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Reusable Homogeneous Catalytic System for Hydrogen Production from Methanol and Water

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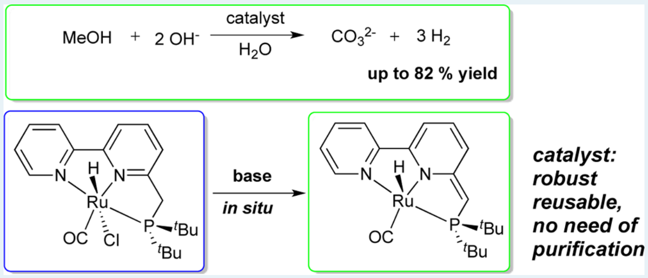
Supporting Information

ABSTRACT: An efficient system catalyzed by a Ru-PNN pincer complex was developed for reforming methanol to H_2 and CO_2 (absorbed by base) under relatively low temperature (around 100 °C), and good yields of H_2 were obtained (~80%). The catalyst solution can be reused without isolation and purification, with no decrease in catalytic activity being observed for a period of ~1 month. Decomposition of formic acid, which is likely to be the last step of the methanol reforming reaction, was also investigated, and the formic acid adduct of the catalyst was fully characterized spectroscopically and by X-ray crystallography.



KEYWORDS: *methanol reforming, hydrogen storage, reusable catalyst, ruthenium pincer complex, dehydrogenation*

Hydrogen is a potentially efficient and clean source of energy,[1] but it is hard to store, being a gas with low density under normal pressure at ambient temperature. On the other hand, methanol, a liquid under ambient conditions and having a high hydrogen storage capacity of 12.6%, is considered as a very good hydrogen carrier.[2−6] Furthermore, methanol can be produced from renewable resources,[2] which makes it even more attractive for use for hydrogen storage purposes. The classic process can produce hydrogen and CO_2 from a mixture of methanol and water and is used in the reformed methanol fuel cell. However, this reforming process is catalyzed by heterogeneous catalysts and requires a high temperature of above 200 °C, which may generate CO, poisoning the fuel cell catalysts. These and some other disadvantages, including the requirement of high pressure, limit the application of the system.[3−7] For practical purposes, efficient processes catalyzed by reusable catalysts, without isolation and purification, are highly desirable for reforming of methanol to hydrogen and CO_2 under relatively low pressure and low temperature.

Recently, Beller reported an important homogeneous ruthenium-catalyzed methanol dehydrogenation reaction at low temperature (<100 °C) to produce hydrogen and carbon dioxide. A high turnover frequency up to 4700 h^{-1} was reported, and the catalyst remained active for a long time (~23 days). However, methanol conversion was low (<30% based on methanol), and the catalytic activity decreased considerably during the reaction.[3,4] In the same year, Grützmacher presented another important example of generation of pure hydrogen from methanol. Catalyzed by 0.5 mol % ruthenium catalyst at 90 °C, conversion of methanol up to 80% was achieved.[5] Shortly after these two reports, Beller reported the reforming of methanol at low temperature catalyzed by iron pincer complexes. Although good turnover numbers were achieved, the catalysts were not very stable, and the reported methanol conversions were low.[6] Our ongoing study on ruthenium pincer complexes has resulted in several efficient and "waste-free" dehydrogenation[8,9] and hydrogenation[9,10] reactions. We have recently reported the transformation of primary alcohols to carboxylic acid salts catalyzed by complex **1** (Figure 1) using H_2O as the oxygen atom source (eq 1) in basic solvent.[11] This finding led us to explore the possibility to produce formic acid from methanol, which would then decompose to hydrogen and carbon dioxide,[12,13] as shown in eq 2. Herein, we present the first example of a reusable homogeneous catalyst system, with no need for catalyst isolation and purification, to promote the

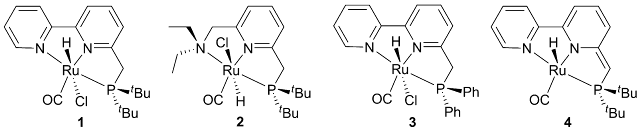
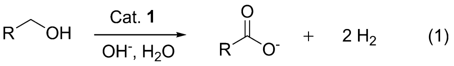


Figure 1. PNN ruthenium pincer complexes **1**−**4**.



$$R\text{CH}_2\text{OH} \xrightarrow[\text{OH}^-,\ H_2O]{\text{Cat. }\mathbf{1}} R\text{COO}^- + 2\,H_2 \qquad (1)$$

$$\text{MeOH} + H_2O \xrightarrow{\text{catalyst}} \text{HCOOH} + 2\,H_2 \xrightarrow{\text{catalyst}} CO_2 + 3\,H_2 \qquad (2)$$

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reforming process of methanol, offering hydrogen and CO_2 (absorbed by base) as products.

First, a mixture of 0.2 mol % complex **1**, 5 mmol MeOH, 10 mmol NaOH, and 0.5 mL H_2O was stirred for 24 h at 115 °C (oil bath temperature), resulting in no observable hydrogen formation (Table 1, entry 1). However, upon addition of 0.5 mL of THF, 71% yield of hydrogen was produced (based on the volume of collected H_2 with respect to MeOH) after 2 days (entry 2). The added THF likely solubilizes the actual catalyst **4** produced in situ (from complex **1** and base). The hydrogen produced was analyzed by GC and IR, showing no observable CO or CO_2 (the latter being captured as carbonate). Using a catalytic amount of KO^{t}Bu (entry 3) or using NEt_3 instead of NaOH (entry 4) resulted in no hydrogen formation. On the basis of conditions of entry 2, use of complex **2** resulted in 54% yield of H_2 after 2 days (entry 5), and with complex **3**, only 3% yield was obtained after 24 h (entry 6).[14] Decreasing the temperature to 60 °C dramatically slowed the reaction, and just a trace amount of hydrogen was produced after 24 h (entry 7). The efficiency of the reaction was significantly influenced by the catalyst loading, and only 28% yield of hydrogen was collected after 4 days when only 0.05 mol % catalyst **1** was used (entry 8).

Table 1. Production of H_2 by Reforming Methanol in Water[a]

$$\mathrm{MeOH + 2OH^-} \xrightarrow{\text{catalyst}} \mathrm{CO_3^{2-} + 3H_2}$$

entry	cat. (mol %)	MeOH (mmol)	H_2O (mL)	solvent (mL)	*t* (days)	yield of H_2 (%)
1	**1** (0.2)	5	0.5		1	
2	**1** (0.2)	5	0.5	THF (0.5)	2	71
3[b]	**1** (0.2)	5	0.5	THF (0.5)	1	
4[c]	**1** (0.2)	5	0.5	THF (0.5)	1	
5	**2** (0.2)	5	0.5	THF (0.5)	2	54
6	**3** (0.2)	5	0.5	THF (0.5)	1	3
7[d]	**1** (0.2)	5	0.5	THF (0.5)	1	trace
8	**1** (0.05)	10	1	THF (0.5)	4	28
9	**1** (0.05)	10	1	toluene (0.5)	4	68
10	**1** (0.025)	20	2	toluene (2)	7	64
11[e]	**1** (0.025)	20	2	toluene (2)	7	70
12[e]	**1** (0.025)	20	2	toluene (2)	9	77
13[e,f]	soln reused	20	2		9	82
14[e,g]	soln reused	20	2		9	80

[a]Reaction conditions: catalyst, 1 equiv of MeOH, 2 equiv of NaOH, and the specified amounts of water and solvent were stirred at 115 °C (oil bath temperature, the actual reaction temperature was 90−95 °C when using THF/H_2O as solvent, and 100−105 °C when using toluene/H_2O as solvent). Yields are based on volume of H_2 collected (with respect to MeOH). [b]Catalytic KO^{t}Bu (1.2 equiv to catalyst) was used without NaOH. [c]Catalytic KO^{t}Bu (1.2 equiv to catalyst) and 2 equiv of NEt_3 were used instead of NaOH. [d]60 °C (oil bath temperature). [e]KOH was used instead of NaOH. [f]Organic layer of entry 12 was used. [g]Organic layer of entry 13 was used.

Further optimization revealed that toluene was a better solvent for the reaction, and 68% yield of hydrogen was observed after 4 days at the same catalyst loading of 0.05 mol % (entry 9). Using a mixed solvent of toluene/H_2O in 1:1 v/v ratio resulted in 64% yield of hydrogen after 7 days, even when a lower catalyst loading of 0.025 mol % was used (entry 10). When KOH was applied instead of NaOH, hydrogen was produced in 70% yield after 7 days (entry 11; the average TOF is 50 h^{-1})[15] and 77% yield after 9 days (entry 12; the average TOF is 43 h^{-1}). Interestingly, when the organic layer of the reaction under the conditions of entry 12 was separated after 9 days and reused directly without adding catalyst **1** and toluene, an 82% yield of hydrogen was collected after 9 days (entry 13; the average TOF is 45 h^{-1}). Further application of the organic layer separated from the reaction under conditions of entry 13 resulted in an 80% yield of hydrogen after 9 days (entry 14; the average TOF is 45 h^{-1}). In all, 0.0024 g of catalyst **1** kept catalytic activity under the conditions of entry 12 for nearly 1 month without any activity decrease: ~1.53 g methanol was fully converted to hydrogen and CO_2 and TON of ~29 000 was achieved. Thus, the catalyst solution can be stored for extended periods and does not lose activity during the course of several heating and cooling (to r.t. or −30 °C) cycles under an inert atmosphere (see the Supporting Information for details).

On the basis of our former research, alcohols can be transformed to carboxylic acid salts upon reaction with water under basic conditions.[11] To get further understanding of the transformation of methanol to H_2 and CO_2, we investigated the decomposition reaction of formic acid in water, which is likely to be the last step of the reforming reaction, using complex **1** as the catalyst.[9] Without stoichiometric base, no gas was produced at room temperature (Table 2, entry 1), whereas 25% yield of hydrogen was collected at 115 °C after 24 h (entry 2). At room temperature, no hydrogen was observed when water was applied, even when stoichiometric KOH (entry 3) and NEt_3 (entry 5) were used. When ~2 equiv of KOH was applied at 115 °C, quantitative hydrogen was produced after 24 h (entry 4). Thus, the formate, which is formed in situ, can undergo smooth decomposition under the reaction conditions. Interestingly, when ~2 equiv of NEt_3 was used in the absence of water, a 98% yield of hydrogen was observed at room temperature after 24 h (entry 6).

Table 2. Decomposition of Formic Acid Promoted by Catalyst 1[a]

$$\mathrm{HCOOH} \xrightarrow{\text{cat.}\,\mathbf{1}} \mathrm{CO_2 + H_2}$$

entry	base (mmol)	H_2O (mL)	*T* (°C)	conv (%)
1		0.5	r.t.	
2		0.5	115	25
3[b]	KOH (5.5)	0.5	r.t.	
4[b]	KOH (5.5)	0.5	115	>99
5	NEt_3 (5.5)	0.5	r.t.	trace
6	NEt_3 (5.5)		r.t.	98

[a]Reaction conditions: 0.09 mol % catalyst **1**, KO^{t}Bu (1.2 equiv relative to catalyst), 0.1 mL HCOOH (2.65 mmol), base (as specified in the Table) and 0.5 mL THF were stirred at r.t. (19−24 °C) or 115 °C (oil bath temperature) for 24 h. Conversion based on volume of H_2 collected. [b]KO^{t}Bu was not used.

Comparing the results of Tables 1 and 2, it seems that (a) Decomposition of formic acid/formate is much easier than formation of formic acid/formate from methanol (Table 2, entry 2 vs Table 1, entry 3; Table 2, entry 6 vs Table 1, entry 4), and the latter (eq 2) is likely to be rate-determining of the whole reaction. (b) A stoichiometric strong base is needed to promote the conversion of methanol to formate. In our former report on the synthesis of carboxylic acids from alcohols, addition of the produced carboxylic acid to the actual catalyst **4** resulted in catalyst deactivation, necessitating the use of stoichiometric base;[11] however, it is unlikely to be the major reason why a strong base is needed in the current case of methanol, because formic acid can be decomposed in the absence of base (Table 2, entry 2) or in the presence of a weak base (Table 2, entry 6), whereas no gas is observed under similar conditions for reforming of methanol (Table 1, entries 3 and 4). Thus, the process from methanol to formic acid is favored in highly basic solvent, although the details are still unclear. (c) Water strongly inhibits the decomposition of formic acid/formate, probably because addition of water across catalyst **4** competes with addition of formic acid, as shown in the following NMR study. This may also be the reason why the reaction proceeds better in toluene, in which the concentration of water is lower than in THF.

To gain insight into the mechanism, the addition of formic acid to complex **4** was studied by NMR spectroscopy. In a J. Young tube, ~0.2 mmol of formic acid was added to a 0.6 mL C_6D_6 solution of complex **4** (0.02 mmol). The solution color instantly changed from dark green to deep red, indicative of formation of the aromatized complex **5** (Figure 2); quantitative formation of **5** was indicated by the ^1H NMR spectrum which showed a doublet at −17.47 ppm (J_{PH} = 23.9 Hz, Ru-*H*), and the $^{31}P\{^1H\}$ NMR spectrum exhibited a singlet at 103.4 ppm. Because the solubility of complex **5** was poor in C_6D_6, more than 1 equiv of formic acid (~10 equiv relative to the catalyst) was needed, forming H-bonds with complex **5** and making it more soluble. However, formic acid slowly decomposed to hydrogen and CO_2 (analyzed by GC) under these conditions, and a dark red crystalline solid of complex **5** was observed after 2 days. To get clean spectra of complex **5** without the influence of formic acid, it was generated in THF-d_8 instead of C_6D_6. Addition of ~10 equiv (0.2 mmol) of formic acid to a THF-d_8 (0.6 mL) solution of complex **4** (0.02 mmol) resulted in a bright red solution. Formic acid decomposition commenced, and bubbles were observed. After 4.5 h, no bubbles were observed, and NMR spectra of the mixture of complex **5** and formic acid were obtained, showing a doublet at −16.04 (J_{PH} = 24.6 Hz, Ru-*H*) in the ^1H NMR spectrum and a singlet at 105.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Three days later, formic acid was fully consumed, and clean NMR spectra of complex **5** were obtained (see the Supporting Information for details). Complex **5** was stable under nitrogen for more than 2 weeks at ambient temperature. NMR follow-up of formic acid decomposition suggested that the decomposition reaction was favored in a high concentration of formic acid and may involve reaction of complex **5** with another molecule of formic acid. Adding ~10 equiv of H_2O to the THF-d_8 solution of complex **5** rapidly resulted in an orange-brown solution of the hydrido−hydroxo complex **6** (Figure 2) in quantitative yield, of which the ^1H NMR spectrum contained a doublet at −16.76 ppm (J_{PH} = 24.6 Hz, Ru-*H*) and the $^{31}P\{^1H\}$ NMR spectrum showed a singlet at 103.27 ppm. As already reported,[11] complex **6** can be obtained by reversible addition of H_2O to complex **4** and can readily lose one molecule of H_2O to regenerate complex **4**.

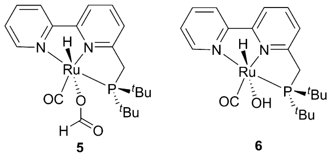

Figure 2. Structures of PNN ruthenium pincer complexes **5** and **6**.

On the basis of these results, the equilibria shown in Figure 3 likely exist among complexes **4**, **5**, and **6** during decomposition of formic acid in water. A higher concentration of water shifts the equilibrium toward complex **6**, inhibiting the generation of complex **5** and, thus, disfavors the decomposition step.

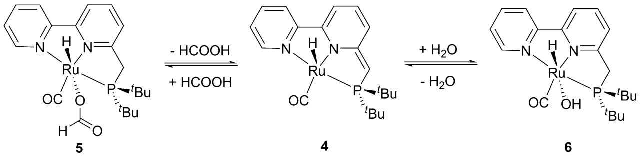

Figure 3. Equilibria among complexes **4**, **5**, and **6**.

Crystals of complex **5** suitable for X-ray diffraction were obtained by slow evaporation of its THF solution. As shown in Figure 4, a distorted octahedral geometry around the Ru(II) center is indicated, with one oxygen atom coordinated (OC(=O)H) cis to two nitrogen atoms and one phosphorus atom of the bipyridine PNN ligand trans to the hydride ligand.

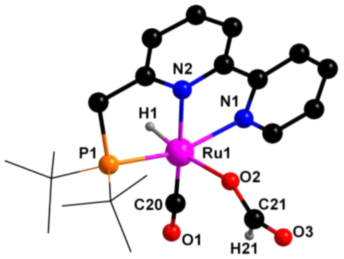

Figure 4. X-ray structure of complex **5**. Hydrogen atoms (except for the hydride and the aldehyde hydrogen) are omitted for clarity. (ᵗBu groups are presented as wireframe for clarity.) Selected bond lengths [Å] and angles [°]: Ru(1)−C(20) 1.847(2), Ru(1)−N(1) 2.1158(17), Ru(1)−N(2) 2.0808(16), Ru(1)−P(1) 2.2939(6), Ru(1)−H(1) 1.47(2), Ru(1)−O(2) 2.2097(14); C(20)−Ru(1)−O(2) 101.29(8), N(1)−Ru(1)−O(2) 81.21(6), N(2)−Ru(1)−O(2) 84.83(6), O(2)−Ru(1)−P(1) 98.79(4).

In conclusion, a reusable, robust catalytic system for the production of hydrogen from methanol and water under relatively low temperature was developed. A high conversion of methanol and good TON were achieved. The outstanding stability of catalyst **1** holds promise for the development of even more efficient reusable catalysts for the methanol reforming procedure.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterization data, and crystallographic data for **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) For base treatment of complexes **1**−**3** to obtain the actual dearomatized catalysts in situ, see refs 8a, 8i, and 10b.

(15) Production of one molecule of hydrogen is counted as one turnover. See the Supporting Information for details.