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Utilization of carbon dioxide in heterogeneous catalytic synthesis†

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Utilization of carbon dioxide as a C_1 building block in chemical synthesis has been stimulated mainly by environmental considerations and its large-scale availability. Catalysis provides several opportunities for using CO_2 in chemical synthesis. The present state of these efforts in heterogeneous catalysis is briefly surveyed, placing special emphasis on more recent developments in the syntheses of methanol, methylamines and formic acid derivatives, and the production of synthesis gas. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: carbon dioxide; chemical synthesis; catalysis; methanol; methylamines; formic acid derivatives; synthesis gas

1. INTRODUCTION

Fixation of carbon dioxide[1] has received considerable attention, mainly triggered by environmental considerations and its large-scale availability at low cost. However, because CO_2 is a highly oxidized, thermodynamically stable compound its utilization in redox reactions requires high energy substances or electroreductive processes. These properties, in conjunction with lower reactivity in various reactions, are probably the major reasons why currently the toxic carbon monoxide, the main competitor as a C_1 building unit for many processes, is used mostly in industry. Although a number of organic syntheses using carbon dioxide are known[2,3] only a few are applied in industry, the main processes being the syntheses of urea and its derivatives,[4,5] and of organic carbonates,[6–8] where phosgene ($COCl_2$) is increasingly being replaced by CO_2 as the C_1 building unit.[8–10] Another important CO_2 consumer is the electrochemical Kolbe–Schmitt process for the production of salicylic acid.

Catalysis, either homogeneous, heterogeneous or enzymatic, is a promising approach to CO_2 fixation. The potential of homogeneous catalysis for CO_2 fixation has been discussed in recent reviews.[3,11] Valuable chemicals that can be synthesized using homogeneous catalytic routes include the production of carbonates,[10] carbamates,[12] urethanes,[13–15] lactones,[16–19] pyrones,[20] and formic acid and its derivatives.[21,22]

Heterogeneous catalysis can offer several technical advantages which are linked with stability, separation, handling and reuse of the catalyst and reactor design. Despite these beneficial practical features, the range of compounds that have been synthesized from CO_2 by heterogeneous catalytic routes is still comparatively narrow. Efforts towards the use of CO_2 for the synthesis of valuable chemicals by heterogeneous catalytic pathways are still mainly confined to methanol synthesis, the syntheses of methylamines and formic acid derivatives, and the production of synthesis gas (CO,H_2). This brief review is intended to provide an overview of the progress in this area, focusing mainly on the most recent developments.

2. METHANOL SYNTHESIS

Hydrogenation of CO_2 can afford various compounds, such as methanol, hydrocarbons, esters and ethers, depending on the catalyst and the reaction conditions applied. Among these products, methanol is by far the most important. It is one of the key petro-chemicals, with a worldwide annual production of nearly 30 million tonnes. In addition to its importance in the syntheses of

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formaldehyde, resins, dimethyl ether, methyl t-butyl ether, acetic acid and other base chemicals, it also finds application as a solvent and gasoline extender. Furthermore, since methanol does not exhibit the storage and transport problems associated with hydrogen, converting carbon dioxide and hydrogen to methanol may offer a great potential for the storage of hydrogen in a future energy scenario.[23]

In principle, methanol can be produced either from CO (Eqn [1]) or CO_2 (Eqn [2]). A disadvantageous feature of the synthesis from CO_2 is that more hydrogen is consumed due to formation of water.

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad [1]$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad [2]$$

The synthesis reactions are interrelated by the water-gas-shift equilibrium:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad [3]$$

Methanol is currently produced on an industrial scale from syngas (CO, H_2) to which a few percent of CO_2 is added to improve catalyst performance. Modern copper-based methanol synthesis catalysts are highly selective (selectivities $>$99.9% are not uncommon).[24] Support materials applied, ranked according to their suitability, are: ZnO, ZrO_2, Al_2O_3, TiO_2 and SiO_2.

Developing high selectivity is the key problem in converting CO_2 to methanol. The challenge is thus to find a catalyst that affords high selectivity to methanol and simultaneously low selectivity to CO, which is formed via the reverse-water-gas-shift (RWGS) reaction ($CO_2 + H_2 \rightarrow CO + H_2O$). As with the industrial methanol production from synthesis gas, copper seems also to be the metal of choice for methanol synthesis starting from CO_2. Another common feature is that the support plays a significant role in the overall catalytic performance.[25–28] Zirconia proved to be an excellent support material for CO_2-based methanol synthesis. The preparation, structural and chemical properties, as well as the mechanistic aspects of metal–zirconia catalysts, for CO_2 hydrogenation have been reviewed recently.[29]

Reaction conditions and catalyst properties strongly affect product distribution in CO_2 hydrogenation; low temperatures and high pressures are favourable for the desired methanol formation. Depending on the active metal and the support/promoter used, various by-products, such as carbon monoxide, methane and dimethyl ether, are observed. However, methanol selectivity is mainly determined by the competition of the methanol synthesis and the reverse-water-gas-shift reaction.[25–30]

From the group IB metal/zirconia catalysts, copper and silver are most selective for methanol formation, with silver being significantly less active than copper.[27] Gold is the most active, but unselective, favouring the undesired reverse-water-gas-shift reaction. Promotion of copper–zirconia with silver results in a distinct increase in methanol selectivity while the activity remains unaffected.[31] The addition of chromium oxide, and to a lesser extent manganese oxide, to copper–zirconia retards sintering of the copper component and shifts the crystallization of the amorphous zirconia to higher temperatures, resulting in increased thermal stability of the catalyst under reaction conditions. For temperatures exceeding 250 °C, the catalyst promoted with chromium oxide exhibits higher activity than the unpromoted copper–zirconia.[32] Clarke and Bell[33] found that the addition of potassium salts accelerates the reverse-water-gas-shift reaction but hinders methanol synthesis in CO_2 hydrogenation reactions. Very recently, copper–zirconia and silver–zirconia aerogels have been prepared via the sol-gel method in combination with supercritical drying.[34] As a consequence of favourable textural properties and high copper surface area, the copper–zirconia aerogel exhibits higher activity than similar catalysts prepared by coprecipitation.

Considerable effort has been expended to unravel the mechanism of CO_2 hydrogenation over copper–zirconia catalysts.[35–38] A complicating factor is that, on all efficient catalysts, hydrogenation (Eqn [2]) and reverse-water-gas-shift reaction (Eqn [3]) occur simultaneously. This problem has led to considerable debate as to whether methanol formation starts from CO or CO_2. However, the relative facility of the water-gas-shift equilibrium (Eqn [3]) renders this question rather hypothetical. The hydration state of the support surface was found to play an important role in providing adsorption sites for the reaction intermediates observed during methanol synthesis. In the presence of surface hydroxyl groups, i.e. on the prereduced catalyst, surface formates, carbonates, formaldehyde and methoxy species are immediately observed in CO_2 and CO hydrogenation reactions. On a non-prereduced surface, formate formation is strongly suppressed, suggesting that formates arise from interaction of the carbon oxides with surface hydroxyl groups. The reverse-water-gas-shift reac-

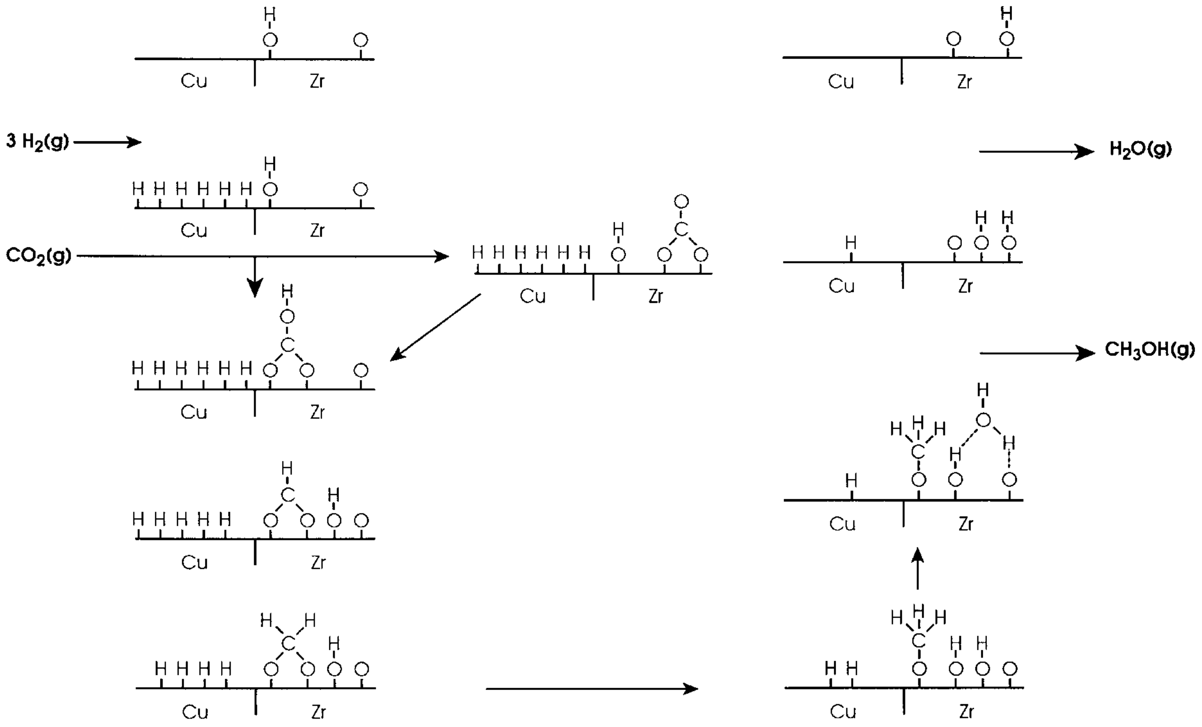

Figure 1 Mechanism proposed for methanol synthesis from CO_2 and hydrogen over Cu–ZrO_2 catalyst, adapted from Ref 38.

tion, which produces gaseous and singly bound CO, involves a carbonate species as intermediate. When starting from CO_2, adsorbed CO is produced via the reverse-water-gas-shift reaction. Although different interpretations exist concerning the role of surface formates in the methanol synthesis mechanism,[37,38] there is agreement that a bifunctional mechanism is governing. CO_2 adsorbs predominantly on zirconia, whereas hydrogen adsorbs and dissociates on copper. Figure 1 shows the mechanism of methanol synthesis from CO_2 and H_2 over copper/zirconia, as proposed recently by Fisher and Bell.[38] According to this mechanism methanol synthesis occurs on the support, with hydrogen coming from the spillover from copper. However, whether the locations where the activations of CO_2 and hydrogen occur can be distinguished so clearly remains to be proven. Another feasible scenario is that the reaction occurs at the copper–zirconia interphase, as suggested previously.[28,30] The important role of the support indicates that precise control of its basicity is important. Finally, it should be noted that the eventual utility of a CO_2-based process assumes the availability of inexpensive hydrogen.

3. SYNTHESIS OF METHYLAMINES

With a worldwide production of approximately 10^6 t per year, monomethylamine (MMA), dimethylamine (DMA), and trimethylamine (TMA) are major industrial chemical intermediates. They are used in such areas as the synthesis of pharmaceuticals, pesticides, surfactants, ion-exchange resins, and in solvent production and water treatment. Methylamines are synthesized on a large scale from methanol and ammonia over a dehydration catalyst such as amorphous silica–alumina.[39] The reaction proceeds to thermodynamic equilibrium, whose position is governed by temperature and the nitrogen/carbon ratio. TMA is the thermodynamically favoured product, whereas market demand is greater for MMA and especially DMA. Recent research has been directed toward improving the selectivity for DMA and MMA through the use of shape-selective zeolite catalysts. The history of the reported routes to, the design of new catalysts for, and the mechanism of the synthesis of methylamines are discussed in a comprehensive recent review.[40]

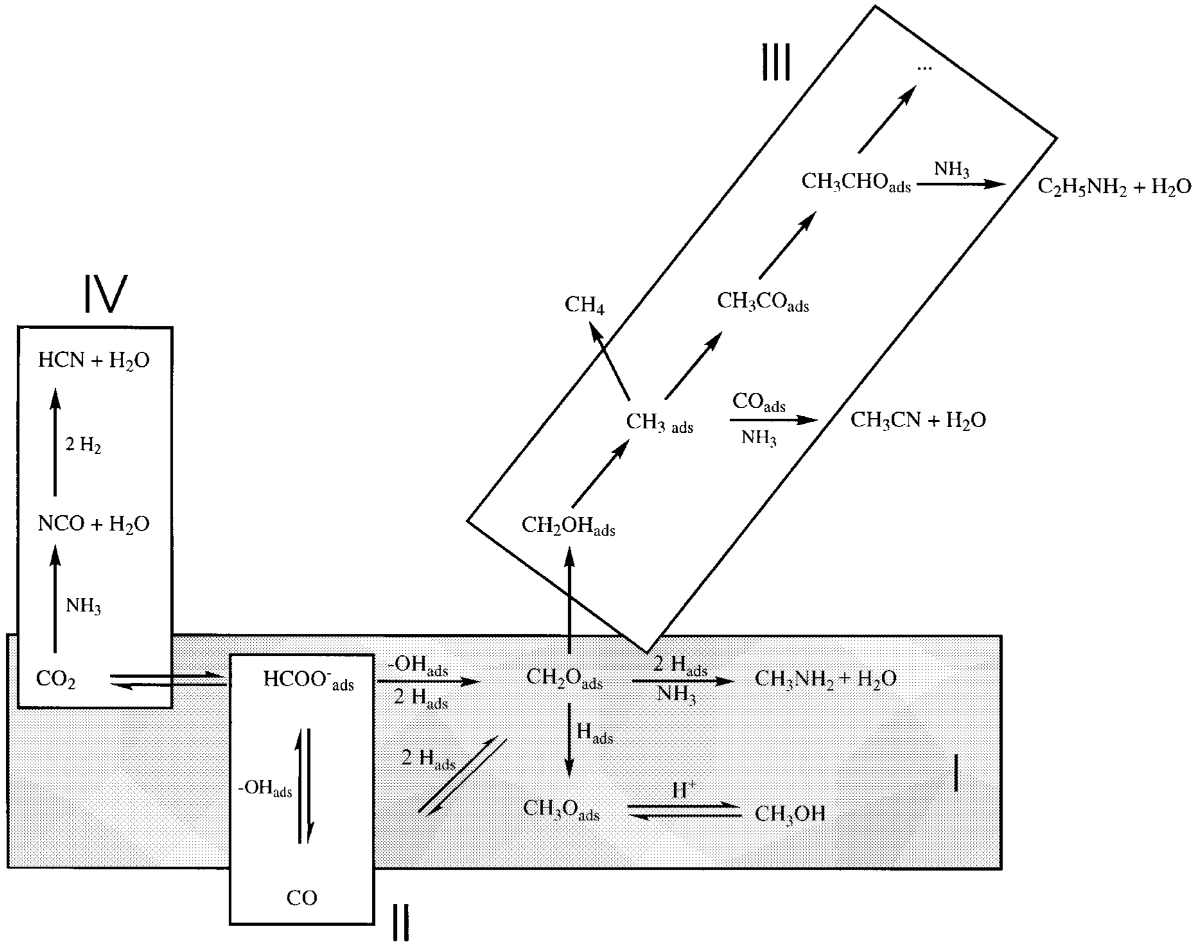

Figure 2 Reaction occurring in the system CO_2, hydrogen and NH_3 over various metal–ZrO_2 catalysts.[43] Note that the reaction to methanol is only observed on copper-based catalysts when ammonia is not present.

A few years ago, it was demonstrated that organo-nitrogen compounds such as methylamines can be directly produced in a continuous fixed-bed reactor starting from CO_2, hydrogen and NH_3 over copper–alumina as a catalyst.[41] MMA and DMA were the major amine products, whereas over the same catalyst in the reaction with methanol instead of CO_2, the thermodynamically favoured TMA was the main product.[42] Increasing the ammonia concentration in the feed resulted in improved selectivity to MMA. The major by-product observed was CO, produced by the reverse-water-gas-shift reaction, which became dominant for temperatures exceeding 300 °C. Copper loading and space velocity were found to be of minor importance for the reaction behaviour. In contrast, ammonia conversion and methylamine distribution were greatly influenced by the reaction temperature and the NH_3/CO_2 ratio, with MMA formation being favoured at higher temperatures and with a stoichiometric NH_3/CO_2 ratio. Methanol formation, which occurs without ammonia in the feed, was already suppressed by small concentrations of ammonia, whereas carbon monoxide formation (reverse-water-gas-shift reaction) was less strongly affected, but also decreased with increasing NH_3 feed concentration. Reactions performed with CO instead of CO_2 showed, under otherwise similar conditions, a slower reaction rate, but higher selectivity to MMA. The favoured production of MMA of the reactions starting from carbon oxides renders this synthesis route particularly interesting. Reactions carried out in the absence of hydrogen in the feed gas resulted in a strong deactivation of the catalyst. This is explained by dissociation of ammonia or amines and subsequent incorporation of nitrogen into the active copper surface, resulting in inactive copper nitride.

A comparative study of the catalytic performance of various alumina-supported metal catalysts,[43,44] including copper, silver, nickel, platinum, palladium, cobalt and iron, indicated that only copper and palladium[44] selectively catalyse MMA production. Figure 2 depicts the reactions observed on the various metal–alumina catalysts in the CO_2, hydrogen and NH_3 system. Copper and palladium catalyse exclusively reaction I (MMA synthesis) and the accompaning reverse-water-gas-shift reaction (reaction II). These reactions are also observed with the other metal catalysts, but the selectivity of these catalysts is biased by several side reactions. For instance, nickel, cobalt, iron and platinum show little methylamine production, but significant methane and Fischer–Tropsch products formation (reaction III). This tendency is ascendant at higher temperatures. Silver produces predominantly CO, H_2O (reaction II) and HCN (reaction IV). Significant HCN formation also occurs with iron–alumina catalysts. Other reactions, not shown in Fig. 2, that can lower the selectivity to MMA include consecutive methylation of MMA, disproportionation ($2MMA \rightarrow DMA + NH_3$) and hydrocracking ($MMA + H_2 \rightarrow CH_4 + NH_3$). Under optimized conditions, the amine selectivities, defined as amine containing hydrocarbon products, not CO_2, reach nearly 100% on the best copper-based catalysts.[41]

Depending on the support material of the copper-based catalysts, distinctly different activity for methylamine synthesis is observed.[45] The surface acidity/basicity of the support seems crucial, as illustrated in Fig. 3, which shows methylamine production as a function of the isoelectric point (IEP) of the support. MMA is the predominant amine product for all supported copper catalysts, with concomitant formation of lower amounts of DMA and TMA. Methylamine yield decreases in the sequence $Cr_2O_3 > ZrO_2 > Al_2O_3$, SiO_2, $ZnO > MgO$. The volcano-type curve can be explained on the basis of the different adsorption strength of ammonia on these support oxides. For catalysts with predominantly basic surface properties, Cu–MgO and Cu–ZnO (IEP > 9), ammonia is not adsorbed strongly enough, resulting in relatively poor NH_3 surface coverage, which has been evidenced by temperature-programmed desorption studies. The decrease of methylamine formation with more acidic supports (e.g. on Cu/SiO_2, IEP 1.8–3.7) has been traced to possible product inhibition by methylamines, which are more strongly adsorbed on acidic surface sites than ammonia.

Very recently, new catalysts effective for MMA synthesis from CO_2 were developed.[46] The catalysts, derived from Cu–Mg–Al lamellar double hydroxides with hydrotalcite-like structure, afford methylamines (MMA, DMA, TMA) with the fraction of MMA being higher than 80%. Further selectivity improvement seems to be possible, which could render methylamine production from CO_2 an interesting alternative to the presently used synthesis from methanol and ammonia.

4. SYNTHESIS OF FORMIC ACID DERIVATIVES

Worldwide, about 300,000 t of formic acid are produced annually. Formic acid is used mainly in the silage of animal feeds, leather and textile industries for tanning and dyeing, and as a coagulating agent in the production of latex rubber. The major process for production of formic acid at present is based on the synthesis of methyl formate with subsequent hydrolysis.[47] The homogeneously catalysed two-stage process uses carbon monoxide and methanol, and $NaOCH_3$ as catalyst. The net reaction can be expressed as the addition of water to CO.

Important derivatives of formic acids include *N,N*-dimethylformamide (DMF) and methyl formate (MF). The world production of DMF amounts

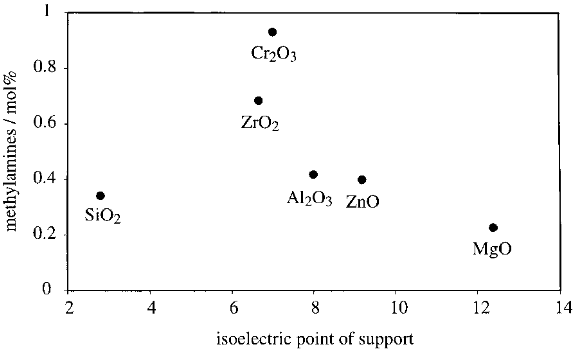

Figure 3 Methylamine production as a function of IEP of the oxidic support material of copper catalysts. Conditions: 3 g catalyst, 300 °C, 0.6 MPa, feed: 150 $cm^3\,min^{-1}$ containing $CO{:}H_2{:}NH_3 = 1{:}3{:}1$. Data from Ref 45.

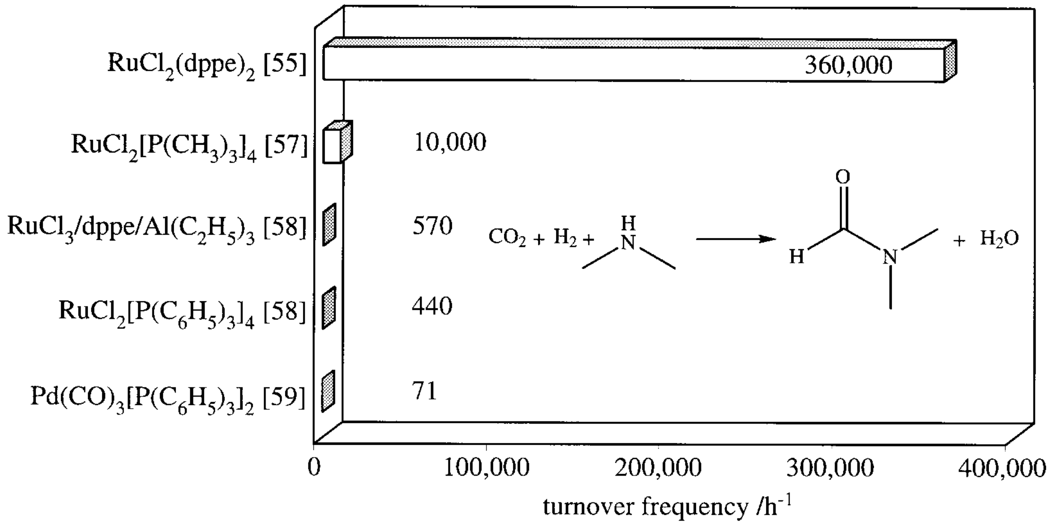

Figure 4 Progress in homogeneously catalysed synthesis of DMF from CO_2, hydrogen and DMA. Selectivities to DMF are generally around 100%.

to *ca* 250,000 t a^{-1}.[48] Most of it is used as a polar solvent, applied as spinning agent in the production of polyacrylonitrile. In the pharmaceutical industry it is used for the production of fine chemicals, especially for recrystallizations and as a reaction medium. Other applications include the use as a solvent for polyurethanes and varnishes, as an extractant, absorbent, and paint stripper. Currently, most of the DMF is produced by carbonylation of dimethylamine with CO at pressures of 5.0 to 11.0 MPa and temperatures between 50 and 200 °C, applying $NaOC_2H_5$ as catalyst. MF is synthesized from CO and methanol using the same base as catalyst.[49] Recent progress in the homogeneously catalysed reactions has triggered very promising developments of corresponding heterogeneous catalytic processes.

4.1 Recent developments in homogeneous catalysis

A promising route to formic acid and its derivatives is the transition-metal-catalysed reduction of CO_2 with hydrogen. Often a third component is added as a trap for the metastable formic acid. In comparison with the reaction of CO_2 and hydrogen alone, the addition of a base lowers the reaction enthalpy, and dissolution of gases increases the reaction entropy.[21] The hydrogenation of CO_2 to formic acid has originally been described by Farlow and Adkins.[50] Inoue *et al.*[51] were the first to demonstrate the homogeneously catalysed synthesis of formic acid. Group VIII metal complexes are the most suitable homogeneous catalysts in organic solvents[21] (and references cited therein).

Noyori's group[52–54] used ruthenium complexes soluble in supercritical CO_2, which enabled them to design a process that does not require any organic solvent. This solvent-free process affords high reaction rates corresponding to turnover frequencies (TOFs) of up to 1400 h^{-1}. For comprehensive reviews the reader is referred to Refs. 21, 22. The formic acid intermediate, formed with the trapping additive, can further react to give esters and amides. MF is produced when triethylamine is used as an additive in combination with methanol. If DMA is added, it plays a double role as stabilizing agent and reactant, yielding DMF as final product. $RuCl_2[P(CH_3)_3]_4$ complexes were found to be highly active and selective for both MF and DMF synthesis from CO_2.

More recently, Kröcher *et al.* [55,56] demonstrated that the efficiency of Noyori's process can be greatly improved by applying ruthenium catalysts with bidentate phosphine ligands, affording TOFs exceeding those previously reported by more than an order of magnitude. Another important advantage for practical application is the higher stability of the bidentate ruthenium complexes. Further improvement of the efficiencies of formic acid, MF and DMF synthesis seems possible. Figures 4 and 5 illustrate the progress made in the hom-

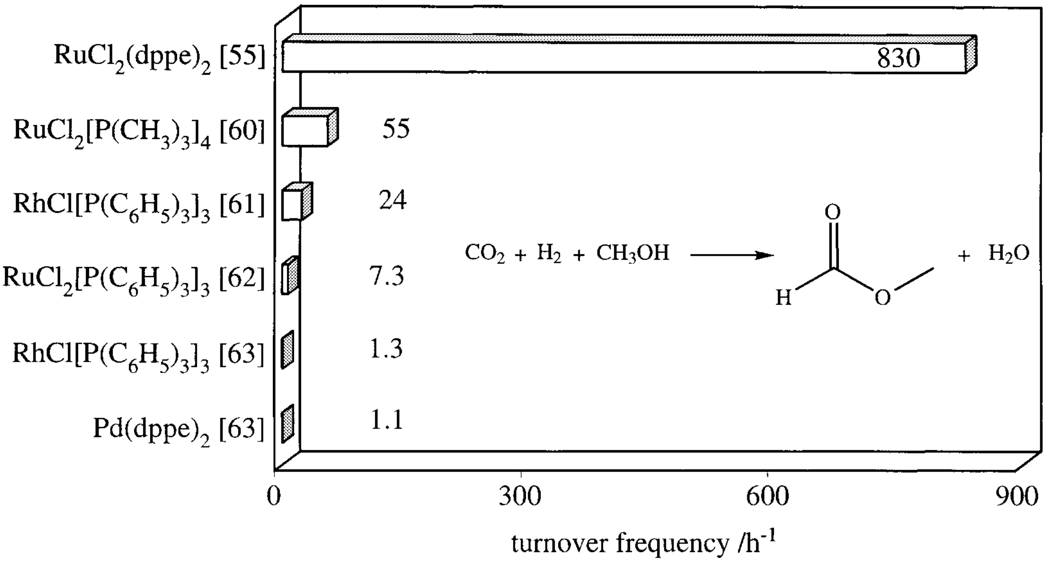

Figure 5 Progress in homogeneously catalysed synthesis of MF from CO_2, hydrogen and ammonia. Selectivities to MF are generally around 100%.

ogeneously catalysed synthesis of DMF and MF respectively.

4.2 Developments in heterogeneous catalysis

Intrigued by the exceptional homogeneous catalytic systems reported in recent years,[52,54,55] we have developed heterogeneous catalysts that combine the excellent properties of the homogeneous catalysts with the practical benefit of solid catalysts.[64–68] The principal design strategy pursued is schematically illustrated for a ruthenium-containing silica hybrid catalyst in Fig. 6. A series of such sol-gel-derived hybrid materials containing different group (VIII) transition metal complexes in a porous silica network was prepared and tested for the catalytic syntheses of DMF and MF from supercritical CO_2, H_2, and $HN(CH_3)_2$, and from CH_3OH and $N(CH_3)_3$ respectively.[65,68] Bifunctional silylether-modified phosphines $X = Ph_2P(CH_2)_2Si(OC_2H_5)_3$ and $Y = (CH_3)_2P(CH_2)_2Si(OC_2H_5)_3$ were used as ligands for the preparation of complexes of the type $RuCl_2X_3$, $RuCl_2Y_3$, $MClX_3$ (M = Ir, Rh), and MCl_2X_2 (M = Pt, Pd). The silylether complexes were anchored in a silica matrix by co-condensation with $Si(OC_2H_5)_4$ (TEOS). All gels were micro- to meso-porous and extended X-ray absorption fine structure measurements[65] indicated no metal–metal interactions, confirming that the organometallic complexes were immobilized as monomers. The hybrid gel catalysts can easily be separated from the reaction mixture. Figure 7 compares the activity of these hybrid xerogels containing monodentate metal complexes. From all catalysts, silica matrix-stabilized ruthenium complexes exhibited highest activities at 100% selectivity in DMF synthesis.[68] Strikingly, the achieved TOF exceeded that of previously reported heterogeneous catalysts[69] by a factor of 600, and this in combination with much higher selectivity (100%). The same hybrid gel catalysts are also suitable for the synthesis of MF. The best ruthenium-containing hybrid catalysts showed an activity (TOF) two times higher than the best hitherto known homogeneous catalyst.[54]

More recently, the performance of the ruthenium–silica hybrid catalysts could be greatly improved further by applying the bidentate $RuCl_2(dppp)_2$ complex[55] as precursor and by optimization of the textural properties (pore size distribution, accessibility of active complexes in solid matrix).[70] Comparative catalytic tests of microporous xerogels and mesoporous aerogels (Fig. 8) indicated that the catalytic performance of the previously prepared xerogel catalysts (Fig. 7) was limited by intraparticle diffusion. This limitation can be eliminated by preparing mesoporous aerogels.[70] This preparation requires supercritical drying instead of conventional evaporative drying in order to avoid the collapse of the tenuous porous

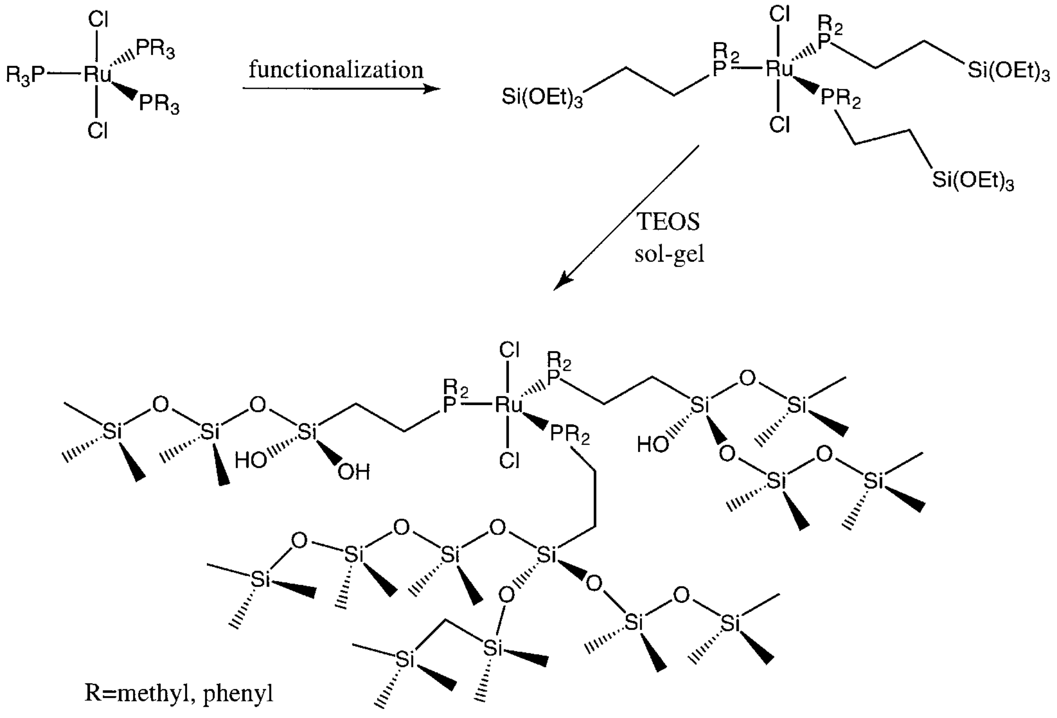

Figure 6 Design strategy for hybrid gel catalysts, illustrated using the example of ruthenium–silica hybrid gel.

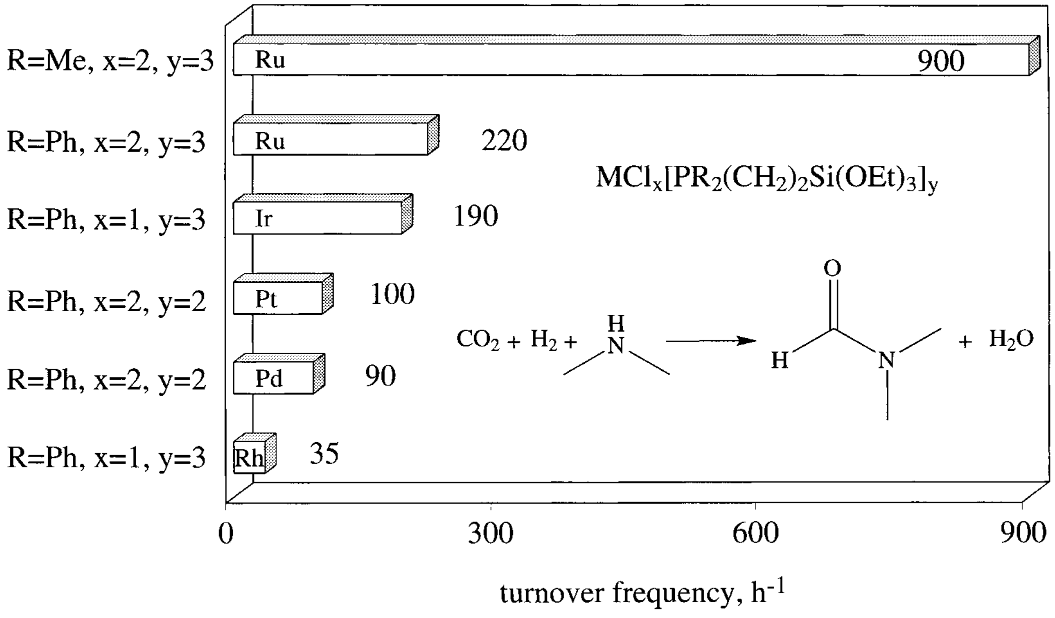

Figure 7 Novel transition-metal-containing silica hybrid xerogel catalysts and their catalytic performance in DMF synthesis from CO_2, hydrogen and DMA. Selectivities to DMF are generally around 100%. Catalysts were prepared from $MCl_x[PR_2(CH_2)_2Si(O\text{-}Et)_3]_y$ transition metal precursors and TEOS according to a procedure described elsewhere.[65] Metal (M):Si ratio of all catalysts 1:50. Conditions of catalytic tests: 500 ml stainless-steel autoclave; $n[Me_2NH] = 0.71$ mol; $p[H_2] = 8.5$ MPa; $p[CO_2] = 13.0$ MPa; $T = 100$ °C; $t = 15$ h; stirring rate: 300 min^{-1}; $n[\text{catalyst}] = 5 \times 10^{-5}$ mol (expressed as amount of Group (VIII) metal).

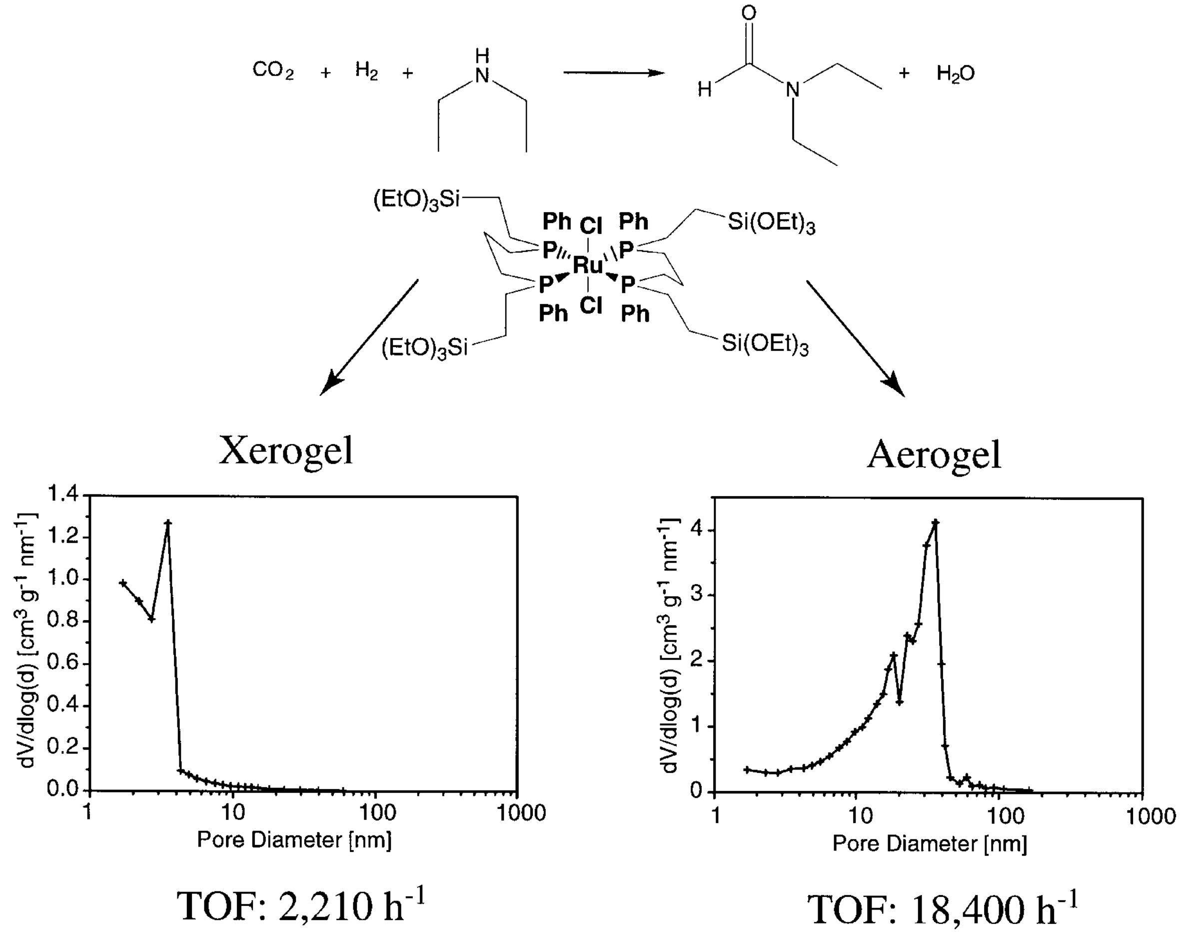

Figure 8 Influence of textural properties (pore size distribution) on catalytic performance (TOF) of ruthenium–silica hybrid gels derived from bidentate $RuCl_2(dppp)_2$ precursor.[70] The microporous xerogel and the mesoporous aerogel were tested in the catalytic synthesis of *N*,*N*-diethylformamide under the following conditions: $n[Et_2NH] = 0.5$ mol; $p[H_2] = 9.0$ MPa; $p[CO_2] = 9.2$ MPa; $T = 110$ °C; $t = 2$ h; stirring rate: 1000 min^{-1}; $n[\text{catalyst}] = 10^{-7}$ mol; metal (Ru):Si ratio = 1:200.

network of the gels due to the detrimental capillary stress during drying.[71] Figure 8 illustrates how these different drying processes affect the pore size distribution of the final hybrid gels and in turn their catalytic performance. The TOF of 18,400 h^{-1} achieved in the synthesis of *N*,*N*-diethylformamide is outstanding. Moreover, the results indicate that the catalysts, originally developed for the synthesis of DMF and MF, should bear a great potential also for the synthesis of other *N*,*N*-dialkylformamides.

5. SYNTHESIS GAS

The heterogeneously catalysed endothermic reaction of CO_2 with aliphatic hydrocarbons for the production of CO–H_2 mixtures ($C_nH_{2n+2} + nCO_2 \rightarrow 2nCO + (n+1)H_2$) has received considerable interest in recent years.[72] Whereas in methane steam reforming ($CH_4 + H_2O \rightarrow CO + 3H_2$) the produced synthesis gas possesses an H_2:CO molar ratio of 3.0, the gas prepared by CO_2 reforming of methane has an H_2:CO molar ratio of 1.0. This feature of CO_2 reforming is important, especially if suitable feed gas for iron ore reduction, Fischer–Tropsch synthesis or other applications is required. The main problem in CO_2 reforming is coke formation by methane decomposition or by CO disproportionation. Generally, catalysts used in steam reforming can also be applied in CO_2 reforming. Nickel catalysts supported on MgO or on carriers composed of α-alumina and of calcium or magnesium aluminate[73] show excellent catalytic performance. A comparative study of CO_2 reforming of methane over MgO-supported nickel, ruthenium, rhodium, palladium, iridium and platinum revealed the following sequence of activity: $Ru > Rh \approx Ni > Ir \approx Pt > Pd$.[74] Very recently, platinum supported on alumina-promoted zirconia was also shown to be effective and resistant to carbon deposition.[75] The platinum–zirconia system appears to be unique for CO_2 reforming, in that CO_2 activation occurs on the zirconia, whereas methane is activated on the platinum crystallites.

6. METHANE

At present, there seems to be no reasonable economical and environmental argument for producing methane from carbon dioxide and hydrogen ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$). Hydrogen and synthesis gas (CO,H_2) are produced on a large scale by the reverse reaction, the steam reforming of methane. Nevertheless, methanation of carbon oxides has been studied extensively in view of a possible utilization of coal. Various metal–support combinations have been described with supported noble metals,[76,77] as well as nickel[76,78] and iron being most active. Possible pathways for the methanation of CO_2 have been discussed in the literature.[79]

7. CONCLUSIONS AND OUTLOOK

Fixation of CO_2 by using it as a C_1 feedstock is making progress. Various processes utilizing CO_2 have been developed; however, their industrial implementation is relatively slow, mostly due to economic considerations. A change from CO- or phosgene-based processes to CO_2 as C_1 feedstock often requires considerable process alterations, and corresponding expenses seem only profitable if environmental aspects are weighed equally as economics. Concerning the scope of chemicals that can be produced from CO_2, the opportunities are numerous and their exploitation is encouraging. Substituting the presently used toxic C_1 feedstocks, CO and $COCl_2$, by the non-toxic, easy to store, transport, and handle CO_2 is an attractive challenge, which can greatly contribute to environmentally benign production of various chemicals. Supercritical CO_2 is an attractive reaction medium because it can be easily separated from product(s) and recycled more efficiently than conventional solvents. Particularly attractive are heterogeneous catalytic processes that make use of supercritical CO_2 as reactant and solvent,[80] as demontrated by the new reaction systems for the synthesis of formic acid derivatives.

Final assessment of the real potential of CO_2 utilization requires the consideration of energetic and economic parameters, and careful comparison of the environmental impact of existing and innovative processes. If hydrogen is to be used in future processes, then the supply of hydrogen must be ensured in some way. At the present time most hydrogen is obtained from steam reforming of hydrocarbons, a process that also produces CO_2 in large quantities. This makes hydrocarbons of questionable value as a hydrogen source for this purpose. Desirable would be non-fossil sources of hydrogen, but none of them seems to bear technical potential at the present time. Expectations concerning the impact of CO_2 utilization for chemical synthesis on atmospheric CO_2 concentration should not be overestimated. Even if CO_2 utilization in chemical synthesis is tremendously increasing, its impact on the atmosphere will probably be relatively small, particularly as long as hydrogen is produced from fossil fuels. However, taking all ecological and economical aspects together, the development of CO_2-based processes is without doubt a rewarding goal.

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