Simple Continuous High-Pressure Hydrogen Production and Separation System from Formic Acid under Mild Temperatures

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A simple and continuous high-pressure (> 120 MPa) hydrogen production system was developed by the selective decomposition of formic acid at 80 °C using an iridium complex as a catalyst, with a view to its application in future hydrogen fuel filling stations. The system is devoid of any compressing system. The described method can provide high-pressure H₂ with 85 % purity after applying an effective gas–liquid separation process to separate the generated gas obtained from the decomposition of formic acid (H₂/CO₂ = 1:1). The efficiency of the catalyst lies with its high turnover frequency (1800 h⁻¹ at 40 MPa) to produce high-pressure H₂ with a good lifetime of >40 h. Interestingly, only very low levels carbon monoxide (less than 6 volppm) were detected in the generated gas, even at 120 MPa.

The increasing demand for energy, especially in the transportation sector, is diminishing fossil fuel resources and escalating environmental concerns. Hydrogen gas (H_2) is considered to be one of the promising alternative clean fuels to replace fossil

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fuels and contributes to the zero-emission technology.^[1] Even though fuel cell vehicles (FCVs) with on-board high-pressure H₂ cylinders up to 70 MPa have recently become available, applications of H₂ as an alternative fuel are still in their infancy due to several challenges, particularly regarding the storage of H₂ and the generation of high-pressure H₂ due to its low volumetric energy density and gaseous properties.^[1,2] The current system at hydrogen stations to feed the high-pressure H₂ to FCVs is expensive because of the use of large mechanical hydrogen compressors and/or the consumption of large amounts of energy in the liquefaction of hydrogen followed by heating to generate high-pressure gas.^[3] To overcome these problems, effective high-pressure H₂ tanks in a cryo-compressed state or liquid state, metal hydrides, and physical H₂ adsorption materials have been developed for H₂ storage system.^[2a,4] However, these methods only allow a low weight density of H₂ and consume a lot of energy to maintain the high pressure for a long time and to release the stored H₂.^[2a, 4b] Recently, some chemicals such as ammonia borane, N-ethyl hydrocarbazole, methyl cyclohexane, hydrazine, methanol, formic acid (FA), and ammonia have received attention as H_2 storage chemicals as they provide significant advantages in terms of availability, recharging, and safety.^[2,4b,c] Within these H₂ storage chemicals, we focused on FA, because it is a low-toxicity, low-flammability, biodegradable liquid at ambient conditions, and has a comparatively high H₂ content. Compared to the other H₂ storage materials, decomposition of FA has a low-reaction enthalpy; thus, H₂ can be produced from FA at mild temperatures, even at < 100 °C.^[5] In addition, FA decomposition is thermodynamically favorable, so that the high-pressure H₂ is generated easily from FA in contrast to other H₂ storage chemicals. Therefore, FA requires less energy for the H₂ production and could be one of the most attractive H₂ storage chemicals. Moreover, FA can function as a renewable material for H₂ storage.^[6] Carbon dioxide (CO₂), which is the co-product of FA decomposition, can be hydrogenated back to FA in water or organic solvents on a catalyst surface or in the presence of specific homogeneous catalysts.^[7] There is a possibility of the formation of carbon monoxide (CO) and water by the dehydration of FA as a side reaction during FA decomposition, which could be fatal to fuel cells due to facile catalyst poisoning by CO.^[8] As mentioned before, in the presence of water, FA undergoes dehydrogenation and dehydration reactions,^[9] but both reactions remain unselective in the aqueous phase. Therefore, to avoid dehydration to generate CO, it is necessary to use an effective catalyst for the decomposition of FA at lower than 100°C. Many catalysts have



been studied for the selective decomposition of FA to generate H₂ with high efficiency.^[10] Recently, we have developed water-soluble iridium catalysts for the decomposition of FA at a temperature of <100 °C.^[7b,11] In particular, the water-soluble Ir catalyst, [Cp*Ir(4DHBP)(H₂O)][SO₄] (Cp*=pentamethylcyclopentadienide, 4DHBP=4,4'-dihydroxy-2,2'-bipyridine), was shown to have a long lifetime (34 h) for decomposition of FA at atmospheric pressure.^[11a]

Here, we have applied the same Ir catalyst ([Cp*Ir(4DHB-P)(H₂O)][SO₄]) for the decomposition of FA to generate high-pressure gases (H₂ and CO₂) at > 70 MPa without any formation of CO at temperatures below 100 °C. Our target is the continuous generation of gas under high-pressure conditions related to its application for FCVs. Furthermore, we also successfully demonstrate a simple and effective method to separate high-pressure H₂ with 85% purity from the generated gases (H₂/CO₂=1:1) by changing the physical state of the product mixture from the supercritical state to the gas–liquid state while maintaining the high-pressure condition (Figure 1).



Figure 1. Continuous, high-pressure H₂ production method involving the decomposition of FA to generate high-pressure H₂+CO₂, followed by gas-liquid separation to purify the H₂ while maintaining a high-pressure condition.

Different reaction parameters to generate high-pressure hydrogen gas from the decomposition of FA were studied by using a high-pressure reactor (Figure 2). Figure 3 shows the time course of the generated gas pressure as a function of the initial concentration of FA at a fixed temperature of 80° C in the presence of the Ir catalyst. The generated gas pressure reached a maximum of 123 MPa within 12 h in the presence of 26 µmol of catalyst when the initial FA concentration was



Figure 2. Schematic diagram of the apparatus for monitoring the pressure evolution during the catalytic decomposition of FA: a) high-pressure reactor made of 316 stainless steel, b) stop valve or back-pressure regulator, c) gas chromatography, d) flow meter. Pressure and temperature are recorded at T1–T3 and p1–p2, respectively.



Figure 3. Time course of the generated pressure by the decomposition of FA at various initial concentrations. The initial concentration of FA is as follows: 4 mol L⁻¹ (black plus), 10 mol L⁻¹ (blue triangle), 15 mol L⁻¹ (green cross), 20 mol L⁻¹ (red circle). Reaction conditions: 80 °C, aqueous solution of FA (4–20 mol L⁻¹, 13 mL), [Cp*Ir(4DHBP)(H₂O)][SO₄] (2.0 mmol L⁻¹, 26 µmol).

20 mol L⁻¹ (Figure 3, red circles). The generated pressure of 123 MPa was much higher than the reported value of 75 MPa at 90 °C in the presence of a ruthenium catalyst.^[10a] After 12 h, the pressure stabilized at 123 MPa, and then remained constant for a further few hours as the chemical equilibrium of the decomposition of FA was attained. When the gas pressure reached 123 MPa, 86 mol% of FA had been decomposed into H₂ and CO₂, with a high turnover number (TON) of 8600. We confirmed that the generated high-pressure gas consisted of only H_2 and CO_2 , with a very small amount of CO (< 6 volppm), which is the detection limit of GC-µTCD (Supporting Information Figure S1 (b)). Depending on the initial FA concentrations of 4, 10, and 15 mol L⁻¹, the final equilibrium gas pressure reached 26, 72, and 105 MPa within the reaction time of 3, 4, and 7 h, respectively (Figure 3). The reaction was repeated 3 times with the same FA concentration of 15 mol L^{-1} , and it was confirmed that a final pressure of \approx 105 MPa was achieved (Supporting information: Table S2). From the results, the final equilibrium gas pressures increase proportionally with the initial concentration of FA (Supporting information: Figure S2). After reaching a constant pressure, the final conversion of FA at each condition is constant (>85 mol%) even in the high-pressure region (Supporting information: Table S2). Therefore, a final equilibrium gas pressure of >120 MPa would be available with a higher initial concentration of FA up to 26 mol L⁻¹, which is 100 mol % of FA. We estimated by thermodynamic considerations that FA could produce 225 MPa as the final equilibrium pressure (Supporting information: Thermodynamic considerations). Thus, decomposition of FA using the Ir catalyst has huge advantages, as it can be used for the production of high-pressure gas (H₂ and CO₂) at > 120 MPa (up to 225 MPa) without formation of CO, which is sufficient to feed FCVs that operate at 70 MPa.



The feeding rate of gas under high-pressure conditions was also studied for the catalytic decomposition of FA by using the high-pressure reactor (Figure 2). In consideration of the fact that a FCV may need to be fed H_2 at 35 MPa in the future, initially the reaction was carried out 40 MPa at 80 °C with 12 mol L⁻¹ of aqueous FA and 0.2 mmol L⁻¹ of catalyst (Figure 4). When the pressure reached the desired pressure of



Figure 4. Time course of the gas volume and the generated pressure from FA decomposition: gas volume (red circle), generated pressure (blue cross), initial generated gas rate of 0.67 L h⁻¹ (black line). Reaction conditions: 80 °C, 40 MPa, aqueous solution of FA (12 mol L⁻¹, 40 mL), [Cp*Ir(4DHBP)(H₂O)][SO₄] (0.2 mmol L⁻¹, 8 µmol). The rate of gas evolution was averaged for the initial 1 h.

40 MPa, the conversion of FA was estimated as 54 mol% and the concentration of FA was 5.4 mol L⁻¹ based on the total volume of decomposition. After the pressure reached 40 MPa, a constant volume of high-pressure gas was exhausted through a back-pressure regulator, and the final FA concentration after 6 h was 3.8 mol L⁻¹. For the first 1 h after the evolution of gas started at 40 MPa, the average gas generation rate was 0.67 Lh⁻¹ and even under the milder conditions, the turnover frequency (TOF) obtained was 1800 h⁻¹, which is significantly higher than 670 h⁻¹ using a ruthenium catalyst (5-25 MPa, and 120 °C) as reported in the literature.^[13] The gas evolution rate was constant for 2-3 h in the beginning, and then gradually decreased with time (Supporting Information: Figure S3). The decrease in the FA decomposition rate with time is attributed to a decrease in the FA concentration.^[11a] According to GC-µTCD analysis of the generated gas, an equimolar mixture of H₂ and CO₂ gases are generated during the gas evolution for 6 h, with a high TON of >41000, and very low levels of CO being detected (< 6 vol ppm, see Supporting information: Figure S1 (c)). Therefore, the catalyst can maintain high selectivity for the FA decomposition even at in the high-pressure region and the long lifetime indicates that the process is free from catalyst poisoning. We also studied the pressure effects on the decomposition rate of FA (Figure 5). A further amount of the generated gas was required to reach the higher

Figure 5. Pressure dependence of the conversion rate of FA at various pressures: atmospheric pressure (blue triangle), 10 MPa (green cross), 30 MPa (red circle). Reaction conditions: 80 °C, aqueous solution of FA (8 molL⁻¹, 30–40 mL), [Cp*Ir(4DHBP)(H₂O)][SO₄] (0.2 mmolL⁻¹, 6–8 µmol). Time is defined as the time after reaching each pressure of the generated gas at 0.1, 10, and 30 MPa, respectively. The conversion of FA is calculated from the generated gas volume.

pressure, so that the initial FA conversion increased with the pressure at 0.1, 10, and 30 MPa, respectively, in Figure 5. When the applied pressure was in the atmospheric condition (0.1 MPa), the initial TOF was 9100 h⁻¹ (Figure 5, blue triangle), which corresponds well with previous work.^[11a] When the pressure was increased to 10 MPa (Figure 5, green cross) and 30 MPa (Figure 5 red circle), the decomposition rate of FA decreased. As a result, TOF values at 10 and 30 MPa decreased to around 2/3 (5700 h⁻¹) and 1/4 (2500 h⁻¹), respectively, compared to that at atmospheric pressure.

By the above-mentioned method from the decomposition of FA, we can generate high-pressure H₂ gas without any compressing procedures, but the generated gas would require purification for use in future FCVs. Hence, to avoid the consumption of compression energy, the development of a purification process under high-pressure conditions is necessary. For the purification under high-pressure conditions, we applied the gas-liquid phase separation method, simply by changing the physical fluid state (Figure 6 and Table 1). The high-pressure gas at > 7.4 MPa, which is generated from FA as a mixture of H_2 and CO_2 at 80 °C, has a lower critical point than CO_2 itself (31.1 $^\circ\text{C},$ 7.4 MPa). $^{[14]}$ Therefore, the generated gas is in the supercritical phase. Thus, to purify H₂ gas from the gas mixture, the gas separator was simply cooled down to a temperature below the critical temperature in order to change the generated gas from the supercritical state to the gas-liquid state without depressurization. When the generated gas entered the gas separator at 80°C and 30 MPa of pressure, the gas separator was set at 35 °C, which is the supercritical condition at 30 MPa. The equimolar mixture of H₂ and CO₂ gases were obtained from the back-pressure regulator attached to the separator.



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Figure 6. Schematic diagram of the apparatus for the kinetic studies on the catalytic decomposition of FA: a) reactor, b) separator, c) backpressure regulator, d) gas chromatography, and e) flow meter. Pressure and temperature are recorded at T1–T4 and p1–p2, respectively.

Table 1. Gas contents of the separated gas generated from the decomposition of FA at various temperatures of the separator at 30 MPa. ^[a]							
Entry	Separator temp. [°C]	X _{H2} [mol%]	X _{co} [mol %]	Initial gas flow $[Lh^{-1}]^{[b]}$	Initial H_2 production $[h^{-1}]^{[c]}$		
1	35	51	n.d. ^[d]	0.93	2560		
2	0	58	n.d.	0.86	2620		
3	-15	69	n.d.	0.75	2790		
4	-40	80	n.d.	0.73	3030		
5	-51	85	n.d.	0.69	3050		
[a] Gas generation condition: 80 °C, 30 MPa. Gas separation condition: $-51-35$ °C, 30 MPa. Aqueous solution of FA: 8 molL ⁻¹ , 40 mL, catalyst ([Cp*Ir(4DHBP)(H ₂ O)][SO ₄]): 0.2 mmolL ⁻¹ , 7–8 µmol. [b] Average gas rate for initial 1 hour. [c] Average rate of H ₂ gas per mole of the catalyst. [d] Not detected (less than 6 volppm).							

The temperature of the separator was then changed to -15 °C and 69 mol% of H₂ gas was obtained. The temperature was further changed to -51 °C and 85 mol% of H₂ gas was obtained at 30 MPa. To confirm these results, we observed the phase behavior through the sapphire windows attached to the high-pressure separation vessel (Figure 7). At 30 MPa and 35 °C, there was a single homogeneous phase as well as atmospheric pressure (Figures 7a,b). As the temperature was lowered to -10 °C, the homogeneous phase separated into two phases comprised of the H₂-rich gas phase and the CO₂-

rich liquid phase (Figure 7 c). As shown in Table 1, the amount of H₂ in the gas phase increased as the separator temperature was set to lower temperatures, and no CO was detected in the H₂-rich gas phase for the first 6 h. At -51 °C, 85 mol% of H₂ gas at 30 MPa was obtained with a good TOF value. We also estimated the vapor-liquid equilibrium value of the H₂ and CO₂ system (Supporting Information: Figure S5), which shows that it is possible to obtain 93 mol% of purified H₂ gas at 30 MPa and -51 °C. Therefore, further improvement of the separation process to achieve highly purified H₂ gas would be possible by allowing the gas mixture to cool down enough during the transfer from the reaction vessel to the separation vessel, and retaining it inside the separator for sufficient time to reach equilibrium. Finally, we found the initial gas flow rate decreases with a decrease in the separator temperature (Table 1). As the separator temperature was set to lower temperatures, a further amount of the generated gas was required to maintain the pressure because of liquefied CO₂ in the separator. As a result, the conversion of FA increases to reach the pressure with a decrease in the separator temperature (Supporting information: Figure S6). After completion of the reaction, 92-93 mol% of FA was converted and a TON of 37000-38000 was achieved at the different separator temperatures (Supporting information: Table S3).

In conclusion, we have developed a simple and continuous high-pressure hydrogen gas (> 120 MPa) production system



Figure 7. Phase behaviour of the gas generated from FA decomposition, observed in the gas separator under various conditions: a) 0.1 MPa and 35 °C, b) 30 MPa and 35 °C, c) 30 MPa and -10 °C. Generation condition (80 °C, 30 MPa), aqueous solution of FA (12 mol L⁻¹, 40 mL), [Cp*lr(4DHBP)(H₂O)][SO₄] (0.2 mmol L⁻¹, 8 µmol). The black vertical tube in the view cell is the inlet tube of the generated gas.

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from FA decomposition catalyzed by the water-soluble homogeneous Ir catalyst, [Cp*Ir(4DHBP)(H₂O)][SO₄], without any compressing procedures. The system can generate high-pressure gas, which is enough to feed FCVs (70 MPa). We further successfully demonstrated high-pressure H₂ gas separation from the generated gas simply by cooling the gas to change the supercritical state to the gas-liquid state. The system can generate hydrogen gas continuously with a high rate (TOF = 2500 h^{-1} at 30 MPa) even at a mild temperature of 80 °C. In addition, > 85% of FA is converted to the gas mixture of H₂ and CO₂, and the CO side product was below the fatal catalyst poisoning level as confirmed from the long catalyst lifetime even at 120 MPa pressure. This system has the potential to be developed further and can be used as a simple and easy to handle system for the generation of high-pressure H₂, not only for FCVs, but also for other applications.

Experimental Section

The general kinetic studies on the catalytic decomposition of FA are as follows. The experiments used the apparatus shown in Figure 3. The Ir catalyst (6–8 μ mol) and the aqueous FA solution (30–40 mL) were introduced into the reactor, and then the apparatus was purged of air with argon. The reactor was heated to 80 °C and the separator was set to the desired temperature. After completing the reaction, the reactor was cooled and then depressurized to atmospheric pressure carefully. The gas was collected during the depressurization and the reaction solution was analyzed by HPLC-UV. Further experimental details are provided in the supporting information.

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