Other major CO_2 sources are energy production in industry and transportation [10] (see Fig. 1). The largest CO_2 emitting point sources in Finland are oil refineries, coal burning plants for energy production and steelworks [11]. Especially the conventional coke-based production of iron from its ores plays a significant role in CO_2 emissions, resulting mostly from the combustion of fossil fuels for producing high-temperature process heat and from various process reactions.

Before its utilization, CO_2 has typically been separated, recovered and purified from concentrated CO_2 sources. Principally, CO_2 capture can be applied to all combustion processes. However, in reality, it will be limited to large scale stationary sources such as power plants and manufacturing industries, in order to achieve economies of scale. CO_2 can be captured either before or after combustion, using a range of existing and emerging technologies [12,13]. It is possible to convert the hydrocarbon fuel into CO_2 and hydrogen, remove CO_2 from the fuel gas and combust hydrogen (pre-combustion capture) or combust fuel using oxygen separated from air, which generates nearly pure CO_2 flue gas (oxyfuel combustion). In conventional processes, CO_2 is captured from the flue gases produced during combustion (post-combustion capture). For post-combustion CO_2 separation from flue gas, there is a wide range of technologies available, namely absorption, adsorption, cryogenic techniques, membrane separation and different combined systems based on physical and chemical processes. Each of these technologies has different benefits and drawbacks, as well as applicability in different situations, and the choice of a suitable technology depends on the characteristics of the flue gas stream [14–16].

Captured CO_2 can be converted in different ways to a large variety of products or utilized directly. Fig. 2 illustrates some of the major direct and indirect uses of CO_2, highlighting catalytic processes. According to Arakawa et al. [7] approximately 110 Mt of CO_2 is used for chemical production annually. The majority of these uses are applied to catalytic reactions. In addition, a range of catalytic reaction routes for CO_2 utilization are presently under research.

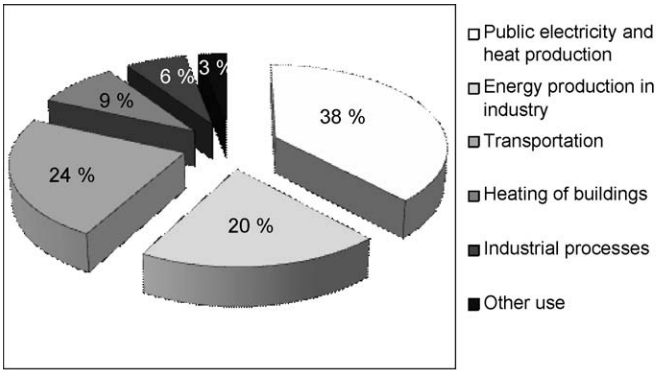

Fig. 1. CO_2 emissions by sources in Finland in 2005. Other use includes other fuel use, fugitive emissions of fuels and solvent use (data from Statistics Finland).

Our research concentrates mainly on reforming of CO_2-containing process and flue gases and methanol synthesis by CO_2 hydrogenation, and is focused on the development of catalysts for CO_2 activation.

3. Reforming using CO_2 as a feedstock

Some of the major CO_2 utilization reactions and their products are illustrated in Fig. 3. One of the most interesting applications for CO_2 is the production of synthesis gas (syngas). Another interesting target is methanol synthesis in which CO_2 is used instead of CO. This article illustrates the research routes printed in bold.

Synthesis gas, a key intermediate in the chemical industry, is a mixture of hydrogen and carbon monoxide. It can be used in a number of syntheses of a wide range of chemicals and fuels, and as a source of pure hydrogen and carbon monoxide. Synthesis gas can be produced by reforming or gasification from almost any carbon-containing source ranging from natural gas and oil products to coal and biomass [17]. Nowadays, natural gas is the dominant feedstock for the production of synthesis gas [18]. However, from an environmental and industrial perspective, there is a growing interest in utilizing alternative raw materials such as renewable sources or different kinds of flue and process gases.

The most dominant reforming technologies are steam reforming, partial oxidation and auto-thermal reforming, a combination of the previous two [19,20]. Recently, the attention to the process

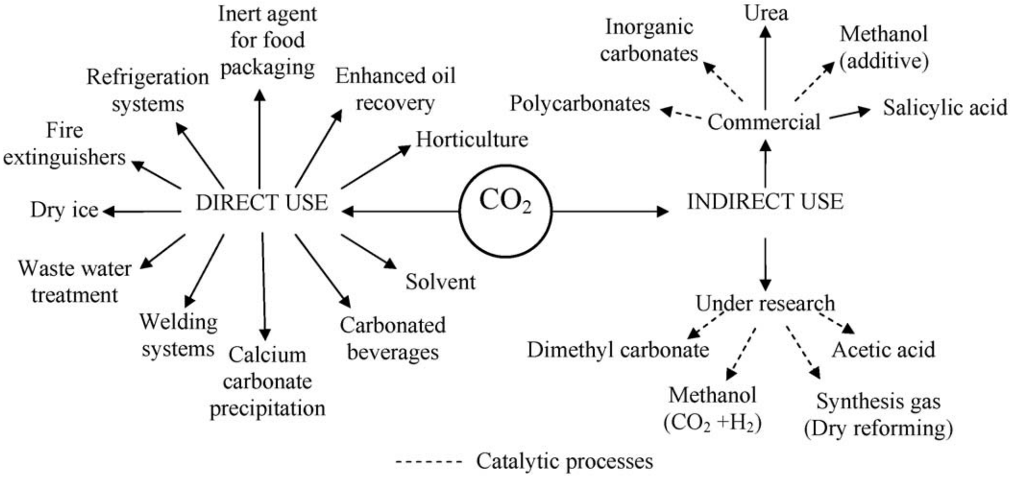

Fig. 2. Some possibilities to direct and indirect utilization of CO_2.

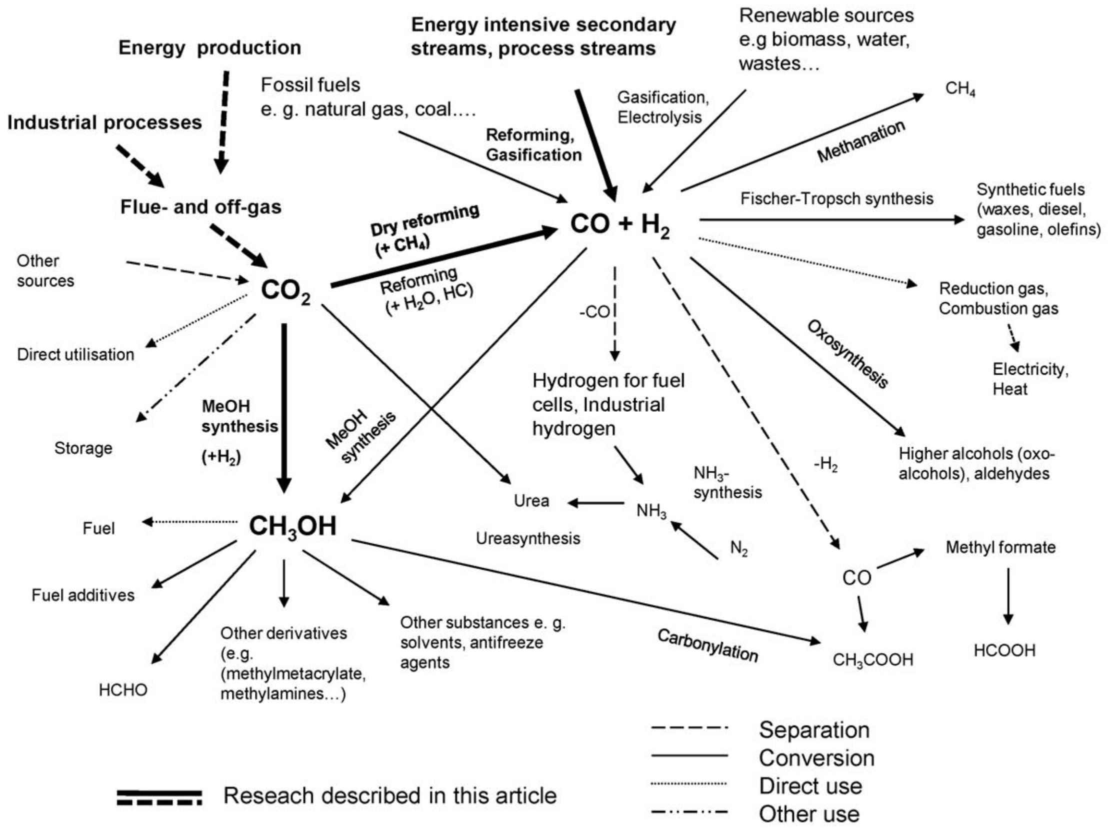

Fig. 3. CO_2 and synthesis gas reaction pathways to products and the scope of this article.

of reforming of CO_2 with methane (called dry reforming, reaction (1)) has increased because of the possibility to use two inexpensive carbon-containing feedstocks for the generation of synthesis gas.

$$CO_2 + CH_4 \leftrightarrow 2H_2 + 2CO, \quad \Delta H^{\circ}{}_{298\,K} = 247\,kJ/mol \tag{1}$$

From the environmental perspective, dry reforming provides the way to consume major greenhouse gases by means of this reaction. From an industrial viewpoint, the dry reforming with CO_2 may be an attractive alternative, especially for applications requiring synthesis gas with low H_2/CO ratio. With a H_2/CO ratio of unity, the synthesis gas produced is a suitable feedstock for the oxo-synthesis or synthesis of oxygenates [21–23]. The major disadvantage of dry reforming is the rapid deactivation of the catalyst caused by coke formation [24,25]. Another drawback is that dry reforming is a highly endothermic reaction and thus requires a large amount of energy. Assuming that the ratio chosen for dry reforming will be unity, it can be seen that remarkable conversion of the reactants (CO_2 and CH_4) will only be achieved at high temperatures (above ca. 800 °C) (Fig. 4). However, even at high temperatures there is a high thermodynamic potential for coke (C) formation. Coke deposition leads to the coverage of active sites and a decrease in catalytic performance up to deactivation of the catalyst. The high positive enthalpy value of the dry reforming reaction indicates that energy has to be supplied to make the reaction to occur. In practice, this energy is probably generated by combustion of fossil fuels, thereby contributing negatively to the overall balance of CO_2. If energy is supplied from renewable or non-fossil sources, the CO_2 balance is not affected. Moreover, when dry reforming is used to provide synthesis gas, the total consumption of CO_2 will depend on the energetics of the subsequent synthesis gas consuming processes. Assuming that the process is exothermic (i.e. methanol synthesis), some energy can be fed back to the reforming phase.

Dry reforming was first studied by Fischer and Tropsch over a number of base metal catalysts [26]. Considerable effort has been devoted to developing high performance dry reforming catalysts. It was reported that most of the group VIII metals are more or less catalytically active toward this reaction [27]. Noble metals, such as ruthenium, rhodium, palladium, platinum and iridium, and some non-noble metals like nickel and cobalt have been studied for the dry reforming reaction (e.g. [28–41]). Generally speaking, noble metal catalysts have higher resistance to carbon deposition than the conventional nickel catalyst [31,42]. However, due to the high price and limited availability of noble metals, nickel catalysts have been the most extensively investigated catalysts [43]. Usually, nickel has been supported on different carriers such as Al_2O_3, MgO,

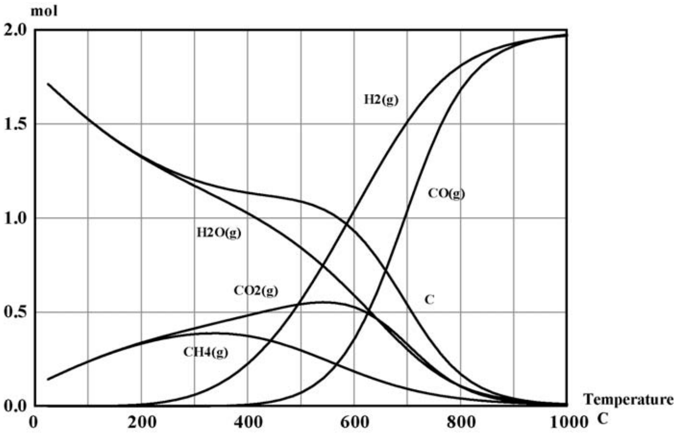

Fig. 4. Product composition of dry reforming as a function of temperature at thermodynamic equilibrium (feed: CH_4:CO_2 = 1, p = 1 atm) calculated by HSC Chemistry®.

TiO_2, ZrO_2 and SiO_2 (e.g. [32,44–48]). Promoters such as CeO_2, La_2O_3 and MnO have been reported to improve the dispersion of nickel and decrease the rate of coke deposition (e.g. [49–51]).

While the thermodynamics of the dry reforming reaction is well understood, knowledge about the reaction mechanism and kinetics is still controversial. It is generally believed that the most likely slow steps are those of methane activation to form CH_x and the reaction between CH_x (x = 0–3) species and the oxidant, either in the form of oxygen atoms originating from CO_2 dissociation or CO_2 itself [52]. However, the results reported in the literature are not consistent, depending on reaction conditions. Generally, it is argued that the dry reforming has either two rate determining steps or one single rate determining step. It has been suggested [53] that both CH_4 dissociation and CH_xO decomposition were rate determining steps in the reforming reaction. Another proposed mechanism [54] indicates that CH_4 decomposes to chemisorbed C in a series of H-abstraction steps, the first H-abstraction being the kinetically significant step.

As referred to earlier, the predominant thinking for CO_2 conversion and utilization begins with the use of pure CO_2. However, CO_2 separation, recovery and purification from concentrated CO_2 streams require substantial energy expenditure. On the other hand, the so called 'tri-reforming' concept uses CO_2 of flue gases from power plants without CO_2 pre-separation. This concept combines dry reforming, steam reforming and partial oxidation and represents a new way of thinking for the production of synthesis gas with desired H_2/CO ratio using flue gas and natural gas [55].

Although thus far the tri-reforming concept has been applied only to power plant's flue gases, the method can be made applicable also to flue or process gases of other sectors as well. Halmann and Steinfeld [56,57] have examined the tri-reforming of natural gas with flue gas from power station and other industries in terms of energy efficiency, fuel saving and CO_2 emission avoidance. Our research is presently directed to CO_2 concentrated gas streams released from iron making and pulp and paper processes, as a potential feedstock for reforming. Resultant gases can then further be upgraded to valuable chemicals or fuels or recycled back to the process. Apart of this method's potential in reducing CO_2 emissions, recycling process gases saves primary energy resources such as fossil fuels and extends the range of products produced in the process, thus improving the resource efficiency of processes.

4. Methanol synthesis

Methanol (CH_3OH) is an industrially important chemical, used mainly as a feedstock in the production of bulk chemicals such as formaldehyde and acetic acid. It has also been used for example in the manufacture of methyl tertiary-butyl ether (MTBE), methyl methacrylate (MMA) and as a solvent [58]. According to the Methanol Institute [59] its demand is nowadays around 32 million tons per year worldwide.

The first commercial process for the production of CH_3OH by the destructive distillation of wood was operational already in the 19th century [60]. The first industrial plant that produced methanol from synthesis gas was built by BASF in 1923. This process used zinc oxide/chromium oxide catalysts operating at 300 °C and 200 atm. The process is also known as high-pressure methanol synthesis [61].

Later on, a number of improvements have been made to early methanol processes, and the predominant technology now is a low-pressure process ($p < 100$ atm) using copper-based catalysts [60,62]. The synthesis gas needed as a feedstock is usually produced by catalytic steam reforming of hydrocarbon feedstocks or by non-catalytic partial oxidation of hydrocarbons or coal. CO_2 is used in the feedstock to adjust the feed compositions [60]. The maximum yield of carbon oxides to methanol is limited by thermodynamic equilibrium. The main reactions taking place in this commercial methanol process are

$$CO + 2H_2 \leftrightarrow CH_3OH, \quad \Delta H^{\circ}_{298\,K} = -90.77\,\text{kJ/mol} \tag{2}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O, \quad \Delta H^{\circ}_{298\,K} = -49.58\,\text{kJ/mol} \tag{3}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O, \quad \Delta H^{\circ}_{298\,K} = 41.19\,\text{kJ/mol} \tag{4}$$

Presently this process is well established, and several companies, including ICI, Lurgi and Mitsubishi, offer commercial technology solutions [61,62]. However, there is still a controversy about many important factors related to catalysts, kinetics and the reaction mechanism of the commercial methanol synthesis reaction. The main question is whether CO or CO_2 is the main source of methanol [63,64]. Some researchers believe that CO hydrogenation (reaction (2)) is the main chemical reaction in commercial methanol synthesis and others assume that the reaction proceeds only via hydrogenation of CO_2 (reaction (3)) [63].

During the last years, CO_2 hydrogenation to CH_3OH (reaction (3)) has gained wide interest to contribute to the reduction of CO_2 emissions. The direct conversion of CO_2 and hydrogen to CH_3OH has already been demonstrated and, according to the literature, CO_2 can be converted with hydrogen into CH_3OH with higher selectivity than CO and at lower reaction temperatures [65 and Ref. 43 therein]. Certainly many challenges still remain. Firstly, the source of hydrogen is a fundamental question when CO_2 is utilized in the hydrogenation reaction to methanol. When considering net CO_2 emissions it is essential that the manufacturing process produces less CO_2 than the methanol synthesis consumes. One solution for that could be the H_2 production via dry reforming (reaction (1)). Instead of producing CO_2, this reaction consumes it. Unfortunately, synthesis gas obtained from the dry reforming contains considerable amount of CO and thereby it is not exploitable in the CO_2-based methanol synthesis as such. Tuning and reduction of CO in the gas mixture increase expenses, but if a profitable application for the utilization of CO can be found, then the treatment of CO is reasoned. Moreover, to get CO_2-based methanol synthesis economically and environmentally reasonable and meaningful, both raw materials, H_2 and CO_2, should be produced or utilized in a sustainable and cost-effective way. Utilization of CO_2 neutral biomass as a carbon source for synthesis, and the electrolysis of water using renewable electrical energy as the source of hydrogen open up a possibility to produce methanol in an environmentally benign way, but especially the cost-effective electrolysis is still far from the commercialization [66]. Secondly, based on thermodynamics the yield of methanol decreases with an increase in the concentration of CO_2 in proportion of CO in the feed gas [67]. As well the kinetics of methanol production in the presence of CO is more advantageous compared to the process without CO [63]. In addition, the CO_2 hydrogenation reaction is dependent on the development of an effective catalyst, because the same methanol synthesis catalysts optimized for commercial processes are not as effective in CO_2 hydrogenation to methanol under similar operation conditions [68,69]. The direct conversion of CO_2 and hydrogen to CH_3OH has been studied extensively, investigating different catalyst compositions and preparation methods. Table 1 summarizes some of the research done with copper-based zirconia-containing catalysts, including our own.

A range of copper-based zirconia-containing catalysts prepared by different methods have already been tested in CO_2 hydrogenation reaction to CH_3OH. This overview (Table 1) illustrates the potential of copper-based zirconia-containing catalysts in methanol synthesis. As a case in point, it has been found e.g. that zirconia addition to copper catalysts enhances copper dispersion [72,74] and the zirconia-containing catalyst can be composed of fine

Table 1
Review of research on zirconia-containing catalysts in CO_2 hydrogenation to methanol.

Catalyst(s)	Preparation method(s)	Aim of research	Main conclusions	Ref.
$Cu/ZnO/ZrO_2$	Co-precipitation	Effect of the solvent used in the catalyst preparation	The properties of the solvent have great influence on surface properties, structure and catalytic performance. The solvent with small surface tension and large viscosity produces a high activity ultrafine catalyst after calcinations	[70]
Cu/ZrO_2	Deposition–precipitation, impregnation, co-precipitation	Effects of the catalyst composition, the catalyst preparation methods and the conditions	The catalyst composition and the catalyst preparation methods and conditions have enormous influence on the surface structure of catalysts. The catalyst prepared by deposition–precipitation has finer particles and higher catalytic activity than the catalysts prepared by impregnation or co-precipitation	[71]
$Cu/\gamma\text{-}Al_2O_3$ $12Cu10Zr/\gamma\text{-}Al_2O_3$	Impregnation	Effect of zirconia modification on $\gamma\text{-}Al_2O_3$ support to the Cu-based catalyst	Both the catalytic activity and selectivity toward methanol improve after Zr addition due to the enhanced dispersion of copper oxide	[72]
$Cu/ZnO/ZrO_2$ $Cu/ZnO/ZrO_2/MgO$ $Cu/ZnO/ZrO_2MnO$	Decomposing the citrate complexes of the metals	Effect of addition of the Mg and Mn promoters on the $Cu/ZnO/ZrO_2$ catalysts	Addition of promoters leads to increase of the copper dispersion in the reduced catalysts and increase of catalytic activity	[73]
Cu/ZnO Zr–Cu/ZnO	Successive-precipitation	Effect of the ZrO_2 doping on Cu/ZnO catalysts	ZrO_2-doped Cu/ZnO catalyst has considerably higher activity and selectivity compared to the catalyst without ZrO_2. The presence of ZrO_2 led to higher copper dispersion	[74]
$Cu/SiO_2/TiO_2$ $Cu/SiO_2/ZrO_2$ $Cu/SiO_2/TiO_2/ZrO_2$	Decomposition of $Cu(NO_3)_2$	Effect of the added ZrO_2 and TiO_2 on the activity of the catalysts	Both the ZrO_2 and the TiO_2 individually enhance the catalyst activity, but a significantly greater enhancement is achieved by the addition of both oxides simultaneously. ZrO_2 addition increases methanol synthesis on both Cu and ZrO_2 surfaces and the TiO_2 addition enhance the reaction occurring on the copper surface	[75]
$Cu/t\text{-}ZrO_2$ $Cu/m\text{-}ZrO_2$	Impregnation	Effect of zirconia phase and copper to zirconia surface on the activity of catalysts	The catalysts prepared on $m\text{-}ZrO_2$ support are 4.5 times more active than the catalysts prepared on $t\text{-}ZrO_2$ support. Higher rate of methanol synthesis on $Cu/m\text{-}ZrO_2$ than on $Cu/t\text{-}ZrO_2$ is due to higher concentration of active intermediates	[76]
$Cu/ZnO/ZrO_2$	Co-precipitation	Effect of ageing time during the co-precipitation	Prolonged suspension ageing time during the catalyst preparation is advantageous for catalyst activity, because with increasing ageing time, the sodium content of the catalyst decreases and finer crystallite structures are formed	[77]

particles [70,71,77]. Due to enhanced copper dispersion both catalytic activity and selectivity toward methanol improve [72,74] and the formation of finer particles leads to higher catalytic activity in CO_2 hydrogenation reaction toward methanol [70,71,77]. In addition, it has been reported e.g. that the crystal type of zirconia influences the performance of the catalyst if zirconia is used as the catalyst support material. The copper catalysts on $m\text{-}ZrO_2$ were 4.5 times more active in methanol synthesis from CO_2 and H_2 compared to those on $t\text{-}ZrO_2$ [76]. Also the addition of promoters could increase the activity of copper-based zirconia-containing catalysts [73,75]. Our research contributes to this field by evaluating the effect of different preparation methods, preparation conditions and catalyst compositions of the copper-based zirconia-containing catalyst on catalytic activity.

5. Discussion

Although being very challenging, utilization of secondary CO_2 originating from production processes and flue gases of CO_2-intensive sectors has a great environmental and industrial potential due to improving the resource efficiency of industry as well as by contributing to the reduction of CO_2 emissions. As a feedstock, CO_2 is non-toxic, stable and, therefore, safe constituent of chemical reactions; however, its activation is challenging. Catalysis plays a crucial role in the chemical utilization of CO_2, as illustrated in this article. Our research has focused on the synthesis of CO_2 to synthesis gas and to methanol, utilizing secondary sources. Further, methanol will provide a reaction pathway to chemical innovations, as well as environmental protection.

Among the innovations in the use of methanol is the production of olefins [78]. Light olefins, such as ethylene and propylene, are important raw materials for polymers production. A novelty application of methanol is in the production of dimethyl carbonate (DMC), further using CO_2 in a supercritical state [79]. DMC in turn is an intermediate for derivatives used in polycarbonates and polyurethanes [80]. Utilization of CO_2 in the production of polymers also provides a long-term fixation of CO_2 and replaces fossil sources otherwise used.

Utilizing methanol produced from secondary CO_2 can also support the energy strategy, especially through promoting sustainable transportation and the use of renewable fuels. In an effort to improve the sustainability of transportation, much research has been done in the area of fuel cell applications [81,82]. Although hydrogen is the most commonly used fuel for fuel cells, also methanol-based fuel cells are suitable for portable applications [83]. Following the European Council Directive 2003/30/EC on the promotion of the use of biofuels or other renewable fuels for transport, EU Member States should ensure that, by 31 December 2010, a minimum of 5.75% proportion (by energy content) of all petrol and diesel for transport purposes placed on

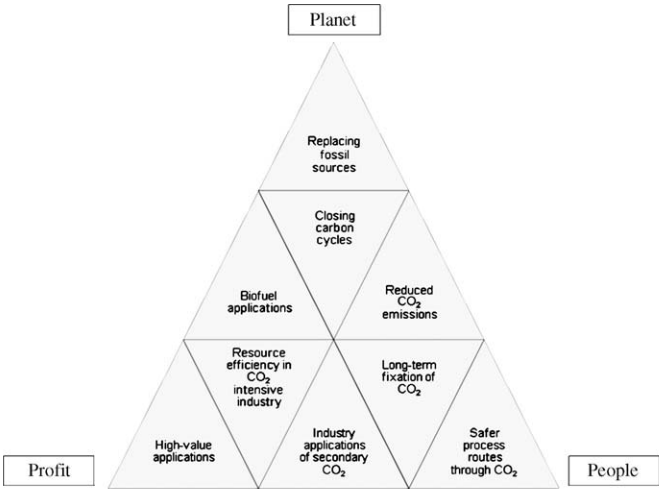

Fig. 5. Chemical utilization of CO_2 satisfying environmental, economic and social concerns, the three facets of sustainability.

markets should be based on renewable sources. Therefore, a noteworthy end-use for methanol is in transesterification for the production of biodiesel.

It can be concluded that direct utilization of secondary CO_2 from industrial sources can be a significant step toward developing sustainable industrial practices and a critical part in sustainable energy strategies. Sustainable processes incorporate environmental considerations, economic benefits and positive social impacts, often expressed as the three Ps: People, Planet and Profit. As illustrated by the fractal diagram in Fig. 5, chemical utilization of CO_2 exemplified in this article can satisfy all facets of sustainability, by closing material cycles, while providing safe and environmentally considerate reaction routes to the manufacture of high-value and high-volume chemicals.

Our research will continue to improve the potential use of flue gases from process industries and to further develop catalysts for the activation of CO_2.

Acknowledgement

The financial support of the Academy of Finland (CO2UTIL Project, No. 118078) for this research is greatly appreciated.

References

[1] R.H. Sokolow, S.W. Pacala, Sci. Am. 295 (2006) 28.
[2] X. Xiaoding, J.A. Moulijn, Energy Fuels 10 (1996) 305.
[3] C.D. Keeling, T.P. Whorf, Atmospheric carbon dioxide record from Mauna Loa, http://cdiac.ornl.gov/trends/co2/sio-mlo.htm.
[4] United Nations Framework Convention on Climate Change, Kyoto Protocol Reference Manual on Accounting of Emissions and Assigned Amounts, http://unfccc.int/files/national_reports/accounting_reporting_and_review_under_the_kyoto_protocol/application/pdf/rm_final.pdf.
[5] European Union, EU Targets, http://ec.europa.eu/environment/climat/campaign/euinitiatives_en.htm.
[6] M. Aresta, I. Tommasi, Energy Convers. Manage. 38 (1997) S373.
[7] H. Arakawa, M. Aresta, J.N. Armor, M.A. Barteau, E.J. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. DuBois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D.W. Goodman, J. Keller, G.J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Murokuma, K.M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielsen, W.M.H. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, P.C. Stair, B.R. Stults, W. Tumas, Chem. Rev. 101 (2001) 953.
[8] C. Song, Catal. Today 115 (2006) 2.
[9] G. Centi, S. Perathoner, Stud. Surf. Sci. Catal. 153 (2004) 1.
[10] Statistics Finland, Greenhouse gas emissions in 1990 and 1995–2005, by source category and gas, http://www.stat.fi/til/khki/2005/khki_2005_2007-04-19_tau_001_en.html.
[11] T. Koljonen, H. Siikavirta, R. Zevenhoven, CO_2 Capture, Storage and Utilization in Finland, Technical Research Centre of Finland, Finland, 2002, p. 98.
[12] G. Göttlicher, R. Pruschek, Energy Convers. Manage. 38 (1997) 173.
[13] K. Damen, M. van Troost, A. Faaij, W. Turkenburg, Prog. Energy Combust. Sci. 32 (2006) 215.
[14] S. Wong, R. Bioletti, Carbon Dioxide Separation Technologies, http://www.aidis.org.br/eng/ftp/CARBON%20DIOXIDE%20SEPARATION%20TECHNLOGIES.pdf.
[15] A. Meisel, S. Xiaoshan, Energy Convers. Manage. 38 (1997) 37.
[16] T.P. Shaw, P.W. Hughes, Hydrocarbon Proc. 80 (2001) 53.
[17] J. Rostrup-Nielsen, J. Sehested, J.K. Norskov, Adv. Catal. 47 (2002) 65.
[18] R. Kothari, D. Buddhi, R.L. Sawhney, Renew. Sustain. Energy Rev. (2006), doi:10.1016/j.rser.2006.07.012.
[19] J.J. McKetta (Ed.), Encyclopedia of Chemical Processing and Design, vol. 56, Marcel Dekker, New York, 1996.
[20] K. Aasberg-Petersen, J.-H. Bak Hansen, T.S. Christensen, I. Dybkjaer, P.S. Christensen, C.S. Nielsen, S.E.L.W. Madsen, J.R. Rostrup-Nielsen, Appl. Catal. A 221 (2001) 379.
[21] R. Burch, M.I. Petch, Appl. Catal. 88 (1992) 39.
[22] E.C. Alyea, J. Wang, Appl. Catal. 104 (1993) 77.
[23] D.L. Trimm, Catal. Rev.-Sci. Eng. 16 (1977) 155.
[24] J.R. Rostrup-Nielsen, Catal. Today 18 (1993) 305.
[25] K.C. Mondal, V.R. Choudhary, U.A. Joshi, Appl. Catal. A 316 (2007) 47.
[26] F. Fischer, H. Tropsch, Brennst. Chem. 9 (1928) 39.
[27] E. Ruckenstein, H.Y. Wang, Appl. Catal. A 204 (2000) 257.
[28] A.M. Gadalla, B. Bower, Chem. Eng. Sci. 43 (1988) 3049.
[29] J.T. Richardson, S.A. Paripatyadar, Appl. Catal. 61 (1990) 293.
[30] A.T. Ashcroft, A.K. Cheetham, M.L.H. Green, P.D.F. Vernon, Nature 352 (1991) 225.
[31] J.R. Rostrup-Nielsen, J.-H.B. Hansen, J. Catal. 144 (1993) 38.
[32] A. Erdöhelyi, J. Cserényi, F. Solymosi, J. Catal. 141 (1993) 287.
[33] E. Ruckenstein, Y.H. Hu, Appl. Catal. A 133 (1995) 149.
[34] Z.L. Zhang, X.E. Verykios, J. Chem. Soc., Chem. Commun. (1995) 71.
[35] V.C.H. Kroll, H.M. Swaan, C. Mirodatos, J. Catal. 161 (1996) 409.
[36] Y.H. Hu, E. Ruckenstein, Catal. Lett. 36 (1996) 145.
[37] R.N. Bhat, W.M.H. Sachtler, Appl. Catal. A 150 (1997) 279.
[38] H.Y. Wang, C.T. Au, Appl. Catal. A 155 (1997) 239.
[39] S.M. Stagg, E. Romeo, C. Padro, D.E. Resasco, J. Catal. 178 (1998) 137.
[40] K. Tomishige, Y. Chen, K. Fujimoto, J. Catal. 181 (1999) 91.
[41] J.H. Bitter, K. Seshan, J.A. Lercher, J. Catal. 183 (1998) 336.
[42] M.F. Mark, M.F. Maier, J. Catal. 164 (1996) 122.
[43] J.R. Rostrup-Nielsen, Catal. Rev. Sci.-Tech. 46 (2004) 247.
[44] E. Ruckenstein, Y.H.J. Hu, J. Catal. 162 (1996) 230.
[45] M.C.J. Bradford, M.A. Vannice, Catal. Today 50 (1999) 87.
[46] J.H. Bitter, W. Hally, K. Seshan, J.G. van Ommen, J.A. Lercher, Catal. Today 29 (1996) 349.
[47] S. Wang, G.Q.M. Lu, Appl. Catal. B 16 (1998) 269.
[48] M. Rezaei, S.M. Alavi, S. Sahebdelfar, Peng Bai, Xinmei Liu, Zi-Feng Yan, App. Catal. B 77 (2008) 346.
[49] S.M. Stagg, D.E. Resasco, Stud. Surf. Sci. Catal. 119 (1998) 813.
[50] G. Xu, K. Shi, Y. Gao, H. Xu, Y. Wei, J. Mol. Catal. A 147 (1999) 47.
[51] A. Nandini, K.K. Pant, S.C. Dhingra, Appl. Catal. A 290 (2005) 166.
[52] S. Wang, G.Q. Lu, Ind. Eng. Chem. Res. 38 (1999) 2615.
[53] M.C.J. Bradford, M.A. Vannice, Appl. Catal. A 142 (1996) 97.
[54] J. Wei, E. Iglesia, J. Catal. 225 (2004).
[55] C. Song, W. Pan, Catal. Today 98 (2004) 463.
[56] M. Halmann, A. Steinfeld, Catal. Today 115 (2006) 170.
[57] M. Halmann, A. Steinfeld, Energy 31 (2006) 3171.
[58] G. Ertl (Ed.), Handbook of Heterogeneous Catalysis, VCH, Weinheim, 1997.
[59] Methanol Institute-World methanol supply/demand http://www.methanol.org/pdfFrame.cfm?pdf=methanolSupplyDemand02.pdf.
[60] J.J. McKetta (Ed.), Encyclopedia of Chemical Processing and Design, vol. 29, Marcel Dekker, New York, 1988.
[61] S. Lee, Methanol Synthesis Technology, CRC Press, The United States, 1990, p. 236.
[62] Methanol Institute, http://www.methanol.org/.
[63] J. Skrzypek, M. Lachowska, M. Grzesik, J. Sloczynski, P. Nowak, Chem. Eng. J. 58 (1995) 101.
[64] V.E. Ostrovskii, Catal. Today 77 (2002) 141.
[65] M. Aresta, A. Dibenedetto, Cat. Today 98 (2004) 455.
[66] J.N. Armor, Catal. Lett. 101 (2005) 131.
[67] J. Wu, M. Saito, M. Takeuchi, T. Watanabe, Appl. Catal. A 218 (2001) 235.
[68] T. Inui, H. Hara, T. Takeguchi, J.B. Kim, Catal. Today 36 (1997) 25.
[69] M. Saito, T. Fujitani, M. Takeuchi, T. Waranabe, Appl. Catal. A 138 (1996) 311.
[70] Y. Ma, Q. Sun, D. Wu, W.-H. Fan, Y.-L. Zhang, J.-F. Deng, Appl. Catal. A 171 (1998) 45.
[71] J. Liu, J. Shi, D. He, Q. Zhang, X. Wu, Y. Liang, Q. Zhu, Appl. Catal. A 218 (2001) 113.
[72] Y. Zhang, J. Fei, Y. Yu, X. Zheng, Energy Convers. Manage. 47 (2006) 3360.
[73] J. Sloczynski, R. Grabowski, A. Kozlowska, P. Olszewski, M. Lachowska, J. Skrzypek, J. Stoch, Appl. Catal. A 249 (2003) 129.
[74] C. Yang, Z. Ma, N. Zhao, W. Wei, T. Hu, Y. Sun, Catal. Today 115 (2006) 222.
[75] T.C. Schilke, I.A. Fisher, A.T. Bell, J. Catal. 184 (1999) 144.
[76] K.T. Jung, A.T. Bell, Catal. Lett. 80 (2002) 63.
[77] R. Raudaskoski, M. Veringa Niemelä, R.L. Keiski, Top. Catal. 45 (2007) 57.
[78] G. Pop, R. Ganea, D. Ivanescu, R. Boeru, G. Ignatescu, R.Birjega, US Patent 6,710,218 (issued 23.3.2004).
[79] D. Ballivet-Tkatchenko, S. Chambrey, R. Keiski, R. Ligabue, L. Plasseraud, P. Richard, H. Turunen, Catal. Today 111 (2006) 80.
[80] F. Rivetti, C. R. Acad. Sci. Paris, Chem. 3 (2000) 497.
[81] B.D. McNicol, D.A.J. Rand, K.R. Williams, J. Power Sources 100 (2001) 47.
[82] M. Sundaresan, S. Ramaswamy, R.M. Moore, M.A. Hoffman, J. Power Sources 113 (2003) 19.
[83] F. de Bruijn, Green Chem. 7 (2005) 132.