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Hydrogen Generation from Formic Acid Decomposition with a Ruthenium Catalyst Promoted by Functionalized Ionic Liquids

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Hydrogen has attracted increasing attention as an important alternative secondary energy resource particularly when combined with fuel-cell technology, which may play a very significant role in power generation in the future.^[1,2] Currently most H₂ is produced industrially by methane or alcohol reforming and by the water-gas-shift reaction at high temperatures. However, special purification steps are needed to remove any remaining CO, which severely inhibits the efficiency of the fuel cell.^[2] On the other hand, the storage and transfer of hydrogen are also problematic because of its low volumetric energy density.^[3] At present most of the hydrogen storage materials, such as metal hydrides, carbon nanotubes, metal-organic frameworks, and ammonia, can only store low amounts; high temperatures are required to release the stored hydrogen;^[4] and metal-based compounds have disadvantages in terms of toxicity, price, and safety.

Formic acid, which is nontoxic and a liquid at room temperature, with a density of 1.22 g cm^{-3} , has been widely used as a hydrogen source for transfer hydrogenation.^[5] The decomposition of formic acid (HCOOH \rightarrow CO₂+H₂),^[6-12] which is the reversible reaction of CO₂ hydrogenation (CO₂+H₂ \rightarrow HCOOH), is considered a promising hydrogen-generation process. Recently, excellent catalytic activities were independently obtained by two groups. Beller and co-workers investigated the catalytic decomposition of formic acid/amine mixtures at 40 °C or room temperature, and excellent catalytic activity was obtained.[13] Although the highest catalytic activity for formic acid decomposition reported to date was obtained, a high ratio of organic amine to formic acid was needed.^[14] The volatile amine should be removed before application in fuel cells, so the use of a large amount of volatile organic amine will result in an increased complexity and, accordingly, increase the cost of application. At the same time, Laurenczy and co-workers developed the decomposition of HCOOH/HCOONa (9:1) under aqueous conditions.^[15] HCOONa is nonvolatile, but was only effectively when heated to 80 °C. This severely inhibits its usage in ambient conditions. Nevertheless, it should be noted that the only products of formic acid decomposition by both of the meth-

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ods mentioned above were gaseous H_2 and $CO_2.$ Fuel-cell-grade hydrogen could be obtained by simple separation. $^{\left[2\right]}$

lonic liquids (ILs), defined as organic salts with melting points below 100 °C, have attracted considerable attention as versatile media and materials because of their peculiar physicochemical properties.^[16] Moreover, functionalized ILs, incorporating different functional groups into the alkyl chains of the imidazolium or pyridinium units, have been synthesized and used as solvents and catalysts in chemical processes. For example, H₂N-functionalized ILs have been used to absorb CO_2 ,^[17] subsequently (CH₃)₂N-functionalized ILs were used to promote the hydrogenation of CO_2 to formic acid.^[18]

Here, the effect of the IL on the decomposition of formic acid is tested for the first time. Furthermore, in order to avoid the use of volatile organic amines, a series of amine-functionalized ILs (Scheme 1) were prepared and their catalytic activities were tested with a commercially available ruthenium-based catalyst, [$\{RuCl_2(p-cymene)\}_2$].



Scheme 1. The cations structure and abbreviations of the amine-functionalized ILs.

We initially investigated the effects of conventional ILs on the decomposition of formic acid (Table 1). The activity was low when *N*,*N*-diisopropylethylamine (*i*Pr₂NEt) or sodium formate (HCOONa) itself was used as base (entries 1 and 2). A much-enhanced catalytic activity was obtained after the addition of the IL BMimBF₄ (entry 3), especially with the addition of BMimCl (entry 4). These results show that the selective catalytic activity can be promoted in the presence of IL. The activity could be further improved when *i*Pr₂NEt was used together with HCOONa (entry 5), and an enhanced activity was also observed after the addition of the ILs BMimBF₄ or BMimCl (entries 6 and 7).

Owing to the volatility of organic amines and the low activity in the presence of HCOONa alone, some amine-group-functionalized ILs (Scheme 1) were prepared and used in the decomposition of formic acid (Table 1, entries 8–13). The results show that the catalytic activity in the presence of Et₂NEMimCl, *i*Pr₂NEMimBF₄, *i*Pr₂NEMimOTf or *i*Pr₂NEMimNTf₂ is low, but good activity is achieved with *i*Pr₂NEMimCl. According to the above results, we tried to synthesize an amine-functionalized IL with formate as anion, *i*Pr₂NEMimHCOO, through ion exchange of *i*Pr₂NEMimCl with HCOONa in acetone. Unfortunate-



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Entry	Base	IL	V_{gas} [m]	_] ^(b)	TON	
	(5 mmol)	(5 mmol)	1 h	2 h	1 h	2 h
1	HCOONa	-	10	19	4	7
2	<i>i</i> Pr ₂ NEt	-	36	61	12	20
3	<i>i</i> Pr ₂ NEt	BMimBF ₄	64	110	21	37
4	<i>i</i> Pr ₂ NEt	BMimCl	173	385	57	128
5	<i>i</i> Pr ₂ NEt/HCOONa ^[c]	-	102	182	34	60
6	<i>i</i> Pr ₂ NEt/HCOONa ^[c]	BMimBF ₄	120	215	40	71
7	<i>i</i> Pr ₂ NEt/HCOONa ^[c]	BMimCl	347	725	115	240
8	-	Et₂NEMimCl	41	71	14	24
9	-	<i>i</i> Pr ₂ NEMimCl	108	206	36	68
10	-	<i>i</i> Pr ₂ NEMimBF ₄	52	87	17	29
11	-	<i>i</i> Pr₂NEMimOTf	74	122	25	40
12	-	<i>i</i> Pr ₂ NEMimNTf ₂	35	55	12	18
13	-	<i>i</i> Pr ₂ NEMimCl/HCOO ^[d]	207	445	69	147
14	HCOONa	<i>i</i> Pr ₂ NEMimCl	382	862	127	286
15	HCOONa	<i>i</i> Pr ₂ NEMimCl ^[e]	38	68	13	23
16	HCOONa	<i>i</i> Pr ₂ NEMimCl ^[e, f]	200	444 ^[g]	66	147 ^[g]
17	HCOONa	<i>i</i> Pr ₂ NEMimCl ^[f, h]	481	971	627	1267

[a] Reaction conditions: 30.85 mmol (1.2 mL) formic acid (97%), 30.85 µmol [{RuCl₂(*p*-cymene)}₂], 60 °C, 2 h. [b] Measured with a gas burette ($H_2/CO_2 = 1:1$). [c] 5 mmol $iPr_2NEt + 5$ mmol HCOONa. [d] $iPr_2NEMimCl/iPr_2NEMimHCOO = 88.2:11.8$ (mol). [e] 40 °C. [f] 10 mmol $iPr_2NEMimCl$. [g] Average number of three reactions. [h] 7.84 µmol [{RuCl₂(*p*-cymene)}₂].

ly the metathesis reaction was incomplete. According to chloride content, measured by using a chloride electrode, only 11.8 mol% of the target *i*Pr₂NEMimHCOO was obtained in the product. However, an acceptable catalytic activity was obtained in this mixed IL (entry 13). To further improve the hydrogen generation system, the catalytic activity of formic acid decomposition with *i*Pr₂NEMimCl and HCOONa was further tested. The results show that excellent activity is obtained (entry 14). Although a relatively low catalytic activity was found when the reaction temperature was lowered from 60 °C to 40 °C (entry 15), the further addition of 5 mmol *i*Pr₂NEMimCl could promote the formic acid decomposition effectively (entry 16). Furthermore, the turn-over number (TON) reached 1267 in 2 h at 60 °C using a high *i*Pr₂NEMimCl content (entry 17).

The use of different ratios of HCOONa to *i*Pr₂NEMimCl was investigated at 40 °C (Figure 1). The activity was low in the presence of *i*Pr₂NEMimCl alone and increased after the addition of HCOONa. However, the rate increase became less pronounced when more than 7 mmol HCOONa was added, for example, the activity with 9 mmol HCOONa was close to the activity with 7 mmol HCOONa. The activity initially increased with increasing HCOONa, proving that free formate was needed for the reaction and that not enough free formate was formed because of the alkalescency of the functionalized IL. Afterwards the increase of the reaction rate almost stopped; we hypothesize that this, with increasing precipitation, was due to the high viscosity and further unchanging ionic polarity of the system.

In addition, the influence of the water content was investigated under optimized conditions. There was no obvious difference in catalytic activity when the water content increased from 1-3% (i.e., 97-99% HCOOH) to 12% (i.e., 88% HCOOH) (Table 2, entries 1–3). The catalytic activity was reduced dis-

tinctly when more water was added. For example, with 97% HCOOH in the presence of 0.3 mL or 1 mL H₂O, the TON in 2 h was reduced to 93 or 58 from 147, respectively. These results are somewhat in contrast to those obtained by Beller et al.,^[13] in which the addition of water showed no influence on the activity towards formic acid decomposition. Hence, the ILs and HCOONa were dried before application each time.

Long-term experiments were investigated with 30.85 mmol (1.2 mL) HCOOH, 5 mmol HCOONa, and 5 mmol or 10 mmol $iPr_2NEMimCl$ at 40 °C. The results showed that the catalytic system with 5 mmol $iPr_2NEMimCl$ could offer hydro-



Figure 1. Hydrogen generation from 30.85 mmol formic acid (97%) with different amounts of HCOONa to 5 mmol *i*Pr₂NEMimCl, using 30.85 μ mol [{RuCl₂(*p*-cymene)}₂] as catalyst at 40 °C, 2 h.

Table 2. Influence of the water content on the decomposition of formic $\operatorname{acid}^{(a)}$								
Entry	% Formic acid	V _{gas} [mL] ^[b] (2 h)	TON (2 h)	% Conv. (2 h)				
1	99	459 ^[c]	152 ^[c]	30.3 ^[c]				
2	97	444 ^[c]	147 ^[c]	29.3 ^[c]				
3	88	381	126	25.2				
4	$97 + 0.3 \text{ mL H}_2\text{O}$	282	93	18.7				
5	$97 + 1.0 \text{ mL H}_2\text{O}$	175	58	11.6				
[a] Reaction conditions: 30.85 mmol formic acid, 30.85 µmol [{RuCl ₂ (<i>p</i> - cymene)}].] 5 mmol HCOONa 10 mmol <i>iP</i> r.NEMimcl 40 °C 2 h [b] Mea-								

cymene)}₂], 5 mmol HCOONa, 10 mmol *i*Pr₂NEMimCl, 40 °C, 2 h. [b] Measured by gas burette (H₂:CO₂=1:1). [c] Average number of three reactions.

gen flow fluently for more than 22 h (Figure 2). The hydrogen generation remained linear for approximately 11 h, and then the formic acid decomposition became faster. This can be ex-



Figure 2. Gas evolution in long-term experiments with 30.85 mmol HCOOH (97%) and 30.85 µmol [{RuCl₂(*p*-cymene)}₂] at 40 °C with 5 mmol HCOONa and (\odot) 5 mmol or (\blacksquare) 10 mmol *i*Pr₂NEMimCl.

plained by the increased ratio of IL to formic acid. In agreement with these results, the experiment with 10 mmol *i*Pr₂NEMimCl showed that the catalytic activity was increased with a higher IL content, and had no induction period. It should be noted that the formic acid could not normally be consumed fully. After careful calibration, we found that the amount of unreacted formic acid was in agreement with the amount of IL added into the system. However, it is still unclear why this amount of formic acid could not be decomposed, and the interaction between IL and formic acid is currently also unknown.

Unfortunately, the reaction could not be restarted if fresh formic acid was added when the reaction finished (Figure 3). However, we did find that the reaction started again after the addition of fresh catalyst (Figure 3, B and D). This suggested



Figure 3. Hydrogen generation with 31.49 mmol formic acid (99%, 1.2 mL), 5 mmol HCOONa and 10 mmol *i*Pr₂NEMimCl using 7.84 µmol [{RuCl₂(p-cymene)}₂] (4.8 mg) as catalyst at 60 °C. When the reaction finished, 0.4 mL formic acid (A and C) and then 4.8 mg catalyst (B and D) were added at different time, respectively.

that the catalyst was deactivated when fresh formic acid was added, but that the IL *i*Pr₂NEMimCl was stable enough during the reaction. We can not provide an explanation at this stage.

In conclusion, we have confirmed for the first time that the generation of hydrogen from formic acid decomposition can be significantly promoted by the addition of ILs such as BMimBF₄, especially by BMimCl. As an alternative to volatile organic amines, a series of amine-functionalized ILs was successfully synthesized and good catalytic activity was obtained under mild conditions. This efficient, simple, and green method to produce H₂ by formic acid selective decomposition has potential applications in industry.

Experimental Section

All solvents and chemicals were obtained from commercial sources and were used as-received. ¹HNMR spectra were recorded on a Bruker AMX FT or DPX-200 spectrometer (400 MHz). All spectra were recorded in CDCl₃ or D₂O and chemical shifts (δ) are reported in ppm relative to tetramethylsilane, referenced to the residual solvent peaks. Spectra were measured at room temperature unless otherwise stated.

1-(2-Diisopropylaminoethyl)-3-methylimidazolium chloride (iPr2NEMimCl): 1-Methylimidazole (99%) was distilled under reduced pressure prior to use and kept hermetically sealed while stored. Typically, 0.2 mol 1-methylimidazole and 2-diisopropylaminoethylchloride hydrochloride (97%) were mixed in anhydrous ethanol (150 mL) in a flask equipped with a magnetic stirrer, and the mixture was refluxed for 48 h. The ethanol was then removed in vacuo and the solid was dissolved in a suitable amount of water. After cooling to ca. 0°C, 1 equivalent of aqueous NaOH was added, and the mixture was stirred for 6 h. After removing the water under reduced pressure, dichloromethane (100 mL) was added. The mixture was stirred for 2 h in ice-water bath, and the resulting solid (NaCl) was removed by filtration. Dichloromethane in the filtrate was removed under reduced pressure and crude iPr₂NEMimCl was obtained. The iPr₂NEMimCl was further washed with absolute diethyl ether 5 times and dried at 70 $^\circ\text{C}$ for 12 h under vacuum (white solid, yield = 89%). Et₂NEMimCl was synthesized according to a similar procedure. *i*Pr₂NEMimOTf, $\mathit{i}Pr_2NEMimBF_4\!,$ and $\mathit{i}Pr_2NEMimNTf_2$ were obtained by the ion-exchange of *i*Pr₂NEMimCl with NaCF₃SO₃ (in ethanol), NaBF₄ (in ethanol) or LiNTf₂ (in water), respectively.

Chloride content was measured by using a SevenMulti instrument (Mettler Toledo) equipped with a chloride electrode. The chloride electrode was activated in a 0.001 molL⁻¹ chloride solution for 1 h with stirring before use. Approximately 0.1 g ionic liquid was dissolved in deionized water in a 100 mL calibrated flask, which was filled to the mark. 1 mL ionic strength adjuster (ISA; 5 molL⁻¹ NaNO₃) was added into 50 mL sample solutions. The chloride concentration was measured according to a calibration diagram, which was prepared with standard solutions of different chloride concentrations. The chloride contents were 12.2 wt% for *i*Pr₂NEMimCl/HCOO, 0.62 wt% for *i*Pr₂NEMimOTf, 0.63 wt% for *i*Pr₂NEMimBF₄, and 750 ppm for *i*Pr₂NEMimNTf₂.

HCOONa was prepared by the neutralization of formic acid by an aqueous NaOH solution. Formic acid (1.1 mol) was added slowly to the NaOH (1 mol) aqueous solution in an ice-water bath. Ethanol was added, after the water was removed at 75 $^\circ$ C under reduced pressure. The solution was filtrated and the white solid HCOONa was obtained.

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The catalyst [{RuCl₂(p-cymene)}₂] (30.85 µmol), HCOONa (5 mmol), $iPr_2NEMimCl$ (5 mmol or 10 mmol) and HCOOH (97 %, 30.85 mmol) were added into a double-walled thermostatic reaction vessel in air. The mixture was stirred for about 10 min and heated to 40 °C. The volume of liberated gas was measured by a gas burette. The produced gaseous sample was captured in a gas-phase cell for FTIR spectroscopy, through which the presence of CO₂ was confirmed.

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