Low-temperature aqueous-phase methanol dehydrogenation to hydrogen and carbon dioxide

Martin Nielsen1, Elisabetta Alberico1,2, Wolfgang Baumann1, Hans-Joachim Drexler1, Henrik Junge1, Serafino Gladiali3 & Matthias Beller1

Hydrogen produced from renewable resources is a promising potential source of clean energy. With the help of low-temperature proton-exchange membrane fuel cells, molecular hydrogen can be converted efficiently to produce electricity1–3. The implementation of sustainable hydrogen production and subsequent hydrogen conversion to energy is called “hydrogen economy”4. Unfortunately, its physical properties make the transport and handling of hydrogen gas difficult. To overcome this, methanol can be used as a material for the storage of hydrogen, because it is a liquid at room temperature and contains 12.6 per cent hydrogen. However, the state-of-the-art method for the production of hydrogen from methanol (methanol reforming) is conducted at high temperatures (over 200 degrees Celsius) and high pressures (25–50 bar), which limits its potential applications4–6. Here we describe an efficient low-temperature aqueous-phase methanol dehydrogenation process, which is facilitated by ruthenium complexes. Hydrogen generation by this method proceeds at 65–95 degrees Celsius and ambient pressure with excellent catalyst turnover frequencies (4,700 per hour) and turnover numbers (exceeding 350,000). This would make the delivery of hydrogen on mobile devices—and hence the use of methanol as a practical hydrogen carrier—feasible.

Of the known hydrogen storage materials6–14, methanol represents a promising energy carrier. Its convenient properties (12.6% hydrogen and being liquid at room temperature) suggest that a “methanol economy” may be possible14. To combine the advantages of simple methanol transportation and the energy efficiency of proton-exchange membrane fuel cells, so-called ‘reformed methanol fuel cells’ have been developed. However, methanol-reforming processes are insufficient unless high temperatures (>200 °C) are used. Therefore, the state-of-the-art efficiency of reformed methanol fuel cells is only approximately 40%. Moreover, very low concentrations of carbon monoxide are tolerated in the fuel cell (<10 parts per million, p.p.m.), which is challenging for current catalytic systems. In general, methanol reforming occurs in the steam phase using heterogeneous catalysis and high temperatures6. Notably, Dumesic et al. have developed a Pt/Al₂O₃-based catalyst that allows for aqueous-phase methanol reforming at more acceptable temperatures (200–225 °C) and pressure (25–50 bar)7,9. In addition, the use of less expensive and more abundant Cu/Zn/Al₂O₃ catalyst systems is also noteworthy, although they need higher temperatures than does the Pt/Al₂O₃ catalyst6.

Our long-term interest in efficient low-temperature hydrogen generation15,16, led us to identify active molecular-defined catalysts for a low-temperature (<100 °C) aqueous-phase methanol dehydrogenation process. We envisioned a one-pot stepwise process including initial dehydrogenation of methanol to hydrogen and formaldehyde, water-promoted dehydrogenation of formaldehyde to formic acid and hydrogen, and final dehydrogenation of formic acid to hydrogen and carbon dioxide. This should lead to an overall yield of three molecules of hydrogen and one of carbon dioxide, thus resembling classic methanol reforming (Fig. 1a). Either methanol (MeOH) or H₂O could be in excess, depending on the potential applications.

To the best of our knowledge, all known molecular-defined organometallic catalysts for alcohol dehydrogenation promote the liberation of only one molecule of hydrogen from each alcohol molecule17–24. Moreover, there exists no example of homogeneously catalysed dehydrogenations of aldehydes in the presence of water. Recently, organometallic complexes containing pincer-type ligands (capable of enabling cooperative metal–ligand catalysis) showed interesting activities in catalytic hydrogenation and dehydrogenation reactions25–29. Therefore, we envisioned that this type of catalyst might be suitable for selective methanol dehydrogenation, and possibly even for methanol reforming. To our delight, testing a variety of ruthenium-based pincer complexes (Supplementary Scheme 1 and Supplementary Table 2) in a 4:1 mixture of MeOH/H₂O containing 0.5 M NaOH revealed significant catalyst activity for complexes 1a and 2a (the turnover frequency is the amount of hydrogen produced by each catalyst molecule per hour, 120 h⁻¹ and 45 h⁻¹, respectively; Fig. 1b). Interestingly, in these reactions hydrogen generation had already occurred at 72.0 °C and all reactions produced very pure hydrogen gas.

**Figure 1 | Methanol reforming by homogeneous catalysis.** a. Schematic pathway for a homogeneously catalysed methanol reforming process via three discrete dehydrogenation steps. b. Best-performing catalysts among those tested (see Supplementary Information) for aqueous-phase methanol dehydrogenation performed with 0.5 M NaOH at 72.0 °C.

1Leibniz-Institut für Katalyse Eingetragener Verein an der Universität Rostock, Albert-Einstein Straße 29a, Rostock, 18059 Germany. 2Istituto di Chimica Biomolecolare, CNR, traversa La Crucca 3, Sassari 07040, Italy. 3Dipartimento di Chimica e Farmacia, Università di Sassari, Sassari 07100, Italy.

©2013 Macmillan Publishers Limited. All rights reserved
Under catalytic conditions (Supplementary Scheme 5) both formate and carbonate ions were observed in the nuclear magnetic resonance (NMR) as traces of the reaction mixtures, showing that the formate is an intermediate in this dehydrogenation sequence and that CO₂ is trapped as carbonate (Supplementary Figs 16 and 19). As shown in Fig. 1a, the first dehydrogenation step of methanol results in formaldehyde, which, however, we never detected in solution. The subsequent conversion to formate and hydrogen occurs rapidly under these conditions, but formate conversion is apparently more sluggish. Moreover, due to the alkaline character of the solution, any evolved CO₂ is initially trapped as carbonate. Hence, in the first phase of the reaction a base-mediated reforming sequence proceeds according to equation (1):

\[
\text{CH}_3\text{OH} + 2\text{NaOH} = 3\text{H}_2 + \text{Na}_2\text{CO}_3
\]

Although no bicarbonate (NaHCO₃) was detected in the reaction mixtures, it should not be conclusively excluded as a possible product given the change in pH observed over time (as discussed below). Owing to the inherent complexity of the overall methanol reforming via dehydrogenation reactions, we assign turnover frequency and turnover number (the amount of hydrogen per catalyst molecule) as measures of the catalyst activity and productivity, respectively, for the production of each H₂ molecule. In fact, the successive production of three H₂ molecules and one CO₂ molecule gives a turnover number of 3.

Investigation into the effect of MeOH/H₂O ratio on catalyst activity. Performed with catalyst 1a or 2a (amounts are given in μmol and loading in μmol mol⁻¹ of MeOH is stated as parts per million) in a 10–40 ml MeOH/H₂O solution containing 8.0 M KOH (molarity based on total MeOH/H₂O volume). For entries 1–7, the reaction mixtures were under reflux. The H₂/CO₂ ratio, determined by gas-phase chromatography, was consistently >500:1. The gas evolution was determined by gas burette measurements. Each molecule of hydrogen is counted as resembling one turnover.
in a 4:1 MeOH/H₂O solution led to the finding that 8.0 M potassium hydroxide (KOH) gave optimal results (Table 1, entry 1). It should be noted that the temperature increase due to such a high base concentration (salt effect) seems to be far more important than the high base concentration itself in boosting activity (Supplementary Scheme 2 and Supplementary Table 3). Using 8.0 M KOH, complex 1a was more active than complex 2a with a turnover frequency of up to 2,687 h⁻¹ (Table 1, entries 2–5). Not surprisingly, increasing the water content (MeOH/H₂O = 3:2) had a detrimental effect on the catalytic activity. The poor solubility of 1a explains the increase in activity over time because it is only slowly transformed into the catalytic active species (Table 1, entry 6). Again using 2a instead of 1a resulted in a more than fivefold improvement of activity (Table 1, entry 7). Even a highly diluted methanol system (MeOH/H₂O = 1:9) still afforded significant hydrogen evolution, albeit with lower activity (Table 1, entry 8). From a practical point of view, this latter result is important because it allows the use of an aqueous methanol solution that may vary in methanol concentration over time. When performing an experiment simply with methanol and potassium hydroxide, a remarkable activity of approximately 4,720 h⁻¹ was obtained (Table 1, entry 9). Moreover, when the experiment in entry 4 of Table 1 was repeated in the presence of a large excess (>500 equivalents) of Hg, no decrease in activity was observed, which supports the homogeneous nature of the catalytic system.

To prove the stability of the catalyst system, a long-term experiment using 0.88 μmol of 2a in 40 ml of a 9:1 MeOH/H₂O solution, corresponding to a catalyst loading of 1 μmol mol⁻¹ of MeOH (1 p.p.m.), was performed (Fig. 2a; Supplementary Scheme 3 and Supplementary Figs 13–15). In this case, MeOH is in excess and is thus taking the role of both the reactant and the solvent. The molecular catalyst was stable for more than three weeks and after 23 days, a total turnover number of 350,000 was achieved. Even after this time, the catalyst was still active with an instant turnover frequency of 200 h⁻¹, measured as an average over the last 24 h. In this case, the hydrogen yield calculated for full methanol reforming was 27% (12% with respect to MeOH, Supplementary Equations (3) and (4)). The reaction showed almost constant activity for the last ten days. Importantly, less than 1 p.p.m. of both CH₄ and CO were observed by gas-phase gas chromatography throughout the reaction. By increasing the catalyst loading, the performance was easily improved. Hence, the same hydrogen yield is reached within 90 min when using 150 μmol mol⁻¹ (150 p.p.m.) of 2a. Within 24 h, the yield of H₂ increases to 59% under these conditions and that of CO₂ approaches 43% (26% and 19%, respectively, if referring solely to MeOH). We did not perform any further optimizations towards higher conversion.

To show that a ‘real’ aqueous methanol–reforming process with a 3:1 H₂/CO₂ gaseous content can be achieved, an experiment in the presence of low amounts of base (0.1 M of NaOH in a 4:1 MeOH/H₂O) was performed (Supplementary Scheme 4). Under these conditions, the majority of CO₂ is released instead of being trapped as carbonate in solution. Indeed, in the presence of 250 p.p.m. of 1a, the expected 3:1 H₂/CO₂ gas composition was observed after approximately 5–6 h and then stayed constant until the reaction was stopped (Fig. 2b). We note

Figure 3 | Proposed catalytic cycle for Ru-promoted aqueous-phase methanol dehydrogenation. Proposed catalyst activation and catalytic cycle for low-temperature methanol reforming catalysed by 2c, made in situ from 2a. The phosphorus iPr substituents have been omitted for clarity. ‡ denotes transition state; solvent-H indicates a molecule of solvent involved in hydrogen bonding.
that a correlation between solution pH and gas composition is observed (Supplementary Table 4). The pH, initially at 13, dropped to approximately 10 over the first 4 h and then stayed constant for the rest of the reaction time. It seems that in the first phase of the reaction an equilibrium among hydroxide/(bi)carbonate/formate is approached, which then leads to a 'steady state' gas evolution, as would be expected if methanol reforming is taking place. The higher-than-expected content in H₂ observed even after onset of the equilibrium is due to the fact that the hydrogen generated in the pre-equilibrium phase has not been discharged. Upon addition of aqueous HCl to a reaction mixture having pH 11 (Supplementary Table 4, entry 4), about 0.7 mmol of CO₂ were evolved, proving that NaOH is actually consumed in the initial course of the reaction. Similar to the long-term reaction experiment, a stable gas evolution (activity) was reached; this time after 2–3 h.

Careful analysis of Fig. 2b shows that the overall process goes through three distinct reaction stages: In the first stage, corresponding to the first hour, the process is mediated by the base and a substantial amount of free hydroxide is still present in the reaction solution. Here, over 90% of the gas is H₂ and the pH stays > 12. The second stage is the equilibrating phase when the gas distribution, hydroxide consumption and pH are approaching a steady state. During this period, the activity changes at a slower rate while approaching the steady-state value as well. In the third stage (after 4–5 h and thereafter), steady-state conditions are established and the hydroxide/(bi)carbonate/formate concentration, gas evolution and distribution, and pH remain constant. Thus, the gas flux contains 3:1 H₂/CO₂, and pH stays at about 10.

Considering the observed general stability of the catalytic system (Fig. 3), the catalytic cycle via 

\[ \text{MeOH} + \text{H}_2 \text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

starts the catalytic cycle by losing formate and reacting with MeOH or formaldehyde. In agreement with previous observations, we suggest that the generation of the first hydrogen molecule occurs through an outer-sphere concerted process as in I, that is, without direct coordination of methanol to the metal. Because formaldehyde itself as well as its hydrates are barely detected in solution, HCHO might undergo a sequence of fast reactions while still coordinated to the metal centre. Attack of hydroxide gives the gem-diol(ate) II, which is probably further stabilized by a solvent-cage of the protic H₂O/MeOH. Again, outer-sphere dehydrogenation releases the second hydrogen molecule and formate is formed. At this point, the catalyst either re-starts the catalytic cycle by losing formate and reacting with MeOH or it performs the final step of the catalytic cycle via III, leading to CO₂ and the third molecule of H₂. Because free formate is actually detected in solution, its dehydrogenation through reaction with 2c must be slow at low formate concentration in competition to MeOH. However, the fact that substantial CO₂ formation is observed at a point where MeOH is still in large excess suggests that formate dehydrogenation might be relatively faster than MeOH dehydrogenation.

Notably, hydride species are observed in solution under catalytic conditions (Supplementary Fig. 17), most probably 2a and 2e–g. It seems that the need for base to keep the catalytic system active is related to the continuous formation of 2c from such species and not to the deprotonation of methanol and formic acid. We may speculate whether the alkalinity of the medium might enhance reactivity by deprotonation of methanol. However, this would most probably require an inner-sphere mechanism, which has been questioned previously.

In conclusion, we have demonstrated aqueous-phase methanol dehydrogenation and reforming at low temperature. Compared to previously known heterogeneous systems, we observe low amounts of contaminant gases CO and CH₄ (<10 p.p.m.). Key to success is the use of molecular-defined [RuHCl(CO)(HN(CH₃)₂PR₂)] (where iPr = (CH₃)₂CH) catalysts, which exhibit high activities up to 4,700 h⁻¹ and catalyst productivities of >350,000. The optimized system is stable under aqueous alkaline conditions and remains active for more than three weeks. Once the relative concentrations of the reagents and possible intermediates competing for the catalyst have reached suitable steady-state values, the ratio of H₂ to CO₂ expected for MeOH aqueous reforming (H₂/CΟ₂ 3:1) is observed. Moreover, this system represents full conversion of all ‘available’ hydrogen atoms in the substrates to hydrogen by homogeneous catalysis. An intrinsic drawback is the base needed for this reaction to stay active. Nevertheless, using this system it might be possible to combine the advantages of methanol as the ‘hydrogen carrier’ and the superior efficiency of proton-exchange membrane fuel cells compared to methanol fuel cells.

METHODS SUMMARY

All reactions were performed under inert atmosphere (argon) with exclusion of air. A solution of MeOH and H₂O in a given ratio, containing a defined amount of base, was heated to a certain temperature and let equilibrate for 30 min. Then an amount of one of five catalysts (1–4, and 5 (ref. 30)) was added to the solution. The amount of catalyst is reported in parts per million relative to MeOH. Gas evolution was measured by a gas burette (100-ml, 500-ml or 1-litre burette). Each molecule of hydrogen is counted as resembling one turnover. After the desired reaction time, the identity of the gas components and their ratio was determined by gas-phase chromatography.

Full Methods and any associated references are available in the online version of the paper.

Received 28 June 2012; accepted 7 January 2013.
Published online 27 February 2013.


**Supplementary Information** is available in the online version of the paper.

**Acknowledgements** M.N. thanks the Alexander von Humboldt Foundation for financial support. We thank the BMBF and the Ministry of Science and Education of Mecklenburg-Western Pommerania for the basic funding of this project.


**Author Information** Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to M.B. (matthias.beller@catalysis.de).
METHODS

All reactions were performed under inert atmosphere (argon) with exclusion of air. Methanol was refluxed over magnesium and distilled under argon atmosphere. Water was distilled and degassed before use. NaOH and KOH were purchased and used as received. \([\text{RuHCl(CO)(PPh}_3\text{)}_3]\), \([\text{RuHCl(CO)(HN(C}_2\text{H}_4\text{PPh}_2\text{)}_2]\) complex 1a (Ru-MACHO), \([\text{RuH(BH}_4\text{(CO)(HN(C}_2\text{H}_4\text{PPh}_2\text{)}_2)]\) complex 1b (Ru-MACHO-BH), \(\text{HN(C}_2\text{H}_4\text{PPr}_2\text{)}_2\), \(\text{HN(C}_2\text{H}_4\text{PCy}_2\text{)}_2\) and carbonylchlorohydrido \(6-(\text{di-t-butylphosphinomethyl})-2-(\text{N,N-diethylaminomethyl})\text{pyridine}\) ruthenium(II) (complex 4; see Supplementary Scheme 1) were purchased from STREM Chemicals Inc., stored under argon, and used as received. \([\text{RuHCl(CO)(HN(C}_2\text{H}_4\text{PPr}_2\text{)}_2)]\) (complex 2a), \([\text{RuH}_2\text{(CO)(HN(C}_2\text{H}_4\text{PPr}_2\text{)}_2)]\) (complex 2b; Supplementary Figs 6 and 7), \([\text{RuH}(\text{CO})(\text{N(C}_2\text{H}_4\text{PPr}_2\text{)}_2)]\) (compound 2c; Supplementary Figs 8 and 9), \([\text{RuHCl(CO)(HN(C}_2\text{H}_4\text{PCy}_2\text{)}_2)]\) (compound 3; Supplementary Figs 10–12), and complex 5 (ref. 30; see Supplementary Scheme 1) were prepared following or adapting procedures in the literature. Catalytic reactions for the measurement of hydrogen gas evolution were carried out in a thermostated double-walled three-necked flask equipped with a high-efficiency reflux condenser. The latter was connected via a three-way stopcock to a gas burette (see Supplementary Figs 4 and 5). At the beginning of each experiment, the reactor system (flask and condenser) was subjected to five consecutive vacuum–argon cycles, while isolated from the burette. Then the whole system, including burette, was purged with argon for at least 15 min. A defined amount of water was then introduced in the flask, followed by the required amount of base and methanol. The system was then heated to the desired temperature by means of a thermostat. Once the temperature set in the thermostat had reached, the system was allowed to equilibrate for 30 min, after which time a homogeneous solution had formed, even in those cases when a very high base concentration was used. The inner temperature reported for each experiment was measured with a ground-glass joint thermometer connected to the reactor (Supplementary Table 1). The desired amount of catalyst was weighed in a Teflon crucible and introduced into the reactor. The reaction solution was stirred at 700 r.p.m. To ascertain the composition of the evolved gas, a sample of the gas phase was withdrawn through a septum in the three-way stopcock with a gas-tight syringe and analysed by gas-phase chromatography using either HP Plot Q/flame ionization detector–hydrocarbons, carboxen/thermoconductivity detector–permanent gases, He carrier gas or carboxen/thermoconductivity detector/methanizer/flame ionization detector–permanent gases, He carrier gas (for representative gas-phase gas chromatography traces, see Supplementary Figs 1–3). The second gas-phase gas chromatography (see Supplementary Experimental Methods GCb) allows the detection of very low levels of CH₄ and CO. The turnover number was calculated from the amount of hydrogen produced. Every hydrogen molecule represents one catalyst turnover number (see Supplementary Equations (1) and (2)).