CO$_2$ Hydrogenation: Supported Nanoparticles vs. Immobilized Catalysts

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Abstract: The conversion of CO$_2$ to more valuable chemicals has been the focus of intense research over the past decades, and this field has become particularly important in view of the continuous increase of CO$_2$ levels in our atmosphere and the need to find alternative ways to store excess energy into fuels. In this review we will discuss different strategies for CO$_2$ conversion with heterogeneous and homogeneous catalysts. In addition, we will introduce some promising research concerning the immobilization of homogeneous catalysts on heterogeneous supports, as a hybrid of hetero- and homogeneous catalysts.

Keywords: CO$_2$ · Heterogeneous catalysis · Hydrogenation · Immobilization

Introduction

Over the last decades the global CO$_2$ emission has continuously increased with fossil fuel combustion and industrial processes such as cement and metal production contributing the largest share. In 2013 a new record of 35.3 billion tons of emitted CO$_2$ has been reached.[1] Due to tougher policies on the emission of green house gases a main focus has been to adapt long-standing processes to reduce CO$_2$ emission in the first place. However, the simple capture and storage of CO$_2$ would increase the energy requirements of an industrial plant by 25–40% presenting challenges in the form of gas separation and fixation.[2] Consequently the simple usage of CO$_2$ as a carbon source and C1-building block for the synthesis of more valuable chemicals or fuels would not only reduce the overall emission but also present a solution in respect to finding alternatives for fossil fuels. Therefore nowadays – at least from the research point of view – CO$_2$ can be considered as an abundant carbon source (Fig. 1) and a part of the methanol economy.[3]

Nevertheless activation of the CO$_2$ molecule is challenging and requires high energies in form of high temperatures, high pressures and/or the use of active reactants. Essentially its considerable Gibbs free energy of formation (CO$_2$ ΔG°$_{298.15K}$ =

–394.4 kJ/mol) has to be overcome. One solution to this thermodynamic problem is the usage of co-reactants with higher Gibbs free energy such as H$_2$, methanol, or even epoxides, the latter being used in the synthesis of (cyclic) carbonates from CO$_2$. The splitting of the C=O double bond and the formation of a C–H or C–C bond can be achieved if a reducing agent is used in the presence of a catalyst. Since renewable energies have been the focus of current research, the usage of H$_2$ as the reducing agent – provided it comes from renewable/excess energy – would greatly contribute to a more environmentally friendly conversion of CO$_2$ and to incorporate CO$_2$ in the fuel cycle.

The application of various mainly transition metal catalysts lowers this activation energy and allows the conversion of CO$_2$ to hydrogenation products such as CO, methane, methanol and dimethyl ether (DME), formic acid and dimethyl-formamide (DMF), but also more complex molecules like (cyclic) carbonates or carboxylic acids.[4]

This review will focus on selected examples of heterogeneous CO$_2$ hydrogenation catalysts and compare them to immobilized homogeneous hydrogenation catalysts.

Supported Nanoparticles as CO$_2$ Hydrogenation Catalysts

As shown in Fig. 1, the hydrogenation of CO$_2$ – depending on the catalytic systems and the reaction conditions – can lead to various products, mainly methane (methanation), hydrocarbons (related to Fischer-Tropsch – FT), CO (reverse water gas shift) and methanol. Below we will illustrate each reaction and the current state of the art.

Reverse Water Gas Shift Reaction

The reverse water gas shift (RWGS) reaction corresponds to the hydrogenation of CO$_2$ into CO and H$_2$O (Eqn. (1)) and is considered to be an intermediate step for CH$_4$ and olefin production in FT-related re-
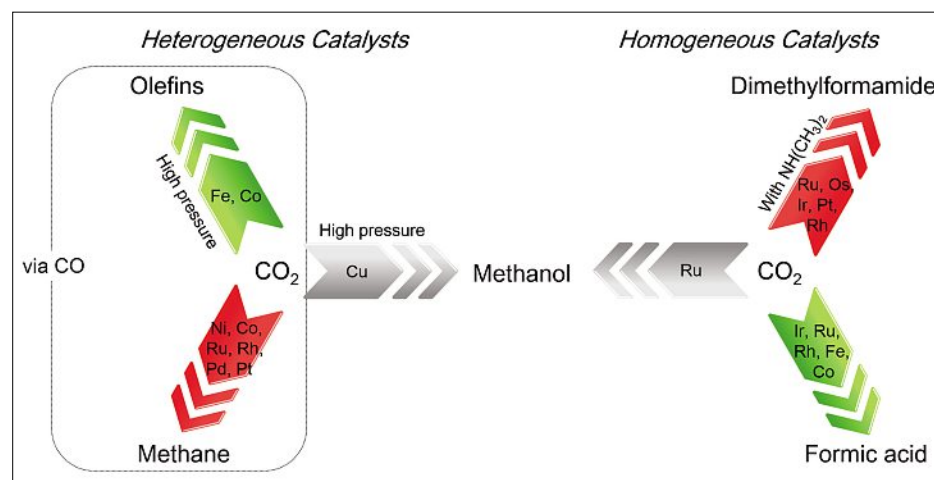
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Fig. 1. CO$_2$ hydrogenation with heterogeneous and homogeneous catalysts, a general view.

actions. This endothermic RWGS reaction – favored at high temperature – is catalyzed by several metals. Much attention has been given to Ni,[5] Pt,[6] Cu,[6] and Au.[7] Three different mechanisms have been proposed for the RWGS reaction: (i) direct dissociation of CO_2 into CO and O*,[8] (ii) formation of formate (HCOO)[9] or (iii) carboxyl (COOH) intermediates.[5,8b,10] While the systems are typically very complex, it has been proposed that the active site under reaction conditions ($CO/CO_2/H_2/H_2O$) in CeO_2 supported Pt and Au catalysts corresponds to partially oxidized Pt and Au species.[11] In addition, based on a kinetic approach of the corresponding reverse reaction (RWGS), corner atoms of Au NPs on TiO_2 are the most likely active sites.[12]

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (1)$$

As discussed above, several reaction pathways are possible. The direct dissociation pathway involves splitting CO_2 on the surface of the metal surface into CO* and O*; the surface O* being then reduced by H_2 or surface H to H_2O*, leading after desorption to CO and H_2O. In the formate mechanism, following the initial H transfer to CO_2, formate species are formed and decomposed into CO.[9b] Alternatively, surface H* can react with CO_2 to generate M-COOH intermediates, which then evolve into CO and surface OH groups. This mechanism has first been proposed by calculations using Cu (111) surfaces.[13] While proposed to be favored on Pt, Ag, and Pd, direct CO_2 dissociation would be favored on Cu, Rh, and Ni.[8b] This process has also been proposed to be favored at the interface between CeO_x and Cu in $CeO_x/Cu(111)$.[10] While under debate, it is clear that the metal the support and the reaction conditions can favor one or the other mechanism, and much work has to be undertaken to understand these systems at a molecular level.

Methanation

Methane can be obtained *via* the hydrogenation of CO_2 (Eqn. (2)). While mainly investigated with supported Ni,[21] noble metals such as Ru,[9b,22] Rh[23] and Pd[8c,24] are also known to participate in this reaction. Since CO_2 methanation is exothermic, lower reaction temperatures favor high methane yields.

$$CO_2 + 4 H_2 \rightarrow CH_4 + 2 H_2O \qquad (2)$$
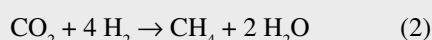
The performance of CO_2 methanation catalysts is affected by the nature of the support materials. For example in the case of CeO_2-based catalysts[21c,22,25] it was

found that CeO_2 increases the amount of adsorbed CO_2[21c] and promotes the conversion of thus-formed surface carbonate into CO.[22] It has been proposed to increase the rates of the first steps associated with the RWGS reaction (Eqn. (1)). In addition, since CeO_2-containing catalysts show high activity in the methanation of CO, it is not too surprising that the overall CO_2 methanation is favored on these catalysts as well, leading to high CH_4 selectivity (close to 100%).[21c,22] ZrO_2-containing materials are also interesting support candidates for CO_2 methanation.[21a] In the related system $Ni/Ce_{0.78}Zr_{0.28}O_2$ the incorporation of a part of Ni species in the fluorite-structured $Ce_{0.78}Zr_{0.28}O_2$ improved the stability of the catalysts for CO_2 methanation at 350 °C ($H_2/CO_2/N_2 = 36/9/10$, GHSV = 43,000 h^{-1} and TOF = 0.4 s^{-1}, Table 1).[16,21b] In addition, Ni sintering can be suppressed by the addition of noble metals (such as Ru and Rh) to the Ni catalyst, leading to longer catalyst lifetime.[26] Adding Pt to Co catalysts also led to an increased catalyst lifetime.[17] The additions of promoters such as Na, K and La to Ru/TiO_2 catalysts can also improve the rate in CO_2 methanation as well.[27]

Methanol and Related Dimethyl Ether Synthesis

In the 1960s ICI developed an efficient low-pressure process (50–100 bar, 200–300 °C) for methanol synthesis from syngas (Eqn. (3)) using $Cu/ZnO/Al_2O_3$ catalysts. More recently, this catalyst and related systems have also been investigated for CO_2 hydrogenation to methanol (Eqn. (4)). For Cu catalysts, the nature of the active sites and the elementary steps are still debated, possibly involving Cu^0 and/or Cu^+. The effect of support and promoter on the Cu catalysts for methanol synthesis has been investigated in depth; for example, reported supports/promoters are ZnO,[28] ZrO_2,[9a,28c] MgO,[28b] TiO_2,[10] and Ga_2O_3.[29]

$$CO + 2 H_2 \rightleftharpoons CH_3OH \qquad (3)$$

$$CO_2 + 3 H_2 \rightleftharpoons CH_3OH + H_2O \qquad (4)$$
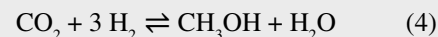
The interaction of Cu with ZnO greatly enhances the activity and selectivity of the methanol synthesis. Possible explanations involve the stabilization of Cu(I) centers[28c] or the better dispersion of Cu species by ZnO. It has also been proposed that the active sites are defective surfaces of nanoparticulate Cu over $Cu/ZnO/Al_2O_3$.[28a] ZrO_2 is also known as one of the promising supports and/or promoters for methanol production from CO_2. For instance, methanol production turnover frequency is 27 times higher (7.3 × 10^{-2} s^{-1}) with $Cu/ZrO_2/SiO_2$ than with Cu/SiO_2 (2.7 × 10^{-3} s^{-1}).[9a] In addition, selectivity of methanol over $Cu/ZrO_2/SiO_2$ was four times higher (43%) than that over Cu/SiO_2 (11%).[9a] This effect of ZrO_2 is likely due to a combination of parameters: improvement of Cu dispersion,[30] increase in CO_2 adsorption[31] and increased number of edges, corners, defects and oxygen vacancies by incorporation of Cu into nanocrystalline ZrO_2.[32] It has also been suggested that $Cu^{\delta+}$ sites at the interface between Cu^0 and ZrO_2 play a key role in the methanol synthesis.[28c]

Recently, catalysts based on Cu/CeO_2 have been reported as an alternative to traditional Cu/ZnO and Cu/ZrO_2 systems, creating a metal-oxide interface that allows a better adsorption and activation of CO_2.[10] Worthy of note the ternary catalyst $Cu/CeO_x/TiO_2(110)$ showed even higher activity for methanol production with TOF of 8.1 s^{-1} at 575 K (Table 1) compared to $Cu/CeO_2(111)$ and $Cu/TiO_2(110)$. Ni_5Ga_3/SiO_2 catalysts are also superior to $Cu/ZnO/Al_2O_3$ owing to low CO production *via* RWGS.[33] Very recently, hybrid oxide catalyst based on MnO_x and mesoporous

Table 1. Selected catalysts for CO, CH_4, and MeOH production *via* CO_2 hydrogenation.

Catalysts	Temp./ °C	Pressure/ bar	Product	TOF/ s^{-1}	Ref.
Cu(110)	237	5.1	CO	0.01	[14]
Pt/TiO$_2$	300	1	CO	0.10	[15]
Ni/CeO$_2$-ZrO$_2$	350	1	CH$_4$	0.429	[16]
Rh/γ-Al$_2$O$_3$	200	1	CH$_4$	0.010	[8c]
Pt/MCF-17+ Co/MCF-17	250	1	CH$_4$	0.038	[17]
Ru/Al$_2$O$_3$	350	1	CH$_4$	0.03	[18]
Ni-Zr alloy	300	1	CH$_4$	0.054	[19]
Cu-Zn-Al-Zr oxides	270	50	MeOH	0.009	[20]
Cu/ZrO$_2$/SiO$_2$	250	6.5	MeOH	0.073	[9a]
Cu/CeO$_x$/TiO$_2$(110)	303	5	MeOH	8.1	[10]

spinel Co_3O_4 catalyzes the CO_2 conversion to methanol in higher yields than the individual catalysts MnO_x-SiO_2 and Co_3O_4 respectively,[34] implying that the interface of MnO_x and Co_3O_4 contains specific active sites for the CO_2 conversion.

Dimethyl ether (DME) is a useful chemical and an attractive alternative to liquefied petroleum gas (LPG), and can be synthesized by a multi-step process involving methanol production *via* CO_2 hydrogenation to methanol (Eqn. (3)) and subsequent methanol dehydration to DME (Eqn. (5)).

$$2\ CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \qquad (5)$$

In a one-step DME synthesis approach, methanol consumption *via* methanol dehydration can abate the catalyst's surface concentration of the intermediate methanol, and in turn overcome the equilibrium limitation of CO_2 conversion at low temperatures. Methanol dehydration takes place on γ-Al_2O_3[35] and acidic zeolites (HZSM-5[35] and SAPO[36]). Therefore DME can be synthesized directly over physical mixtures of solid acids and methanol synthesis catalysts. Note that methanol dehydration is an exothermic reaction, leading to higher DME selectivity at lower reaction temperatures. It is reported that the methanol synthesis is the rate-determining step when Cu-based methanol synthesis catalysts were physically mixed with high acidity materials.[36]

Olefins

The hydrogenation of CO_2 to olefins derives from the combination of RWGS reaction (Eqn. (1)) converting CO_2 to CO and the Fischer-Tropsch (FT) process (Eqn. (6)), yielding hydrocarbons.

$$CO + 2\ H_2 \rightarrow (CH_2) + H_2O \qquad (6)$$
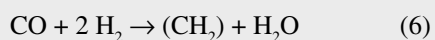
Accordingly, the reaction has been studied mainly on traditional catalysts for FT synthesis such as iron and cobalt catalysts with promoters. The olefins are likely produced on surface carbides, which are formed *in situ via* decomposition of CO on metal surfaces, following the Boudard reaction (Eqn. (7)).

$$CO + CO \rightarrow C + CO_2 \qquad (7)$$

The role of promoters, such as K,[37] Na,[37b] Li,[37b] Mn[37a,38] and La[39] species, is considered to enhance the activity of the catalyst in RWGS (due to improvement of CO/CO_2 adsorption) and the carburization of Fe or Co species. In addition, Mn has

been proposed to play the role of structural promoter as well, leading to higher dispersion of Fe species on support materials.[38] The presence of noble metals such as Ru on Co-K catalysts further enhanced the conversion of CO_2 and the selectivity of C5+ hydrocarbons.[37b]

Immobilized Homogeneous Catalysts for CO_2 Hydrogenation

The most prominent reactions in homogeneous CO_2 hydrogenation are the syntheses of formic acid and methanol, however the generation of formic acid and its derivatives yields much higher TONs and TOFs than that of methanol, since the conversion of CO_2 to methanol usually requires the combination of several catalysts or concurrent reactions. In general, the conversion of CO_2 to formic acid is highly reversible in the presence of the catalyst; hence the employment of a base to remove the formic acid from the equilibrium is necessary.

State of the Art in Homogeneous Catalysis

Pioneering work on the hydrogenation reactions of CO_2 started in the 1970s, using various transition-metal complexes of Ru, Os, Rh, Ir and Pt.[40] Greater performances were reached much later using Ru catalysts such as **2-(a)** and supercritical CO_2 (scCO_2) as a solvent, resolving miscibility issues reported previously.[41]

Since 2000 ruthenium[42] and iridium[43] have been used the most frequently for the hydrogenation of CO_2 to formic acid derivatives (Figs. 2 and 3). Worthy of note, [$RuCl_2(PTA)_4$] (PTA = 1,3,5-tri-
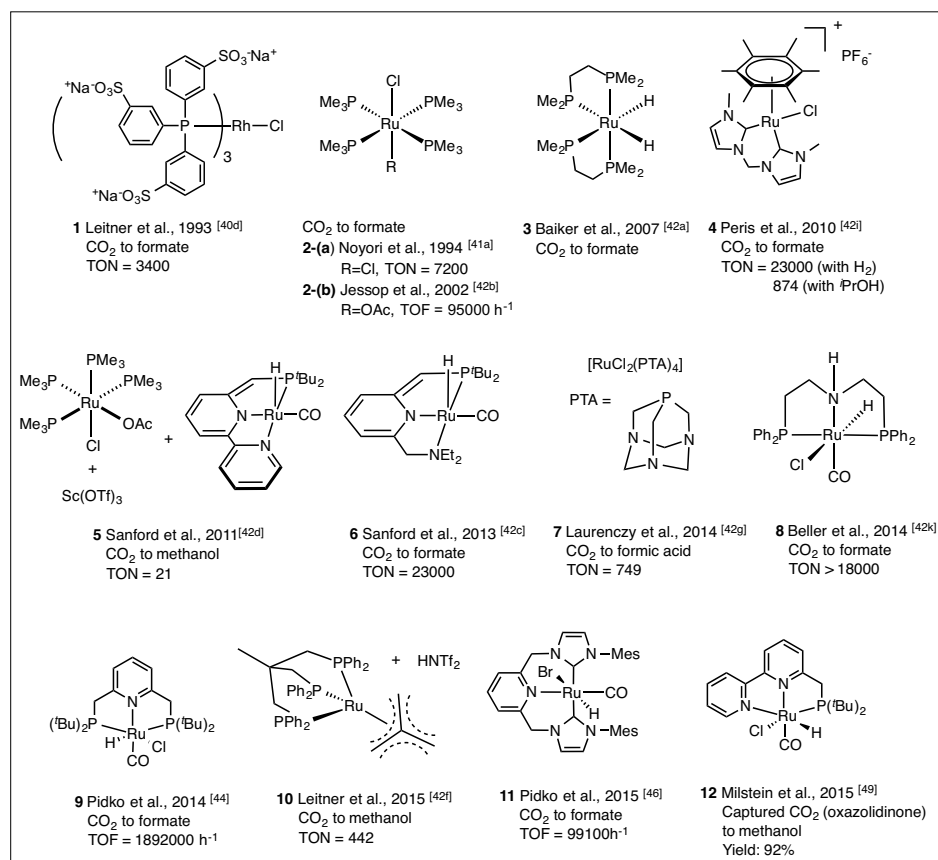
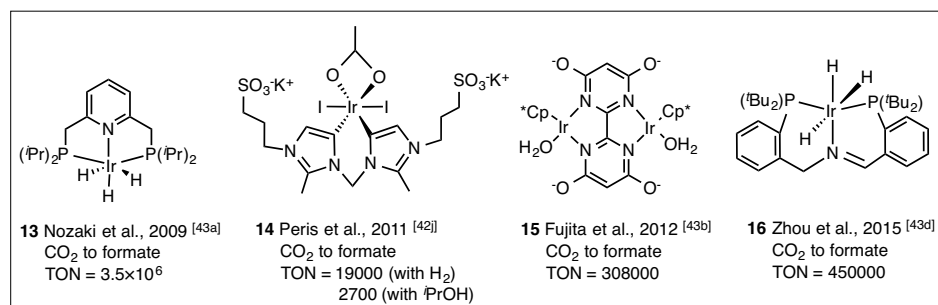Fig. 2. Selected ruthenium catalysts used in CO_2 hydrogenation reactions.

Fig. 3. Iridium catalysts used in CO_2 hydrogenation reactions.

aza-7- phosphaadamantane) (**7**) allows the conversion of CO_2 to formic acid without the addition of base at low temperatures in DMSO.[42g] Applying other hydrogen sources than H_2, such as isopropanol or methanol, ruthenium and iridium complex with N-heterocyclic carbenes (**4**, **14**)[42h–j] as well as PNP pincer-type[42k,44] ligands (**8**, **9**) were used to convert CO_2 to formate.

Iridium catalysts have also proven to be very effective to promote CO_2 hydrogenation. Ir^{III}-pincer trihydride complex **13** catalyzes the hydrogenation of CO_2 into potassium formate (HCOOK) with a TON of 3.5×10^6 and TOF of 150 000 h^{-1} using an aqueous KOH solution at 120 °C and 6 MPa (H_2:CO_2=1:1).[43a,45] The pincer ligand, which is believed to be non-innocent in the catalytic cycle,[43a] seems to be superior to other ligand systems such as N^N-bidentate (**15**),[43b,c] imine-diphosphine (**16**)[43d,e] or N-heterocyclic carbenes.[46]

Non-precious-metal-based catalysts based on Fe,[47] Co[48] and Cu[49] have also been discovered (Fig. 4), but suffer from relatively low TON/TOF compared to the precious-metal-based catalysts.

More recently the direct synthesis of methanol from CO_2 with homogenous catalysts was reported using (i) a cascade reaction applying two different ruthenium catalysts together with Sc(OTf)$_3$ as a Bronsted/Lewis acid catalyst (**5**),[42c,d] (ii) a tandem capture of CO_2 with aminoethanols combined with the subsequent hydrogenation with a PNN Ru catalyst (**12**)[50] and (iii) a specific ruthenium phosphine complex, generated *in situ* from [Ru(acac)$_3$] and the tridentate ligand Triphos (1,1,1-tris (diphenylphosphinomethyl)ethane) (**10**) in the presence of HNTf$_2$ as an acid cocatalyst.[42e,f]

Immobilization Strategies

With the associated difficulty to separate reactants/products from the active phase, a large research effort has focused on immobilizing highly active homogenous catalysts on a variety of supports. Different strategies have been applied including encapsulation, intercalation or entrapment of the catalyst as well as anchoring the ligand to a support.[51] However, efficient, immobilized CO_2 hydrogenation catalysts are still rare. Organo-silica hybrid materials based on the co-condensation of silylated derivatives of [Ru(dppp)$_2$Cl$_2$] (dppp = bis-(diphenylphosphino)propane) (Fig. 5) with tetraorthosilicate (TEOS) were the first to be reported.[52] While molecular [Ru(dppm)$_2$Cl$_2$] and [Ru(dppp)$_2$Cl$_2$] display very good activities for the formation of DMF from CO_2 and H_2 with TOFs of 190000 h^{-1} and 2650 h^{-1} respectively,[53] the corresponding immobilized systems display much lower TOFs: materials purely consisting of the silylated precursors
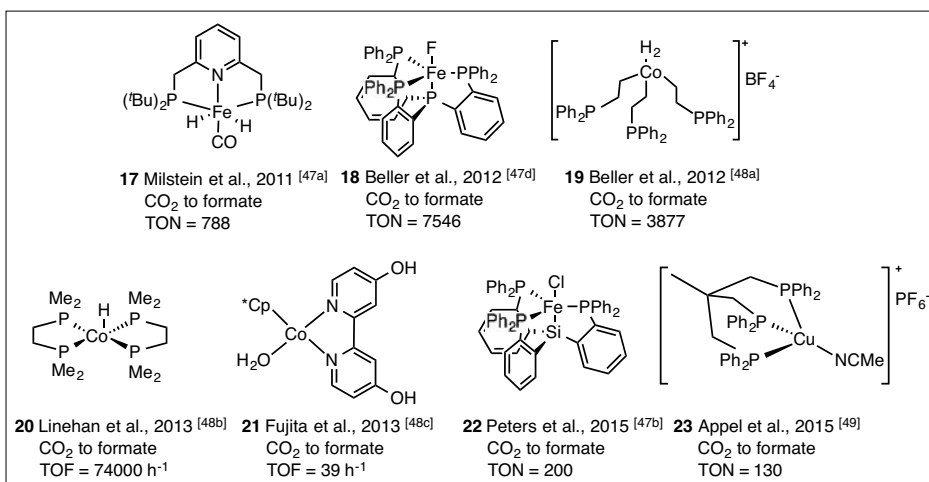

Fig. 4. Non-precious-metal-based catalysts used in CO_2 hydrogenation reactions.

24 or **25** (no TEOS added) reach TOFs of 3030 h^{-1} and 2300 h^{-1} respectively, while dilution with 20 to 200 equiv. TEOS dramatically decreased the TOFs to 500–970 h^{-1}.[52c]

Alternatively, immobilization of [Ru(TPPTS)$_2$]$^{4-}$ (TPPTS = tris(3-sulfophenyl) phosphine trisodium salt) was possible on a Dowex ion exchange resin, phosphine functionalized polymers as well as zeolites.[54] While solely applied for the decomposition of formic acid into H_2 and CO_2, both the ion exchange resin and the polymer support led to stable catalysts that did not leach and maintained their activity over several cycles. Most of the zeolites however could not withstand the acidic reaction conditions.

Furthermore, immobilization was also accomplished by the post-functionalization

of a poly(styrene)-block-poly(ethylene glycol) polymer (ArgoGel-NH$_2$®) containing free amine moieties.[55] Condensation of the free amine with formaldehyde and a secondary phosphine led to supported bidentate phosphine ligands that could easily substitute the ligands in [RuCl$_2$(PPh$_3$)$_3$] or *cis*-[RuH$_2$(PPh$_3$)$_4$] yielding the bound compounds **26**–**27** and **28**–**29** respectively (Fig. 5). The functionalized beads showed a similar activity compared to the homogeneous equivalent in the synthesis of DMF in supercritical CO_2 (scCO$_2$) at 100 °C and could easily be recovered and reused. **26** in contrast to **27**–**29** showed no decrease in activity over four cycles (TON 1560–1960). Similar anchoring strategies have described for the coordination of IrCl$_3$ or RuCl$_3$ to hybrid organosilica materials containing propylamine or alkylphosphine
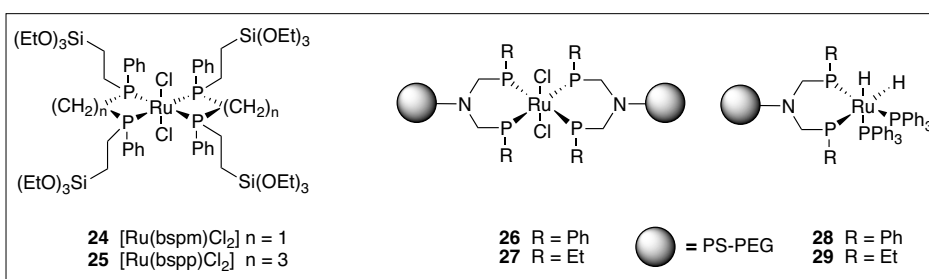

Fig. 5. Immobilization strategies for Ru^{II}-hydrogenation catalysts.
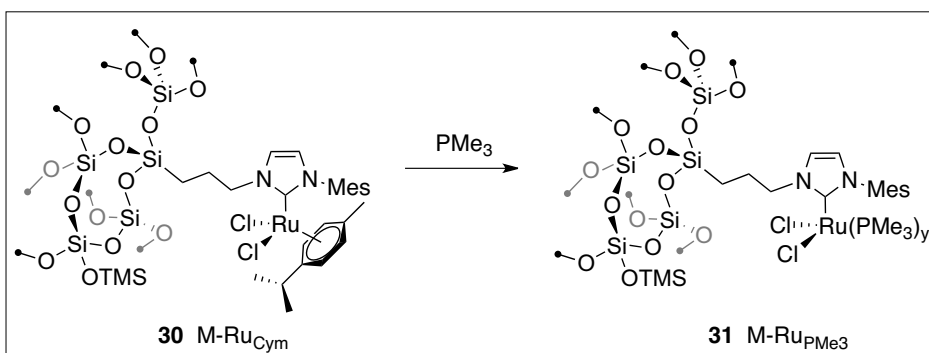

Fig. 6. Immobilized Ru-NHC complexes on mesoporous silica.

moities. While reported as active and re-cyclable, the nature of the catalyst is not clear.[56]

More recently, the immobilization of a ruthenium N-heterocyclic carbene (NHC) complex for the CO_2 hydrogenation to amides was accomplished by a different strategy, where the density of the organic functionalities (ligands) is controlled through a templating approach and the metal is covalently anchored to a N-heterocyclic carbene ligand.[57] The immobilized catalyst is prepared by reacting imidazolium-functionalized mesoporous silica with $[\{RuCl_2(p\text{-cymene})\}_2]$ yielding the surface bound Ru-NHC compound in 60% yield (30).[58] Substitution of the cymene ligand with PMe_3 resulted in the respective surface bound Ru-phosphine-NHC compound (31) (Fig. 6).

Hydrogenation reactions of CO_2 in the presence of pyrrolidine yielding 1-formyl-pyrrolidine (50 bar CO_2, 30 bar H_2, 100 °C) showed that 30 had a very low TON while 31 was almost as active as $[RuCl_2(PMe_3)_4]$, which is one of the best catalysts under the chosen reaction conditions (TON 2900 and 3100 respectively). However metal leaching proved to be a problem concerning the recyclability of the materials.

Conclusion

Heterogeneous catalysts are already used in industrial applications due to their high thermal stability and recyclability leading to low operation costs for chemical processes.[59] Generally in ambient pressure reactions CO_2 is converted into CO over transition metal catalysts and into CH_4 over Ni, Ru and Rh catalysts, whereas CO_2 is hydrogenated to methanol (and dimethyl ether) under high-pressure over Cu-based catalysts and to olefins over Fe- and Co-based catalysts. ZnO, ZrO_2 and CeO_2 are so far the best support materials for most of the CO_2 hydrogenation reactions, probably due to their large CO_2 adsorption capacity and high activity towards the conversion of CO_2 into CO. The addition of alkali or lanthanide metals has been shown to enhance CO_2 conversion and help to furnish olefins under high pressure.

On the other hand, numerous homogeneous catalysts have appeared more recently with tailored properties by tuning of the organic ligands. They have become consequently more active and/or selective, but they still suffer from lower thermal stability, difficulty of regeneration as well as separation from the products, limiting their industrial applications. While immobilization on supports appears to be a promising strategy, immobilized CO_2 hydrogenation catalysts always show lower TON/TOFs compared to the homogeneous analogues.

Here deactivation by interaction with the support, metal leaching and simple regeneration protocols still present great challenges, which need to be surmounted. The right combination and choice of support, linker and homogeneous catalyst will be important for the generation of stable and active immobilized catalysts.

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