Towards a methanol economy based on homogeneous catalysis: methanol to H₂ and CO₂ to methanol

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The possibility to implement both the exhaustive dehydrogenation of aqueous methanol to hydrogen and CO₂ and the reverse reaction, the hydrogenation of CO₂ to methanol and water, may pave the way to a methanol based economy as part of a promising renewable energy system. Recently, homogeneous catalytic systems have been reported which are able to promote either one or the other of the two reactions under mild conditions. Here, we review and discuss these developments.

Introduction

More than 80% of the total worldwide energy consumption is today based on fossil fuels,¹ resulting in an increase of anthropogenic CO₂ in the atmosphere. Moreover, it is well known that oil sources are likely to be near-depleted by the end of this century if we maintain or increase the present rate of their consumption. Hence, there is an urgency to develop techniques for exploiting alternative energy resources such as wind, sunlight, and biomass in order to generate electricity and/or H₂, the latter being equivalent to chemically stored electrical energy. The capability of storing electricity is important because of the intermittent supply of most renewable energy sources.²–⁴

Hydrogen is an ideal fuel as its combustion releases energy and water as the sole by-product. However, mainly because of its physical and chemical properties, hydrogen is not an ideal energy vector: it is a gas with a limited volumetric energy density which, as fuel, especially in the field of automotive applications,

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The chemical storage of hydrogen in solid or liquid compounds from which it can be released as gas through a suitable (and ideally fully reversible) dehydrogenation reaction has been intensively investigated as a possibility to overcome some of these limitations. Several criteria have to be considered when evaluating the potential of a chemical substance as hydrogen carrier, among others, its storage capacity (H₂ wt%), its volumetric hydrogen content (kg H₂ m⁻³ carrier) and the energy efficiency of the whole process of carrier hydrogenation–dehydrogenation, from hydrogen production to final hydrogen utilization. Methanol belongs to the broader class of liquid storage compounds which includes liquid organic hydrogen carriers (LOHC i.e. methylcyclohexane and N-ethylperhydrocarbazole), alcohols and formic acid. It is a key platform chemical for existing fuel and chemical infrastructures and contains 12.6% w/w hydrogen, which can be released through aqueous reforming. Heterogeneous catalysts, which promote this reaction and the reverse one, the conversion of CO₂ and H₂ to MeOH, operate at high temperatures (> 200 °C) and/or applied pressures (>25 bar). Indeed the high temperature required for dehydrogenation is one of the main factors which so far has made MeOH less suitable as energy carrier in the field of portable applications. Therefore, developing milder routes for these two conversions is highly desirable in order to reach a viable H₂ energy system based on a CO₂-MeOH cycle. Moreover, the carbon dioxide released in the process and from any other source might be hydrogenated back to methanol using hydrogen obtained from renewable sources, ideally from water electrolysis powered by solar energy, thus completing a carbon neutral cycle.

The advantages and limitations of a methanol based economy, how far this is from being implemented, especially in relation to technologies currently available for carbon dioxide capture and sequestration and water electrolysis for hydrogen production, have been reviewed in excellent monographs and articles and the reader is referred to them for an in-depth acquaintance with the topic.

In this review we would like to draw the readers’ attention to recent reports on the development and application of homogeneous catalysts for MeOH dehydrogenation (≤ 95 °C and atmospheric pressure) and CO₂ hydrogenation to MeOH (≤ 145 °C and ≤ 60 bars) which are active under comparatively mild conditions.

Looking into the mechanism of a homogeneously catalysed CO₂/Methanol hydrogenation/dehydrogenation system, it becomes evident that a few organic intermediates must exist alongside this stepwise transformation. As shown in Scheme 1, the generally proposed MeOH dehydrogenation pathway by homogeneous catalysis commences with the formation of formaldehyde, which is then converted to formic acid promoted by a H₂O molecule. The final step is CO₂ production from formic acid. In each of these three steps, a H₂ molecule is liberated. The CO₂ hydrogenation pathway is envisioned to follow the reversed sequence of the same reaction steps.

In the absence of water and in the presence of suitable catalysts, methanol may decompose to hydrogen and formaldehyde (the latter may further react to afford other products, depending on the catalyst and the reaction conditions) (eqn (1)) or be fully dehydrogenated to hydrogen and carbon monoxide (eqn (2)). The catalysts which were found able to promote such processes in the absence of a hydrogen acceptor in almost all cases were applied with much greater success to the dehydrogenation of ethanol and isopropanol, the latter being often the substrate of choice to test new catalysts, because of the more favourable thermodynamics and the possibility of a higher operational temperature.

\[
\text{CH}_3\text{OH}(l) \rightarrow \text{H}_2\text{CO}(g) + \text{H}_2(g) \quad \Delta H_{298} = 129.8 \text{ kJ mol}^{-1} \\
\Delta G_{298} = 63.5 \text{ kJ mol}^{-1}
\]

(1)

\[
\text{CH}_3\text{OH}(l) \rightarrow \text{CO}(g) + 2\text{H}_2(g) \quad \Delta H_{298} = 127.9 \text{ kJ mol}^{-1} \\
\Delta G_{298} = 29.0 \text{ kJ mol}^{-1}
\]

(2)

**Methanol dehydrogenation**

**Partial methanol conversion**

The first examples of homogeneously catalysed methanol dehydrogenation were published approximately 30 years ago. However, because reactions were carried out in the absence of water, the possibility for the full conversion of methanol to CO₂ and three H₂ was precluded. Yet they will be briefly discussed here as they set the very early stage for future developments towards the successful sustainable production of hydrogen from alcohols.

**Thermal decomposition of methanol.** Early accounts on the thermal dehydrogenation of methanol with hydrogen evolution promoted by a homogeneous catalyst were reported by the groups of Saito, Maitlis, Shinoda and Cole-Hamilton. These reactions were carried out using ruthenium catalyst precursors modified by phosphines and other ancillary ligands. The dehydrogenation of methanol to formaldehyde and hydrogen (eqn (1)) is an endergonic and endothermic process, which becomes feasible under relatively mild conditions (65 °C, reflux) if the reaction is carried out in an open vessel from which hydrogen easily escapes the reaction medium due to its very limited solubility, thus shifting the equilibrium.

Saito could show that catalyst [Ru(OAc)₂(Cl)(PEtPPh₂)]₂ prepared in situ from [Ru₂(OAc)₆(Cl)] and PEtPPh₂ is competent for the dehydrogenation of methanol to formaldehyde at reflux with an initial TOF of 0.96 h⁻¹ and a total TON of 34 over 90 hour reaction time (Table 1, entry 1). An optimum of two equivalents of acetic acid to ruthenium is required to achieve this result as compared to TOF 0.60 h⁻¹ without any. While formaldehyde was the only
product in the early stage of the reaction, at higher conversion both methylformate (the product of a Tishchenko-like dimerization of formaldehyde) and dimethoxymethane (formaldehyde dimethyl acetal) could eventually be detected in solution. No carbon monoxide or methane contaminants were detected in the gas phase.

Almost at the same time Maitlis reported the dehydrogenation of methanol to methylformate and dimethoxymethane catalysed by [RuCl₂(PPh₃)₃] at 150 °C achieving a total TON = 65 for hydrogen evolution over 18 hours, at which time activity ceased likely due to formation of inactive [[PPh₃]₂Ru(CO)[μ-H][μ-Cl]](CO)[PPh₃]₁. Which was isolated from the reaction mixture (Table 1, entry 2).13 Cole-Hamilton showed that the rate of hydrogen evolution from methanol over 2 h at 150 °C could be greatly improved by performing the reaction in the presence of a 10 fold excess of base (NaOH) as to the catalyst when using preformed [Ru(H)₂(N₂)(PPh₃)₃] (TOF = 6.4 h⁻¹, Table 1, entry 3) or [Ru(H)₂(PPh₃)₄] (TOF = 7.5 h⁻¹, Table 1, entry 4).15 Notably, RuCl₃ with no ancillary ligand is able to promote methanol dehydrogenation if sodium methoxide is added to the reaction mixture, thus showing the critical role played by the base.12d

Table 1 summarizes and compares the activity of complexes which were able to promote, although with poor activity, the thermal decomposition of methanol.

A more detailed study concerning methanol dehydrogenation was carried out using [Pd₄Cl₆(dpm)₃] and cis[Rh₂Cl₆(dpm)₂] (dpm = bis(diphenylphosphino)methane) which proved effective in promoting hydrogen evolution from a 9 : 1 MeOH/acetone solution at reflux under photolysis with a 400 high-pressure mercury lamp affording a maximum TOF of 360 nm which is formed during the catalytic cycle following formaldehyde decarbonylation and provide a vacant coordination site for a new alcohol molecule to bind. Also in the case of catalysts [Ru(H)₂(N₂)(PPh₃)₃] and [Ru(H)₂(PPh₃)₄] the rate enhancement observed in hydrogen evolution from methanol upon irradiation has been ascribed to the labilization of a coordinated ligand, more specifically to the release of dihydrogen from intermediate [Ru(H)₂(H)(PPh₃)₄].15

Aqueous methanol dehydrogenation to hydrogen and carbon dioxide: methanol reforming

In 2013, the first examples of homogeneously catalysed complete methanol dehydrogenation to CO₂ and three molecules of H₂ were disclosed.11
Exhaustive methanol dehydrogenation is currently realized through steam reforming according to eqn (3) using heterogeneous catalysts which operate between 200 and 300 °C.\(^7\)\(^a\) Established catalysts fall into two main classes: copper-based and group 8–10 metal-based catalysts.\(^7\)\(^a\)\(^b\) Commercially available CuO/ZnO/Al\(_2\)O\(_3\) is a catalyst formulation which belongs to the first class and highlights the constitutional elements of a competent heterogeneous catalyst: copper is the active metal, ZnO is a metal oxide which ensures active site segregation to prevent copper sintering at high temperatures and alumina provides a high surface support which increases copper dispersion and contributes minimizing sintering as well. Copper-based catalysts are highly active and selective for methanol steam-reforming and are outstandingly cost effective, but suffer from deactivation problems due to the sintering of metal particles above 300 °C and are pyrophoric. Palladium–zinc alloy-based catalysts are representative of the second class; its members enjoy improved thermal stability compared to the copper ones but, in general, are less active and, with the exception of those based on Pd– and Pt–metal alloy, can favour decomposition of methanol according to eqn (4), thus increasing the relative amount of CO contamination.

Lower operational temperatures are highly desirable, especially in view of the application of methanol as fuel in Reformed Methanol Fuel Cells (RMFC) for mobile applications: here methanol reforming takes place on board to directly fuel the cell with hydrogen. Because of the high temperature required by heterogeneous catalysts, the overall efficiency of state of the art devices does not exceed 40%. Furthermore high temperatures favour formation of CO\(^2\) which, already at few ppm concentration, may poison the precious electro-catalyst at the cell anode. It should be mentioned that another possible source of CO contamination under the conditions of steam reforming is the reverse water gas shift reaction (eqn (5)).

A very first report concerning the possibility of applying an homogeneous catalyst to the thermal dehydrogenation of alcohols in the presence of water was published by Cole-Hamilton and relied on the use of [Rh(bipy)\(_2\)]\(^+\)Cl as catalyst.\(^2\)\(^a\) The rationale behind the use of water is the possibility to open a new decomposition path according to eqn (3) and Scheme 1, which is thermodynamically less demanding than simple dehydrogenation as to eqn (1) or (2). Reactions were carried out using a 95 : 5 v/v solution of alcohol/\(\text{H}_2\text{O}\) in the presence of NaOH \((0.25–5 \times 10^{-3} \text{ mol})\) with [Rh(bipy)\(_2\)]\(^+\)Cl \((5 \times 10^{-6} \text{ mol})\) at \(120 \text{ °C}\) in a closed system for 3 h.

Alcohols other than methanol, such as ethanol, isopropanol and butane-2,3-diol, afforded almost a 100 fold higher rate of hydrogen production compared to methanol, which had a TOF = \(7 \text{ h}^{-1}\) (Table 2, entry 1). No detail though was provided for the gas- and liquid-phase composition of the system after reaction; however, in the case of ethanol, beside \(\text{H}_2\) in the gas phase and ethanol and its condensation products in the liquid phase, \(\text{CH}_4\) and \(\text{CO}_2\) in a 1:1 ratio were detected (the latter after acid addition to the solution) showing the ability of the catalyst to promote intermediate aldehyde decarbonylation and formation of \(\text{CO}_2\). 25 years later, almost at the same time, two groups, Grützmacher’s\(^2\)\(^2\) and Beller’s\(^2\)\(^3\) reported the efficient aqueous dehydrogenation of methanol to hydrogen and carbon dioxide below 100 °C promoted by homogenous ruthenium catalysts (Fig. 1, 1 and 2, respectively), with almost no trace of CO contamination, setting the stage for a foreseeable application in RMFC. Very recently Milstein has shown that also ruthenium catalyst 3 (Fig. 1) is able to promote the same transformation.\(^2\)\(^4\)

A common feature of these catalysts is that they possess multideterminate ligands which confer improved thermal stability to the resulting metal complexes while blocking three (like in 2 and 3) or four (like in 1) of the possible metal coordination sites; this is particular useful in order to hamper the possible decarbonylation of formaldehyde arising from methanol dehydrogenation.

Most importantly, the abstraction of hydrogen from the alcohol relies on a cooperative mechanism involving both the metal and the ligand, the latter being therefore termed “non-innocent”.\(^2\)\(^5\) Experimental evidence suggests that, when catalysed by such complexes, exhaustive dehydrogenation of methanol might proceed through three consecutive steps: dehydrogenation of methanol to hydrogen and formaldehyde (eqn (1)), dehydrogenation of the gem-diol arising from the reaction of formaldehyde with water (eqn (6)),\(^2\)\(^6\) final dehydrogenation of the resulting formic acid to hydrogen and carbon dioxide (eqn (7)). This sequence is identical to the general reaction pathway shown in Scheme 1.\(^1\)\(^1\)

\[
\text{CH}_3\text{OH}(l) \rightarrow \text{H}_2\text{CO}(g) + \text{H}_2(g) \quad \Delta H_{298}^\circ = 129.8 \text{ kJ mol}^{-1} \quad (1)
\]

\[
\text{H}_2\text{CO}(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2(g) + \text{HCOOH}(l) \quad \Delta H_{298}^\circ = -30.7 \text{ kJ mol}^{-1} \quad (6)
\]

\[
\text{HCOOH}(l) \rightarrow \text{CO}_2(g) + \text{H}_2(g) \quad \Delta H_{298}^\circ = 31.6 \text{ kJ mol}^{-1} \quad (7)
\]

\[
\text{CH}_3\text{OH}(l) + \text{H}_2\text{O}(l) \rightarrow 3\text{H}_2(g) + \text{CO}_2(g) \quad \Delta H_{298}^\circ = 130.7 \text{ kJ mol}^{-1} \quad (8)
\]

The structure of ruthenium hydride [K(dme),][Rhu(trop2dad)] (dme = dimethoxyethane, trop2dad = N\(_N\)N\(_N\)-bis(5H-dibenzo[a,d]cyclohepten-5-yl)-1,4-diaminoethane) 1 has been confirmed by X-ray analysis. It is a 16-electron valence Ru(0) complex which catalyses

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Fig. 1 Homogeneous catalysts which promote the aqueous dehydrogenation of methanol to hydrogen and carbon dioxide.

Table 2 Active homogeneous catalysts for methanol reforming

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (10^{-3} mmol; ppm to MeOH)</th>
<th>MeOH (mmol)</th>
<th>H2O (mmol)</th>
<th>Solvent (mL)</th>
<th>Additive</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>H2 (mmol)</th>
<th>Yield(^a) (%)</th>
<th>TOF(^b) (h^{-1})</th>
<th>TON</th>
<th>Conv. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Rh(bipy)2]Cl(^f) 5; 45</td>
<td>111</td>
<td>27.8</td>
<td>—</td>
<td>NaOH</td>
<td>120</td>
<td>3</td>
<td>0.105</td>
<td>0.03</td>
<td>7</td>
<td>21</td>
<td>n.r.</td>
</tr>
<tr>
<td>2</td>
<td>[K(dme)3][RuH(trop,dad)](^f) 10; 500</td>
<td>2</td>
<td>2.6</td>
<td>THF 1</td>
<td>—</td>
<td>90</td>
<td>10</td>
<td>5.0</td>
<td>84.0</td>
<td>54</td>
<td>540</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>[Ru(H)(Cl)(CO)(PNP(^f)iPr)] 0.88; 1</td>
<td>890</td>
<td>222</td>
<td>—</td>
<td>KOH</td>
<td>91</td>
<td>576</td>
<td>311</td>
<td>11.6</td>
<td>613</td>
<td>353</td>
<td>409(^f)</td>
</tr>
<tr>
<td>4</td>
<td>[Ru(H)(Cl)(CO)(PNP(^f)iPr)] 150; 130</td>
<td>890</td>
<td>222</td>
<td>—</td>
<td>KOH 320</td>
<td>91</td>
<td>24</td>
<td>231</td>
<td>26</td>
<td>64</td>
<td>192</td>
<td>(^f)</td>
</tr>
<tr>
<td>5</td>
<td>[Ru(H)(Cl)(CO)(PNP(^f)iPr)] 49.3; 250</td>
<td>198</td>
<td>111</td>
<td>NaOH 1</td>
<td>72</td>
<td>2</td>
<td>3.4</td>
<td>0.57</td>
<td>0.34</td>
<td>68</td>
<td>(^f)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>[Fe(H)(BH(_4))(CO)(PNP(^f)iPr)] 1; 4.5</td>
<td>222</td>
<td>55.5</td>
<td>—</td>
<td>KOH 80</td>
<td>91</td>
<td>46</td>
<td>9.8</td>
<td>1.5</td>
<td>214</td>
<td>9834</td>
<td>(^f)</td>
</tr>
<tr>
<td>7</td>
<td>[Ru(H)(BH(_4))(CO)(PNP(^f)Ph)] 3; 22.5</td>
<td>222</td>
<td>55.5</td>
<td>Triglyme 4</td>
<td>—</td>
<td>93.5</td>
<td>192</td>
<td>42.8</td>
<td>6.4</td>
<td>22</td>
<td>4286</td>
<td>6.4</td>
</tr>
<tr>
<td>8</td>
<td>[Ru(H)(Cl)(CO)(PNP(^f)Ph)] 3; 22.5</td>
<td>20</td>
<td>111</td>
<td>Toluene 2</td>
<td>KOH 40</td>
<td>100–105</td>
<td>648</td>
<td>131</td>
<td>72.8(^i)</td>
<td>44</td>
<td>28</td>
<td>661(^i)</td>
</tr>
</tbody>
</table>

\(\text{n.r. = not reported.} \)\(^a\) The yield is referred to methanol and is calculated assuming that each mmol of converted methanol has been fully dehydrogenated providing three mmoles of hydrogen.\(^a\) The TOF is the average value measured over the entire reaction time. Data extracted from ref. 21, Table 1, experiment performed in a closed vessel.\(^a\) Data extracted from ref. 22, SI pag. 14, base-free experiment. Data extracted from ref. 23a, SI pag. 21, long-term experiment with focus on catalyst stability. Data extracted from ref. 22, SI pag. 14, base-free experiment. Data extracted from ref. 24, SI pag. 2 Table S1.\(^f\) The TON is the total one over three consecutive uses (recycling) of the organic phase containing the catalyst; likewise, the yield has been calculated based on the total amount of methanol, 3 × 20 mmol, used over the three experiments.

The reaction of methanol and water to afford H2 and CO2 below 100 °C without addition of exogenous base.\(^\text{22}\) When the reaction was carried out in an open vessel at 90 °C in MeOH (2 mmol, 81 µL), H2O (2.6 mmol, 47 µL), toluene (1 mmol, 110 µL as internal standard), and THF (1 mL) with 1 (10 × 10^{-3} mmol, 0.5 mol%) to MeOH, a TON = 540 over 10 hours was achieved corresponding to an average TOF = 54 h^{-1} (each mole of hydrogen gas produced per mole of catalyst is considered as a turnover) (Table 2, entry 2). Neither formaldehyde nor its acetal were detected in solution, suggesting that attack of water may proceed on still coordinated formaldehyde and dehydrogenation of the acetal to formic acid be faster than that of methanol to formaldehyde, as predicted by DFT for primary alcohol dehydrogenation. Indirect evidence of the intermediacy of HCOOH was provided by the ability of 1 (0.01% mol) to decompose a 1 M solution of HCCOH in dioxane at 90 °C within minutes affording an initial turnover frequency of 24 000 h^{-1}. Based on the isolation and characterisation of some relevant intermediates and following investigation into their reactivity, the authors have suggested the catalytic cycle illustrated in Scheme 2. The hydride 1 does not react appreciably with alcohols but it does with H2O (or carboxylic acid) to generate a very reactive neutral Ru species (characterized by NMR), with release of one molecule of H2 and one equivalent of base. This is therefore considered to be the first step of the catalytic cycle. Addition of the OH bond of a substrate molecule, either methanol (this case is illustrated in Scheme 2), gem-diol (arising from hydration of formaldehyde), or formic acid, across the Ru–N bond affords the enamiido complex 5. This activates the ν-CH of the coordinated substrate which is then transferred to the ligand to give an imino–amino Ru(0) complex 6 after release of the dehydrogenation product. 6 can reiterate this process with a second substrate molecule to provide diamino complex 7 from which one equivalent of hydrogen is then released, aided by base and heat, to regenerate 1. Intermediates 7 and its adduct with benzaldehyde have been synthesized via stoichiometric reactions and characterized by X-ray analysis. Species 4 and 6 are competent for dehydrogenation of either MeOH, formaldehyde gem-diol or formic acid (in Scheme 2 the dehydrogenation of formic acid as by 4 to afford 6 and CO2 is shown in grey). This is an example of cooperative catalysis in which the ligand is both redox- and chemically active, supporting the metal shuttle between oxidation states 2 and 0 and adding the hydrogen...
optimised conditions, neat MeOH (10 mL), KOH = 8 M, catalyst 
tration and even in the presence of 90% v/v of water. Under 
amount of base, temperature and water content. The reaction 
turned out to be favoured by a high base content with KOH as 
base of choice, high temperature and low water amount, yet 
availability was observed already at 75 °C at 0.1 M base concen-
tration and even in the presence of 90% v/v of water. Under 
optimised conditions, neat MeOH (10 mL), KOH = 8 M, catalyst 
2b (1.58 µmol, 6.4 ppm), at 95 °C, an average TOF = 4723 h⁻¹ 
was achieved over three hours. The evolved gas was pure 
hydrogen with almost no trace of CO contamination (below 
1 ppm) while CO₂ was trapped as carbonate. By performing a 
longer term experiment in the presence of less base and a 
higher amount of catalyst (MeOH 8 mL, H₂O 2 mL, NaOH = 
0.1 M, catalyst 2a 49.3 µmol, 250 ppm, 72 °C) a steady-state 
condition was achieved within hours when CO₂ could escape 
the reaction medium and the expected H₂/CO₂ 3:1 ratio was 
observed. Complex 2b proved extremely robust as hydrogen 
evolution continued for three weeks affording a TON = 350 000 
with an average TOF = 200 h⁻¹ (using 1.0 ppm 2b in a 9:1 ratio 
of MeOH/H₂O), measured over the last 24 h (Table 2, entry 3). 
Parallel to base consumption and the ensuing decrease of 
boiling temperature, in fact, a decrease in activity was observed. 

Compound 2b is merely a catalyst precursor which needs 
one equivalent of base to be converted into amido complex 8 
(Scheme 3). The amido complex has been reported to react with 
iso-propanol or hydrogen gas to afford dihydride 9:²⁷b the 
protic hydrogen of the –OH moiety in the alcohol would add 
to the basic nitrogen of the ligand in 8 whereas the hydride of 
the α-CH would be transferred to the metal centre. It was 
therefore suggested that 8 and 9 are the two key species 
between which dehydrogenation of methanol, formaldehyde 
gem-diol(ate) and formate (which was detected in solution 
under catalytic-like conditions) occurs with ensuing hydrogen 
evolution.²³,b

DFT calculations have provided support to the proposed 
metal–ligand cooperative mechanism, highlighting the decisive 
role of the protic solvent, either water or methanol, in relaying a 
proton shuttle from the ligand nitrogen to the ruthenium 
ylide for the formation of a ruthenium dihydrogen complex 
from which hydrogen is eventually released.²³,b However it has 
been suggested, based on calculations, that formate decom-
position to hydrogen and carbon dioxide could take place 
through both inner- and outer-sphere mechanisms.²³,b According 
to the calculated free-energy landscape of the overall reac-
tion, dehydrogenation of gemdial(ate) has the lowest rate 
constant and dehydrogenation of formate the highest among 
the three steps,²³,b which is in line with the experimental 
observation that free formate, but neither formaldehyde nor 
gem-diolate, was observed in solution The actual rate of each 
step would however depend on the relative concentration of the 
species involved (‘‘steady-state regime’’).

The outer-sphere, cooperative mechanism does not require a 
change in the formal oxidation state of the central metal to 
trigger substrate reactivity and is hence open to 1st row transi-
tion metals. These metals usually prefer one-electron redox 
changes, making it more challenging to stabilise and maintain

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**Scheme 2** Proposed catalytic cycle for the aqueous dehydrogenation of MeOH promoted by [K(dme)₂][RuH(trop₂dad)].

**Scheme 3** Oversimplified proposed catalytic cycle for the aqueous dehydrogenation of MeOH promoted by [Ru(H)(Cl)(CO)(PNP³)] 2b.
the catalyst functionality, should the reaction proceed according to classical oxidative addition, insertion and reductive elimination. Indeed the analogous iron complex 2c was synthesized and proved effective in aqueous methanol reforming. Under optimised conditions, MeOH/H2O 9/1 v/v (10 mL), KOH = 8 M, catalyst 2c (4.18 μmol, 18.8 ppm to MeOH), at 91 °C, a TOF = 702 h⁻¹ was achieved in the first hour, and a TON = 6270 over 43 hours. By adding 5 equivalents of free ligand to the solution it was possible to extend the catalyst lifespan over almost five days, affording, under otherwise identical conditions, a TON = 9184 (111 h) (Table 2, entry 6). Although based on a far cheaper and abundant metal, the iron system is clearly less active than the ruthenium one, as correctly anticipated by theoretical calculations. However if the turnover activity per unit cost, recently suggested by Crabtree as a further “green” parameter to judge a catalyst, then the advantage based catalysts.

One drawback associated with the use of catalysts 2 in methanol reforming is the need for a high base concentration. The role of the base is many-fold: on the one hand it allows, by means of the salt effect, to increase the operational temperature and thus both the thermodynamic driving force and the rate of reaction; it provides an additional free energy advantage because of the acid–base reaction with the generated CO2; it is likely necessary to regenerate the catalytic active species from dormant resting states. Furthermore, because free formate is actually detected in solution when using catalysts 2 under basic conditions, it was suspected that its dehydrogenation might be slow at low methanol conversion. Therefore it was envisioned that either the addition of a higher catalyst amount, of a second catalyst which had proved effective in formic acid decomposition or of a high-boiling solvent might contribute to achieve methanol reforming even in the absence of base. Indeed, after catalyst and solvent screening, it was found that the combined use of catalyst Ru-MACHO-BH, which does not need an exogenous base to be activated, and [Ru(H)2(dppe)2] (dppe = 1,2-bis(diphenylphosphino)ethane) in the presence of triglyme (MeOH 9 mL, H2O 1 mL, triglyme 4 mL, 2d 5 μmol, 5 μmol) allows to dehydrogenate methanol at 93.5 °C with an average TOF = 93 h⁻¹ over 7 hours. The catalyst system stayed active for 8 days affording an overall TON of 4286 (Table 2, entry 7). Interestingly the two catalysts operate in a synergistic manner, as their combined activity is superior to the sum of the activities displayed by each of them alone in the same transformation.

Very recently Milstein et al. have added catalyst 3 (Fig. 1) to those amenable to methanol reforming: under optimised conditions, MeOH 20 mmol, 0.8 mL, H2O 111 mmol, 2 mL, toluene 2 mL, KOH 40 mmol, catalyst 3 5 × 10⁻³ mmol, 250 ppm to MeOH, Tset = 115 °C (effective T = 100–105 °C), a 70% yield of hydrogen was achieved over 9 day reaction time, corresponding to an average TOF = 45 h⁻¹. The base is necessary in order to generate the true catalytic species 11 from 3 (1 equivalent to the catalyst) and, according to the authors, to generate formate from methanol. In fact, while no hydrogen is produced from methanol in the absence of base, conversion of formic acid to hydrogen and CO2 with the same catalyst is instead possible. Toluene is likely necessary to increase catalyst solubility as no activity was detected in the absence of an organic solvent. Furthermore, the presence of a biphasic system allows for the easy recovery and recycling of the catalyst: the organic phase of the experiment under optimised conditions was separated and used twice for the reforming of new batches of methanol, showing undiminished activity and affording, after an overall reaction time of almost 1 month, a remarkable TON of about 29 000 (Table 2, entry 8). Like in the cases of catalysts 1 and 2, catalyst 3, or rather its activated form 11 (Scheme 4), relies on ligand–metal cooperation to abstract hydrogen from the substrate, either methanol, formaldelyde gem diolate or formate. The deearomatised complex 11, resulting from deprotonation at the pyridinylmethylene carbon, can in fact regain aromatisation at the pyridine moiety by interacting with the substrate, adding a “proton-like” hydrogen to the side-arm of the ligand and a “hydride-like” hydrogen to ruthenium (Scheme 4). The resulting dihydride 12 then releases hydrogen.

Very recently Crabtree et al. have reported the acceptorless dehydrogenation of methanol using homogeneous iridium bis(N-heterocyclic carbene) catalysts: under optimised conditions (dry MeOH, 3 mL, KOH 6.7 M, [Ir] 1 μmol, 91 °C) using a bis(N-heterocyclic) carbene complex stabilised with CO ligands an overall TON of 2900 over 15 hours was achieved which could be increased to 8000 over 40 hours. However, by measuring the relative amounts of HCOOK and K2CO3 produced, it turned out that only 5% of the converted MeOH had been exhaustively dehydrogenated to CO2 (trapped as carbonate) and H2, the rest being transformed into formate. Yet the catalysts are noteworthy

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**Scheme 4** Proposed key-intermediates in the aqueous dehydrogenation of MeOH promoted by 3, through aromatisation–dearomatisation of the pyridine pincer based ligand.
in that they can operate in air with undiminished efficiency and rely on simpler and cheaper ancillary ligands as to catalyst 1–3.

For the sake of comparison, selected data concerning the homogeneous catalysts able to promote aqueous reforming of methanol are collected in Table 2. For catalyst 2b, two further experiments with a higher catalyst loading (Table 2, entries 4 and 5) are reported.

Comparison between data reported in Table 1 for methanol decomposition and in Table 2 for aqueous methanol dehydrogenation clearly show that ruthenium catalysts bearing “non-innocent” pincer ligands (Table 2) have proved so far more active in methanol dehydrogenation than those whose ancillary ligands are not directly involved in substrate transformation (Table 1). This is probably due to the higher energy demanding events taking place at the metal in the latter case, like labilisation of a coordinated ligand or change in the oxidation state which is not necessary for the former, or if so, like in the case of catalyst 1 developed by Grützmacher et al., is supported by the ligand.22

Among homogeneous catalysts for aqueous methanol dehydrogenation, catalyst 2b stands out for the high average TOF of 613 h⁻¹ over 23 days (although the average TOF during the last 24 hours of the reaction was 200 h⁻¹, which is however still higher than the average TOF for catalysts 1 and 3). Yet yield is quite limited if compared to those recorded with 1 and 3: use of a higher catalyst loading serves to improve it although at the expenses of activity (TOF) (compare entries 3 and 4 in Table 2). Unlike others in Table 2, catalysts 2 do not require any added solvent to allow for better catalyst solubilisation and are tolerant of various methanol/water ratios. The robustness of aliphatic PNP pincer ruthenium catalysts has been further demonstrated in the dehydrogenation of higher alcohols, such as biomass derived ethanol33 and glycerol,34 a by-product of biodiesel production, selectively afford, in the last case, valuable lactic acid. Catalyst 2a could be applied directly to industrial batches of bioethanol and glycerol with undiminished, if not superior, efficiency compared to solutions of the pure substrates.

The main drawback of catalysts 2 and 3 is the requirement of high base loads, whereas catalyst 1 operates smoothly without. At the present stage of development, it has been pointed out that the capturing of CO₂ from small and widespread sources may be technically feasible but economically prohibitive and CO₂ should be eventually captured from the atmosphere itself.35 On the other hand, the high base concentration required by catalysts 2 and 3 might be advantageously exploited to sequester CO₂ for its later recycle, for example by hydrogenation of the resulting bicarbonate to formate salts,36 while awaiting for a fully reversible charge–discharge CH₃OH ↔ CO₂ process.

Aqueous methanol dehydrogenation actually combines three catalytic cycles running at the same time, each of which might require a different catalyst for optimal efficiency. Entry 7 in Table 2 shows the feasibility of such approach, without the need for catalyst confinement. The possibility of replacing precious metals with non-noble ones has been demonstrated with catalyst 2c. Designing phosphorus-free ligands would help reducing catalyst cost further.

The activities and productivities of the homogeneous catalysts developed so far for methanol reforming lie far behind those required for practical applications and, at present, do not compare favourably with those achieved with supported metal catalysts.36 Yet, they operate under milder conditions and are thus more selective (no CO contamination). In addition, the mechanism of a catalytic process promoted by a homogeneous catalyst is in general more easily disclosed and this opens the possibility to tailor an optimized catalyst by modifying its structural electronic and steric properties. This will certainly stimulate further intense effort to develop improved systems for methanol reforming.

**Carbon dioxide hydrogenation**

Numerous reports have focussed on partial hydrogenation of CO₂, especially to formic acid, a topic which has been recently reviewed in depth by several authors37 and readers are referred to them for detailed descriptions on this topic.

For selective reduction to MeOH–H₂O, activated hydrides such as boranes18 or silanes39 have usually been employed. However, examples of homogeneously catalysed reduction of CO₂ to MeOH/H₂O using molecular H₂ as reducing agent have until recently remained elusive.40 In this account, the direct hydrogenation of CO₂ to MeOH using H₂ as reductant and homogeneous catalysts will be discussed. In addition, procedures that employ CO₂-derivatives will be mentioned.

Sanford et al. presented the first successful example of homogeneous catalytic CO₂ hydrogenation to MeOH and H₂O in 2011.41 This was achieved through cascade catalysis using a combination of three catalytic systems in order to accommodate the sequential reduction as illustrated in Scheme 5.

The first step is the hydrogenation of CO₂ to formic acid using catalyst 13,42 which is followed by a Sc(OTf)₃ catalysed esterification to methyl formate. Overall, it was found that, in a one-pot procedure, methyl formate could be formed from CO₂ with a TON of 40 after 16 hours at 135 °C. For the further hydrogenation of the ester to MeOH, complex 11, one of Milstein’s catalysts,25a,f,43 was employed. This led to an optimised system, which produced MeOH with a TON of 2.5 after 16 hours at 135 °C under 30/10 bars of H₂/CO₂ pressure. A low CO₂ pressure was necessary in order to avoid inactivation of 11 due to covalent bond formation between CO₂ and the complex.44 A further problem was the inactivation of 11 by...
Sc(OTf)₃, which explained the low overall TON of CO₂ conversion to MeOH. These issues were partially circumvented by setting up a two-compartment system in which catalysts 13 and 11 are confined in one compartment, and Sc(OTf)₃ in the other. This led to an improved TON of 21.

The system described by Sanford et al. illustrates the possibility for homogeneous catalytic CO₂ hydrogenation. When comparing this procedure with the general hydrogenation approach shown in Scheme 1, catalyst 13 is responsible for the first reduction, Sc(OTf)₃ is present as a Lewis acid for activating formic acid to form methyl formate, and 11 promotes the other two reduction steps towards methanol. Therefore, developing a catalytic system capable of hydrogenating formic acid directly would allow to dispense with Sc(OTf)₃. Moreover, finding a catalyst that not only tolerates CO₂, but also effectively hydrogenates it all the way to MeOH is of obvious interest. This would allow to use a single catalyst for the whole procedure and to adjust more freely the applied CO₂ pressure.

Almost simultaneously with Sanford, Milstein et al. showed that the CO₂-derivative dimethyl carbonate can be hydrogenated to MeOH using a single catalyst (Scheme 6). Under optimised conditions, a TON of 4000 could be achieved using catalyst 11, whereas a TON of 2500 was obtained with 14. Yields of 88% and >99% were obtained, respectively. In addition, when using 11 as catalyst (0.01 mol%), the reaction could be performed neat at 100 °C under 10.1 bar of H₂ pressure leading to a quantitative yield of MeOH after 8 hours with a TON > 990. Hence, this procedure represents a mild, solvent- and waste free procedure. However, the use of dimethyl carbonate reduces the overall gravimetric H₂ capacity of the system. In addition, no long term reactivity was provided.

A mechanism for the catalytic cycle has been proposed based on experimental evidence and calculations. All studies suggest methyl formate and formaldehyde as intermediates, which supports the general pathway shown in Scheme 1. There is, however, some dispute as to how rupture of the OCH₂ group on the resulting ruthenium alkoxide is mediated. One suggestion is that one hydrogen from the ligand arm is transferred to afford CH₃OH in a cooperative metal–ligand fashion. An alternative lower energy lying route has been put forward where a CH₃O group is actually transferred to the metal after transfer of the Ru–H hydride to the carbonyl group [Ru–H/Ru-OCH₃ metathesis].

Ding et al. showed that 2a (Fig. 1), is also capable of reducing carbonates to MeOH. At 140 °C, a catalyst loading of 0.001–0.1 mol% suffices to form MeOH in 84–99% yield from a range of carbonate substrates. An impressive TON up to 87 000 and TOF of 1200 h⁻¹ were obtained.

Another indirect approach, where CO₂ is initially transformed into an urea derivative before being hydrogenated to MeOH and amines, was also suggested by Milstein et al. When using 2 mol% of catalyst 11, yields up to 94% were obtained; however, with 1 mol% of 11 the yields did not exceed 63%, limiting the applicability of the system. Moreover, as opposed to the system shown in Scheme 6, using ureas as CO₂-derivatives inevitably creates undesired amine side products. Even if these amines became part of a cycle encompassing urea to MeOH–amine, they would still represent unnecessary ballast compared to the optimal CO₂–MeOH hydrogenation–dehydrogenation system.

In 2012, Klankermayer and Leitner et al. demonstrated for the first time that a single catalyst is capable of hydrogenating CO₂ to MeOH (Scheme 7). This was achieved by mixing the precursors of catalyst 15 in THF at 140 °C with 60/20 bars of pressurised H₂ and CO₂, respectively. In addition, EtOH (400 eq. with respect to 15) and an acid additive (MSA or HNT₅₂, 1.0–1.5 eq. with respect to 15) were required in order to achieve TON values exceeding 10. The precursors of 15 can be either a mixture of [Ru(acac)₃] and triphos or 16. When employing [Ru(acac)₃]/triphos a TON up to 135 could be achieved after 24 hours. With 16, the TON could reach 221. Moreover, it was shown that the system was active for at least 3 days, demonstrating the robustness of the system. EtOH could be replaced by MeOH but at the expense of the efficiency. Under otherwise identical reaction conditions, TONs of 52 and 24 were observed after 24 hours with EtOH and MeOH, respectively. The role of the alcohol was suggested to be ester formation by reaction with formic acid. Using the double amount of ethanol did not result in an increased reaction rate, which the authors ascribed to the fact that ethyl formate formation is not rate-limiting.
However, the efficiency in the absence of an alcohol additive, under otherwise identical reaction conditions, was not reported.

Clear advantages of this system are that CO₂ is directly hydrogenated to MeOH and H₂O by a single catalyst and that the system is stable on the scale of days. As such, this system is a proof of principle that a single molecular organometallic complex can encompass all three hydrogenation steps. Moreover, avoiding THF as solvent would increase the gravimetric H₂ yield of the produced MeOH.

Two years later, Klankermayer and Leitner reported that the same system is capable of performing the full hydrogenation of CO₂ to MeOH without the need of an alcohol additive.50 In fact, the conditions that provide a TOF of 221 in the presence of 400 equivalents of EtOH (Scheme 7, using 16) gave a very similar TOF of 228 without any alcohol additive. Using half the amount of 16 (12.5 μmol) led to an initial TOF of 79 h⁻¹, which is comparable to state-of-the-art heterogeneous Cu/ZnO catalysts.51 Moreover, re-pressurising the reaction mixture with CO₂ and H₂ after 16 and 32 hours allowed for a total TOF of 603 after 48 hours.

Exchanging THF with 2-MeTHF (2-methyltetrahydrofuran) led to a biphasic system, which allowed for easy separation of the aqueous product phase (H₂O and MeOH) from the organic phase containing the catalyst, though a small decrease in reactivity compared to THF was observed (TON of 186 after 24 hours). A total TON of 769 could be achieved after 4 cycles of CO₂ hydrogenation when using 12.5 μmol of 16, showing the potential of this reaction system. However, the reactivity of the fourth cycle was merely 50% compared to the first cycle (TON of 110 compared to 247).

Due to the fact that this system represents the first example of a homogeneous catalytic system capable of catalysing the hydrogenation of CO₂ to MeOH, the mechanism proposed by Klankermayer and Leitner is of interest. The mechanistic aspects of all three hydrogenation steps were studied in depth by NMR and in silico experiments. Based on this, a very detailed mechanism was proposed, which is presented here in a highly simplified manner in Scheme 8 for the sake of brevity.

Initially, the solvent (S = THF) in 15 is replaced by CO₂ forming complex A. After migratory insertion of CO₂ into the ruthenium-hydride bond a solvent molecule coordinates to form B. It is proposed that a H₂ molecule is released and re-attached during this process. At this stage, the central CO₂-carbon atom has reached the oxidation state of formic acid.

A heterolytic cleavage of the Ru-bound H₂ followed by a hydride transfer to the carbon atom leads to C. To facilitate these events, a H₂ molecule is replacing the solvent and eventually detaches again (not shown). Moreover, the catalytic cycle has at this point reached the stage where the carbon atom has the oxidation state equivalent to that of formaldehyde.

Complex C is then converted to D by collapse of the ruthenium methanediolate to a ruthenium-formaldehyde adduct assisted by protonation by a carboxylic acid, which acts as proton shuttle. Acetic acid was used as model for the calculations in this instance. The presence of a D like intermediate was corroborated by in situ NMR studies. Furthermore, it was found that the acid-mediated path is energetically favoured over the water-assisted pathway and D represents a low energy intermediate for the formation of E. As for the step from B to C, intermediate F is formed from E via a transient bound H₂ (which replaces the solvent), and transfer of a hydride to the carbon atom, rendering it in the oxidation state of a methanol.

As for the collapse of methanediol (C to E), a low energy pathway towards H is found when introducing a carboxylic acid as assisting unit. Hence, intermediate G has a similar function for the F to H transformation as D has it for C to E. Finally, 15 is regenerated by ligation of H₂ and extrusion of MeOH.

As shown in the catalytic cycle, a single complex is proposed to perform all three hydrogenation stages. Moreover, both formic acid and formaldehyde were shown to be hydrogenated by 15, supporting the notion of a single complex catalysed hydrogenation of CO₂ to MeOH.

Overall, an exergonic reaction is predicted by the calculations, which is in accordance with (reverse) eqn (8).

Because of the limited number of reports on direct hydrogenation of CO₂ to MeOH by a single molecular catalyst, the work by Klankermayer and Leitner represents a guideline for future studies in this area. Developing more active catalysts for this process is of obvious necessity in order to meet any demands for a practical application of hydrogen storage in a cycle CO₂–MeOH based on homogeneous catalysis. Furthermore, it would be interesting to test the activity of the Klankermayer and Leitner catalyst for the opposite directed reaction, MeOH dehydrogenation.

Complex 16 has also been shown to be active for the hydrogenation of dimethyl carbonate.55 Using 1 mol% and 1.5 equivalent of HNTF₂ under 50 bar H₂ at 140 °C in dioxane allowed for 99% conversion with 94% selectivity towards MeOH after 16 hours.

Conclusions

Very recently, methanol dehydrogenation to carbon dioxide and the reverse reaction catalysed by homogeneous catalysis have...
witnessed great progress. Whereas several efficient catalytic systems comprising a single catalyst have already been devised for the former reaction, only a single example of the latter has been published to date. Moreover, much more efficient systems need to be developed for both directions in order to approach practical applicability.

To date, there are no examples of any homogeneous catalytic system capable of catalysing both directions of the CO₂/MeOH cycle. Perhaps combining a system from the dehydrogenation direction that would work under the Klankemeyer and Leitner system, such as the Gützmacher system, could show some insight to this intriguing endeavour.

Considering the sudden increase of homogeneous catalytic systems capable of performing MeOH dehydrogenation or CO₂ hydrogenation within the last very few years, it will be very interesting to follow the further developments to come in this area in the near future.

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Notes and references

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