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Hydrogenation of Carbon Dioxide is Promoted by a Task-Specific Ionic Liquid**

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Carbon dioxide has become the focus of attention recently because it is a major greenhouse gas and a cheap C1 resource. The conversion of CO_2 into value-added chemicals has also attracted much attention in recent years.[1] The hydrogenation of CO_2 to produce formic acid ($CO_2 + H_2 \rightarrow HCOOH$) is an attractive reaction that has been carried out in organic solvents,[2] water,[3] and supercritical CO_2.[4] Homogeneous catalysts are widely used for this reaction, and satisfactory reaction rates have been achieved.[2–5] Heterogeneous catalysts fabricated by immobilizing ruthenium on silica and polystyrene (PS) resin have also been used.[6] The reaction is thermodynamically unfavorable because the standard Gibbs free energy ΔG_{298}° of the reaction is $+32.9\ \mathrm{kJ\,mol^{-1}}$. Inorganic or organic bases, including high-boiling organic bases, such as imidozoles, quinoline, and other heterocyclic nitrogen compounds, are often added to the reaction mixture to achieve reasonable conversions,[7] although formate salts are formed when performing the reaction under basic conditions. However, the best way to recover the formic acid and reuse the bases and catalysts is still a problem that has not been well solved. This problem is one of the main obstacles for industrialization of this reaction.

Ionic liquids (ILs), which are organic salts with a melting point below 100 °C, have attracted much attention in recent years.[8] ILs have a negligible vapor pressure, high thermal stability, wide liquid-temperature range, and are excellent solvents for both organic and inorganic substances. Many reactions have been carried out in ILs, including hydrogenation of CO_2 in the conventional IL 1-butyl-3-methylimidazolium hexafluorophosphate in the presence of dialkyl amines.[9] Furthermore, ILs can readily be functionalized and some of these derivatives have been applied in the separation of CO_2 and SO_2 from gas streams,[10] the extraction of metal ions,[11] and catalysis,[12] and this topic has been reviewed.[13]

Herein we demonstrate the first use of an IL as a base that promotes the hydrogenation of CO_2 to form formic acid. Ruthenium immobilized on silica was used as a heterogeneous catalyst, which was dispersed in an IL aqueous solution during the reaction. This catalytic system has satisfactory activity and high selectivity. The unique feature of this approach is that the formic acid can be recovered easily and both the IL and catalyst can be reused after a simple separation process.

The reaction and separation process for the catalyst and IL is shown schematically in Figure 1. The catalyst is first dispersed in the IL aqueous solution and H_2 and CO_2 are added. The catalyst is recovered after the reaction by filtration and can be reused directly. The filtrate, which contains the IL, water, and formic acid, is heated to 110 °C to evaporate the water quickly. The formic acid and IL are then separated at 130 °C by evaporating the former with the aid of a nitrogen flow, and the remaining IL can be reused directly. This separation method is possible because formic acid is stable at these temperatures in the absence of catalyst.[14]

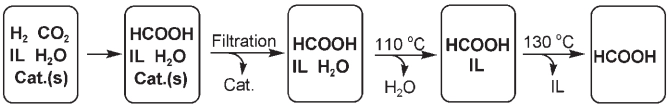
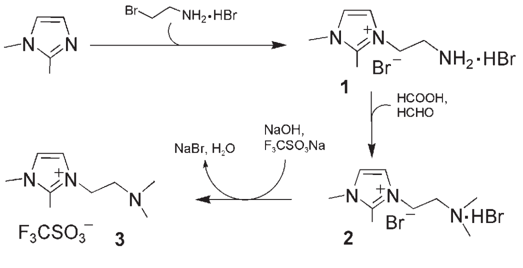


Figure 1. Hydrogenation reaction and recovery of the product, catalyst, and IL.

An IL containing a primary amino group (NH_2) has been used to absorb CO_2.[10a] However, this NH_2 group can form formamide with the formic acid in our system, thus making it very difficult to isolate the formic acid and recover the IL. We therefore synthesized a new basic IL that has a tertiary amino group ($N(CH_3)_2$) on the cation, namely 1-(*N*,*N*-dimethylaminoethyl)-2,3-dimethylimidazolium trifluoromethanesulfonate ([mammim][TfO], **3**), which can form a salt with formic acid and can be reused after separation. The synthesis of this IL is shown in Scheme 1.

3-Chloropropyltrialkoxysilanes ($(RO)_3Si(CH_2)_3Cl$) can be used to functionalize the surface of silica for different applications.[15] For instance, polystyrene-$CH_2NH(CSCH_3)$-



Scheme 1. Synthesis of the IL [mammim][TfO] (**3**).

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$RuCl_3$-PPh_3 has been used to catalyze the hydrogenation of CO_2 to produce formic acid.[6b] In light of these results, we prepared the catalyst "Si"-$(CH_2)_3NH(CSCH_3)$-$RuCl_3$-PPh_3 (see Experimental Section). The particle size of this catalyst is in the range 1–5 μm (see the Supporting information). The Ru content of the catalyst was determined by ICP-AES to be 3.8 $mg\,g^{-1}$.

Table 1 shows the turnover frequency (TOF) of the reaction under different conditions. No by-products were detectable under our experimental conditions. The TOF of the reaction increases with an increase of hydrogen pressure (Table 1, entries 1–3 and 5–7). Similarly, an increase in CO_2 pressure also results in larger TOF values (Table 1, entries 2, 4, and 7–9). The reason for this is that both hydrogen and CO_2 are reactants in the reaction and the concentration of the two gases in the catalytic system (liquid phase) increases with increasing pressure. The TOF also increases as the amount of IL is raised from 0.5 to 1.5 g. This is understandable because the IL is used to shift the reaction equilibrium and therefore it is easier for the IL to form a salt with formic acid at higher concentrations.

Table 1: Turnover frequencies (TOFs) for the hydrogenation of CO_2 to formic acid under different conditions.[a]

Entry	IL [g]	P_{H_2} [MPa][b]	P_T [MPa][b]	t [h]	AIR[c]	TOF [h^{-1}][d]
1	0.5	1	4	2	0.20	14
2	0.5	3	6	2	0.35	24
3	0.5	9	12	2	0.60	42
4	0.5	3	12	2	0.65	45
4-1[e]	0.5	3	12	2	0.63	44
4-2[e]	0.5	3	12	2	0.61	43
4-3[e]	0.5	3	12	2	0.63	44
4-4[e]	0.5	3	12	2	0.62	43
5	1.5	3	6	2	0.17	36
6	1.5	6	9	2	0.27	57
7	1.5	9	12	2	0.31	65
8	1.5	9	15	2	0.46	96
9	1.5	9	18	2	0.49	103
10	1.5	9	18	5	0.87	73
11	1.5	9	18	10	0.96	40
12[f]	1.5	9	12	2	0.04	8

[a] Reaction conditions: 0.3 g of catalyst (3.8 $mg\,g^{-1}$), 5 g of H_2O, 60 °C; [b] P_{H_2} and P_T are the initial partial pressure of hydrogen and total pressure, respectively. [c] AIR is the molar ratio of formic acid formed to IL added. [d] Mols of formic acid per mol of Ru per hour. [e] Entries 4-1, 4-2, 4-3, and 4-4 are the results of recycling the IL and catalyst under the conditions of entry 4. [f] No water was added to the reaction system.

As expected, the molar ratio of formic acid to IL becomes larger as the reaction time is increased from 2 to 10 h (Table 1, entries 9–11), although the TOF drops at longer reaction times. The main reason for this is that more of the IL forms a salt with the formic acid with increasing reaction time, which decreases the effective concentration of the IL. This situation is consistent with the result where the TOF increases with the amount of IL, as discussed above. We also conducted the reaction without additional water (Table 1, entry 12). It can be seen that the TOF of this reaction is very low, probably as a result of the high viscosity of the IL.

We also investigated the reusability of the catalyst and IL. The experiments were carried out under the conditions of entry 4 in Table 1. The catalyst and IL were recovered after reaction as described above and were reused directly. The TOFs for the four recycling experiments are listed in Table 1 (entries 4-1, 4-2, 4-3, and 4-4). No decrease of TOF is evident after recycling the catalyst and IL five times, thus demonstrating that both the catalyst and the IL can be reused after this simple separation process, which is very favorable from a practical point of view. ICP-AES analysis indicated that Ru content in the pristine catalyst and that in the catalyst after being used five times are nearly the same, thus indicating that no significant loss of Ru occurs during the recycling process. Similarly, ^1H NMR spectroscopic characterization showed that there was no difference between the virgin IL and the IL after being used five times.

Thermogravimetric analysis (TGA) indicated that the IL is stable up to 220 °C (see the Supporting Information), which is much higher than the temperature needed to separate the IL and formic acid (130 °C). This provides further evidence for the excellent reusability of the IL. The easy reuse of the IL is due to three factors. First, the basicity of the IL is appropriate for both promoting the reaction and easy separation as it cannot promote the reaction effectively if it is too weak a base, whereas it will be difficult to separate the IL and formic acid if it is too strong a base. Second, the IL is nonvolatile and formic acid is volatile, which makes their complete separation much easier by simple distillation. Finally, the IL is thermally stable, therefore the separation of the IL and formic acid can be performed at a suitable temperature.

In summary, the basic IL [mammim][TfO] and the heterogeneous catalyst "Si"-$(CH_2)_3$-$NH(CSCH_3)$-$RuCl_3$-PPh_3 can be combined in aqueous solution to catalyze the hydrogenation of CO_2 and produce formic acid with satisfactory activity and high selectivity. This process has some unique features. In particular, the IL and catalyst can be reused directly after easy separation, no volatile organic substance is used, and no waste is produced. These features suggest that this reaction could be developed into a commercial process.

Experimental Section

1: 1,2-Dimethylimidazolium (12.5 g, 0.13 mol) and acetonitrile (50 mL) were added to a two-necked flask equipped with a magnetic stirrer and the mixture was heated under reflux in an oil bath at 78 °C under nitrogen. 2-Bromoethylamine hydrobromide (20.5 g, 0.10 mol) was then added to the flask in portions over 24 h. After this time the liquid was separated and the remaining solid washed three times with ethanol. Drying under vacuum gave 16.0 g of 1-aminoethyl-2,3-dimethylimidazolium bromide hydrobromide (**1**).

2: Compound **1** (15.0 g), water (30 mL), formic acid (15 g), and aqueous formaldehyde solution (15 g) were placed in a two-neck flask and the mixture was stirred and heated under reflux in an oil bath at 100 °C for 36 h. Formic acid, formaldehyde, and water were then removed under reduced pressure and the remaining solid was washed with ethanol to give 15.9 g of 1-(*N*,*N*-dimethylaminoethyl)-2,3-dimethylimidazolium bromide hydrobromide (**2**).

3: NaOH (1 equiv) and **2** (1 equiv) were added to methanol (100 mL) and the mixture stirred for 1 h. Sodium trifluoromethanesulfonate (1 equiv) was then added and the mixture stirred for 2 h. After this time the methanol was evaporated under reduced pressure, dichloromethane (100 mL) was added, and the mixed was stirred for a further 2 h. The solid (NaBr) was removed by filtration, dichloromethane was removed from the filtrate under reduced pressure, and the resulting IL **3** was dried at 50 °C for 12 h under vacuum. The concentration of water in the IL, as determined by Karl–Fischer analysis, was 0.1 wt %.

Catalyst preparation: Silica (200–300 mesh; 12.0 g) and $(EtO)_3Si(CH_2)_3Cl$ (8.0 g) were stirred in a flask containing refluxing toluene (60 mL) for 8 h. Water (40 mL) was then added and the mixture stirred for 4 h. The resulting solid “Si”-$(CH_2)_3Cl$ was collected by filtration, washed with ethanol, and dried. “Si”-$(CH_2)_3Cl$ (5.0 g) was added to a solution of thioacetamide (20 g in 50 mL H_2O) containing Na_2CO_3 (4 g) and the mixture stirred at 50 °C for 15 h. The resulting solid “Si”-$(CH_2)_3NH(CSCH_3)$ was collected by filtration, washed with water, and dried. $RuCl_3{\cdot}3H_2O$ (0.10 g) and “Si”-$(CH_2)_3NH(CSCH_3)$ (5.0 g) were added to ethanol (30 mL) and the mixture was stirred for 2 h at room temperature. The solid was collected by filtration, washed with ethanol, and dried under vacuum to give “Si”-$(CH_2)_3NH(CSCH_3)$-$RuCl_3$, which was then added to an ethanol solution of PPh_3 (P/Ru 4:1) and stirred for 1 h. The catalyst was obtained after filtration under nitrogen and drying.

All catalytic reactions were carried out in a 50-mL stainless-steel view-reactor equipped with a magnetic stirrer. In a typical experiment, catalyst (0.3 g), water (5 g), and the desired amount of IL were placed in the reactor, the air in the reactor was replaced with CO_2, and the reactor was placed in a constant-temperature water bath at 60 °C. The reactor was pressurized to the desired partial pressure of H_2 and CO_2 was added until the desired total pressure was reached. After the appropriate reaction time the reactor was cooled and the H_2 and CO_2 pressure was released. The catalyst was recovered by filtration and the filtrate was placed in a stainless-steel cell fitted with a Teflon liner and heated to 110 °C. The water evaporates quickly at this temperature. Nitrogen at ambient pressure was passed through the cell at 130 °C to remove the formic acid, which was absorbed in distilled water. The amount of formic acid was determined by a conventional titration method with NaOH as base and phenolphthalein as indicator. The reliability of the analytical procedure was confirmed by simulation experiments in which a known amount of formic acid was added to a mixture of catalyst, water, and IL and then the amount of formic acid was determined as described above. The amount determined agreed well with the amount of formic acid added in three independent experiments. The presence of possible by-products was examined by recording the ^1H NMR (400 MHz) spectrum of the filtrate, which indicated that no by-products were formed and that only the IL was left in the cell after removing the formic acid. The recovered catalyst and IL were reused directly in subsequent experiments.

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