Hydrogen Storage

DOI: 10.1002/anie.200705972

Controlled Generation of Hydrogen from Formic Acid Amine Adducts at Room Temperature and Application in H_2/O_2 Fuel Cells**

*Björn Loges, Albert Boddien, Henrik Junge, and Matthias Beller**

Dedicated to Professor Boy Cornils on the occasion of his 70th birthday

One of the central challenges of this century is the sufficient and sustainable supply of energy. In this respect, advancements in hydrogen technology, such as the generation of hydrogen from suitable starting materials, its storage and conversion into electrical energy, are of particular interest.

Besides methane and methanol, renewable resources, such as (bio)ethanol and glycerol, are considered as promising sources for hydrogen production.[1] Nevertheless, their use remains difficult, as the applied reforming processes run at high temperature ($>200\,°C$). Thus, improved technologies for generating hydrogen at higher reaction rates and under milder conditions are required. At present, hydrogen can be only produced at ambient temperatures by the reaction of metals or metal compounds, for example, $NaBH_4$, with water. However, these compounds have obvious disadvantages, such as toxicity, price, and safety.

To the best of our knowledge there is no reaction system known at present which is able to generate hydrogen from organic products in a controlled manner at room temperature.[2] Herein we demonstrate the possibility of generating hydrogen on demand from mixtures of formic acid and amines at room temperature. Notably, formic acid as a hydrogen source is non-toxic and can be handled and stored easily.[3]

Our previous work on the development of low-temperature hydrogen generating systems used alcohols as feedstock.[2e–g] More recently, we had the idea to apply carbon dioxide as storage media for hydrogen. Based on the catalytic processes of formation and decomposition of formic acid, a power supply system should be possible. Figure 1 depicts a CO_2-neutral hydrogen storage cycle. Although CO_2 is available in huge amounts on the earth, the use of carbon dioxide for hydrogen storage has been largely neglected until now and should be paid more attention in future.[4]

Hydrogenation of carbon dioxide is thermodynamically an uphill process, and therefore a base is needed to give formic acid base adducts, which is a favorable enthalpy-driven reaction.[5]

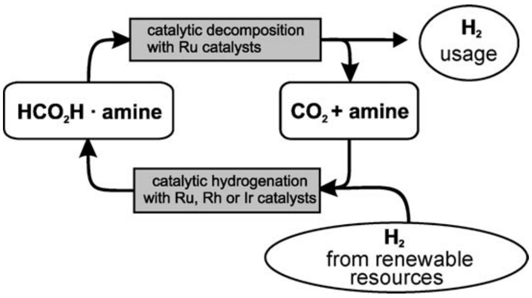

Figure 1. A CO_2-neutral cycle for the storage of hydrogen in formic acid base adducts.

In contrast to hydrogen generation from formic acid, the homogeneous hydrogenation of CO_2 in the presence of base is well established, and high catalyst activities and selectivities have been achieved. The reaction was first reported in 1976 by Inoue et al.[6] Later, seminal work was carried out by Noyori, Jessop, Leitner, Jóo, and Himeda.[5,7] However, the decomposition of formic acid was almost disregarded, although it is the prerequisite for catalytic transfer hydrogenations with formic acid as the hydrogen donor. Few examples include the reports of Coffey[8] and the groups of Otsuka,[9] Strauss,[10] and Trogler et al.,[11] who between 1967 and 1982 described the decomposition of formic acid with platinum, ruthenium, iridium, or rhodium complexes. Catalyst activities are low with two exceptions: A turnover frequency (TOF) of $100\,h^{-1}$ after 15 min at room temperature was observed applying a platinum phosphine catalyst,[9] and a TOF of $1187\,h^{-1}$ at 100–117 °C with an iridium phosphine complex.[8] Alternatively, Pd/C has been used for the decomposition of formic acid at room temperature,[4b] and of formate salts at 70 to 140 °C.[4d,e,12,13]

From the mid-1990s, the decomposition of formates or formic acid base adducts has been studied as the undesired back-reaction in catalytic CO_2 hydrogenation. With rhodium phosphine catalysts, Leitner et al.[4a] and Jóo et al.[14] reached turnover frequencies of approximately $30\,h^{-1}$ at room temperature and 70 °C, respectively. Himeda et al. obtained TOFs of $238\,h^{-1}$ with rhodium bipyridine catalysts at 40 °C.[15] Puddephatt's group used the dinuclear complex $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-dppm})_2]$ for the decomposition of formic acid without base, and reported TOFs up to $500\,h^{-1}$ after 20 min in NMR spectroscopic studies.[16] Furthermore, this reaction has been investigated with nitrite-promoted rhodium[17] and

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[*] Dipl.-Chem. B. Loges, A. Boddien, Dr. H. Junge, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Str. 29a, 18059 Rostock (Germany)
Fax: (+49) 381-1281-5000
E-mail: matthias.beller@catalysis.de
Homepage: http://www.catalysis.de

[**] This work has been supported by the State of Mecklenburg-Vorpommern, the BMBF, the DFG (Leibniz prize), and the Fonds der Chemischen Industrie (FCI). We thank Dr. C. Fischer, S. Bucholz, and C. Mewes (LIKAT) for their excellent analytical and technical support and Carbo-Tex GmbH Paderborn for a free sample of CarboTex.

molybdenum phosphine[18] catalysts, and efforts have been made in the field of heterogeneous catalysis.[19]

Initially, we investigated the decomposition of formic acid in the presence of different homogeneous catalysts at 40 °C. As a starting point, $5\,HCO_2H/2\,NEt_3$ was chosen as model system, as it is known to act as a hydrogen source in transfer hydrogenation.[20]

Table 2: Decomposition of formic acid amine adducts using $[\{RuCl_2(p\text{-cymene})\}_2]$.

Entry	Amine	V_{gas} (2 h) [mL][a]	TON (2 h)	V_{gas} (3 h) [mL][a]	TON (3 h)
1	NEt_3	41	14	61	21
2	NH_3	35	12	50	17
3	$EtNMe_2$	25	8.6	38	13
4	$BuNMe_2$	50	17	76	26
5	$HexNMe_2$	59	20	88	30
6	$OctNMe_2$	53	18	82	28
7	Bu_2NMe	35	12	56	19
8	$PhNMe_2$	14	4.7	20	6.8
9	DMAE	59	20	88	30
10	TMEDA	33	11	50	17
11	NEt_3[b]	41	14	62	21
12	NEt_3[c]	44	15	67	23

Reaction conditions: 5.0 mL preformed formic acid/amine mixture, 29.75 μmol $[\{RuCl_2(p\text{-cymene})\}_2]$, 40 °C, 3 h, ratio $HCO_2H/N = 5{:}2$. [a] Measured by gas burette ($H_2{:}CO_2 = 1{:}1$). [b] 5.0 mL water added; [c] 5.0 mL ethanol added.

Without catalyst, no gas evolution is detected. $RhCl_3{\cdot}x\,H_2O$ showed slow formation of hydrogen, whereas $RuCl_3{\cdot}x\,H_2O$ is not active (Table 1, entries 1 and 2). However, $[\{RuCl_2(p\text{-cymene})\}_2]$ is an appropriate catalyst precursor, as it showed significant activity at catalyst concentrations from 320 to 10 000 ppm (Table 1, entries 3–5). $[RuCl_2(p\text{-cymene})(tmeda)]$ is also active, but needed a longer induction period (Table 1, entry 6). For comparison, the common heterogeneous transfer hydrogenation catalyst Pd/C was investigated (Table 1, entry 7). However, it is only active within the first two hours, and thereafter the system is deactivated. Also other metal precursors, for example, iron compounds (Table 1, entries 8–10) were included in the screening, but none of them showed any significant activity.

Table 1: Study of various catalysts for the generation of H_2 from $5\,HCO_2H/2\,NEt_3$ adduct.

Entry	V_{subst} [mL]	Catalyst	n_{metal} [μmol]	V_{gas} (2 h) [mL][a]	TON (2 h)	V_{gas} (6 h) [mL][a]	TON (6 h)
1	5	$RhCl_3{\cdot}x\,H_2O$	19.1	1.9	2.0	18	19
2	5	$RuCl_3{\cdot}x\,H_2O$	19.1	0.6[b]	-	0.1[b]	–
3	5	$[\{RuCl_2(p\text{-cymene})\}_2]$	19.1	12	13	36	38
4	5	$[\{RuCl_2(p\text{-cymene})\}_2]$	59.5	41	14	123	42
5	10	$[\{RuCl_2(p\text{-cymene})\}_2]$	1191	215[c]	3.7[c]	666[c]	11[c]
6	5	$[RuCl_2(tmeda)(p\text{-cymene})]$	59.5	23	7.7	99	34
7	5	Pd/C	19.1	19	20	21	22
8	5	Fe_2O_3/silica	19.1	0.4[b]	–	0.9[b]	–
9	5	nano-Fe_2O_3	59.5	0.6[b]	–	–	–
10	5	$[CpFe(CO)_2I]$	59.5	3.6[d]	–	4.1[d]	–

Reaction conditions: substrate (subst): preformed formic acid/amine mixture, 40 °C, 6 h. [a] Measured by gas burette ($H_2{:}CO_2 = 1{:}1$). [b] No hydrogen detected by GC. [c] Reaction performed at 26.5 °C. [d] Only CO and no hydrogen detected by GC.

The influence of different amines was investigated using 1000 ppm $[\{RuCl_2(p\text{-cymene})\}_2]$ as the standard catalyst precursor, and a formic acid to nitrogen atom ratio of 5:2. In comparison to the standard system (Table 2, entry 1), formic acid in the presence of ammonia (Table 2, entry 2) is less easily decomposed. The investigation of a series of homologous aliphatic dimethyl amines (Table 2, entries 3–6) revealed an increase of activity with increasing carbon chain length.

The maximum volume of hydrogen is obtained in the presence of *N*,*N*-dimethylhexylamine and *N*,*N*-dimethylaminoethanol (DMAE) (Table 2, entries 5 and 9), and the lowest amount of gas generated is observed using *N*,*N*-dimethylaniline (Table 2, entry 8). Interestingly, the addition of water or ethanol showed no influence on the activity towards formic acid decomposition demonstrating the robustness of the system (Table 2, entries 11–12).

In a long-term experiment, the catalytic system was active for more than 42 h (Figure 2). During this time, 2728 mL of gas is generated, which corresponds to a conversion of 93 %. After an induction period, the hydrogen generation remained linear for approximately 24 hours before a rate acceleration occurred. This could be explained by the increase in the ratio of amine to formic acid. In agreement with these results, additional experiments with varying ratios of NEt_3 to HCO_2H showed that the catalyst activity is increased by a higher amine content (TON after 2 h: 0.9 for $NEt_3/HCO_2H = 1{:}10$ and TON after 2 h: 38 for $NEt_3/HCO_2H = 3{:}4$). Notably, after full conversion and addition of new HCO_2H, the catalyst is active again.

After demonstrating the possibility to generate hydrogen at low temperature from formic acid amine adducts with $[\{RuCl_2(p\text{-cymene})\}_2]$, we turned our attention to phosphine-containing ruthenium complexes. As a starting point we chose the commercially available complex $[RuCl_2(PPh_3)_3]$. To our

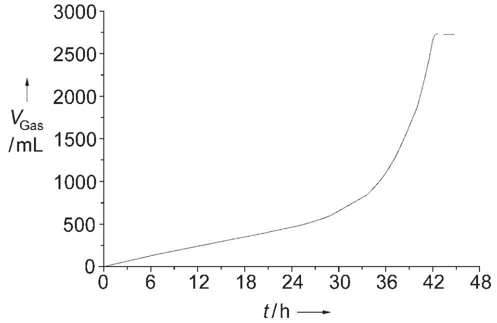

Figure 2. Gas evolution in a long-term experiment with 5.0 mL $5\,HCO_2H/2\,NEt_3$ and 29.75 μmol $[\{RuCl_2(p\text{-cymene})\}_2]$ at 40 °C.

delight this catalyst precursor gave much higher turnover frequencies: up to 417 and 302 h^{-1} after 2 and 3 hours, respectively, and a formic acid conversion of 90% after 3 hours (Table 3, entry 1). $[RuCl_2(PPh_3)_3]$ is only slightly less active at 26.5 °C compared to 40 °C (Table 3, entries 2 and 3). Owing to the slow dissolution of $[RuCl_2(PPh_3)_3]$, we applied dimethylformamide as solvent for a pretreatment of the catalyst precursor, which increased the activity further (TOF: up to 445 h^{-1} after 2 h; Table 3, entries 4 and 5) and improved the reproducibility. It is noteworthy that the molecularly defined pre-catalyst gave a TOF after 20 min of 2688 h^{-1}, which is the highest activity for formic acid decomposition known to date (Table 3, entry 5). For comparison, a catalyst formed in situ from $RuCl_3{\cdot}x\,H_2O$ and 3 equivalents of triphenylphosphine (Table 3, entry 6) was about 23% less active than $[RuCl_2(PPh_3)_3]$.

Table 3: Decomposition of $5\,HCO_2H/2\,NEt_3$ adduct with Ru/PPh_3 catalyst systems.

Entry	n_{Ru} [µmol]	Solvent	T [°C]	V_{gas}[a] (2 h) [mL]	TON (2 h)	V_{gas}[a] (3 h) [mL]	TON (3 h)	Conv. (3 h) [%]
1[b]	59.5	–	40	2436	834	2641	905	90
2[b]	5.95	–	40	139	477	143	490	4.9
3[b]	5.95	–	26.5	106	362	119	408	4.1
4[b]	5.95	DMF[c]	40	258	882	258	882	8.8
5[b]	5.95	DMF[d]	40	260	891[e]	261	893	8.9
6[f]	5.95	DMF[d]	40	202	691	204	700	7.0

Conditions: 5.0 mL $5\,HCO_2H/2\,NEt_3$, 3 h, catalyst. [a] Measured by gas burette (H_2:CO_2 = 1:1). [b] Catalyst: $[RuCl_2(PPh_3)_3]$. [c] 1.0 mL dimethylformamide (DMF) added to substrate. [d] Catalyst pretreated in 1.0 mL DMF (2 h, 80 °C). [e] TOF 2688 h^{-1} after 20 min. [f] Catalyst: $RuCl_3{\cdot}x\,H_2O + 3\,PPh_3$.

In the gas phase of all the experiments, only hydrogen and carbon dioxide are detected alongside the inert atmosphere, argon, and traces of the evaporated substrates. Thus, and importantly for fuel cell applications, formic acid is selectively converted into hydrogen and CO_2.

We demonstrated that it is indeed possible to generate hydrogen from organic compounds under mild conditions and to directly use it for power generation. Thus, we combined the hydrogen generation unit with a H_2/O_2 PEM fuel cell. An easy gas cleaning by charcoal (CarboTex) is sufficient to remove traces of the volatile amine. A gas mixture generated according to entry 5 in Table 1 is converted into a maximum electric power of approximately 47 mW at a potential of 374 mV for more than 29 h. Similar power densities are observed for 1:1 mixtures of commercial hydrogen and carbon dioxide.

In conclusion, we have shown for the first time the generation of hydrogen from formic acid amine adducts at such high rates at room temperature with the commercially available complex $[RuCl_2(PPh_3)_3]$. Compared to previously known organic hydrogen generating systems the system presented can be run at low temperatures without the need of high-temperature reforming processes. The hydrogen produced can be directly used in fuel cells, thus combining the advantages of liquid fuels and established H_2/O_2 fuel cells.[21] This might be interesting for new applications in portable electric devices.

Experimental Section

All catalytic experiments were carried out under an inert gas atmosphere (argon) with exclusion of air. The substrates were dried by standard laboratory methods prior to use. The formic acid to amine ratio was determined by ^1H NMR spectroscopy on a Bruker Avance 300 spectrometer. The catalyst precursors were purchased from commercial suppliers: $[RuCl_2(PPh_3)_3]$ (ABCR), Pd/C (10 wt.%) (Fluka), $RuCl_3{\cdot}x\,H_2O$, $RhCl_3{\cdot}x\,H_2O$, $[\{RuCl_2(p\text{-cymene})\}_2]$, $[CpFe(CO)_2I]$, nano-Fe_2O_3 (all Aldrich). We prepared $[RuCl_2(p\text{-cymene})(tmeda)]$ and Fe_2O_3/silica (5 wt.%).

The amount of gas liberated was measured by a gas burette. In addition, a GC for analyzing gases was applied (Agilent 6890N, permanent gases: Carboxen 1000, TCD, external calibration; amines: HP Plot Q, 30 m, FID), and a hydrogen sensor (Hach Ultra Analytics GmbH) was used for analysis of hydrogen.

Fuel cell experiments were performed with a fuel cell from AMT Analysenmesstechnik GmbH[22] applying Pt–Ru/C as anode (20/10 wt.%, catalyst loading 1.5 mg cm^{-2}, electrode area 6.25 cm^2) and Pt/C as cathode catalyst (20 wt.%, catalyst loading 1.5 mg cm^{-2}, electrode area 6.25 cm^2). Gas flow on the anode side was set by the gas generation reaction; as oxidant, compressed air was used at a flow rate of 36.66 mL min^{-1}.

For the fuel-cell experiments, the generated gas was cleaned by leading it through a column (internal diameter 10 mm, length 170 mm) filled with 7.36 g CarboTex (BET 1200 $m^2 g^{-1}$-MP/I 1200, diameter 0.4 mm). CarboTex was purchased from CarboTex Produktions- und Veredelungsbetriebe GmbH Paderborn.

Typical procedure for the decomposition of formic acid/amine adducts: The premixed solution of $5\,HCO_2H/2\,NEt_3$ (5.0 mL, 0.0595 mol HCO_2H) was warmed to 26.5 or 40.0 °C in a double-walled thermostatic reaction vessel. The vessel was purged with argon to remove any other gas before the reaction was started by addition of the catalyst $[\{RuCl_2(p\text{-cymene})\}_2]$ (18.23 mg, 29.75 µmol).

Typically, the standard deviation for the volumetrically determined hydrogen volumes and calculated activities is between 1–20%.

Received: December 28, 2007
Revised: February 15, 2008

Keywords: catalysis · formic acid · fuel cells · hydrogen · ruthenium

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[21] Alternatively, liquid fuels such as methanol, ethanol, or formic acid could be directly converted in direct fuel cells into electric energy. Although the direct methanol fuel cell (DMFC) has been announced as power supply for portable electronic devices, it still suffers from a slow methanol oxidation and a performance loss resulting from methanol "crossover" and poisoning of the cathode catalyst. The direct formic acid fuel cell (DFAFC) is still under investigation, and only some prototypes have been reported. In particular, the catalysts for the anode and cathode reactions have to be improved regarding increased efficiency and stability to reach the same power densities as H_2/O_2 fuel cells.

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