Highly efficient hydrogen evolution by decomposition of formic acid using an iridium catalyst with 4,4′-dihydroxy-2,2′-bipyridine

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The efficient evolution of CO-free hydrogen by the decomposition of formic acid using iridium catalyst with 4,4′-dihydroxy-2,2′-bipyridine as a ligand in H_2O was demonstrated. The highest catalytic activity (turnover frequency (TOF) of up to 14000 h^{-1} at 90 °C) and an almost complete consumption of formic acid were obtained for the catalytic system. Furthermore, it was found that hydrogen could be generated even at elevated pressures. We discuss the possibility of a cycle for CO_2 as a hydrogen carrier by combining the decomposition of formic acid (evolution of H_2) with the hydrogenation of bicarbonate (fixation of CO_2 and storage of H_2) using the iridium catalyst.

Introduction

Hydrogen has attracted increasing attention as an alternative energy resource. Currently, the most widely used procedures for the production of hydrogen are the steam reforming of methane and the water-gas shift reaction, which occurs at high temperatures (>200 °C). However, the actual use of hydrogen is limited, mainly because of storage and delivery problems.[1,2] In recent times, extensive research has been carried out for the development of novel materials such as metal hydrides, carbon nanotubes, metal-organic frameworks, ammonia, amine boranes, phosphonium borates, and doped polymers for the storage and liberation of hydrogen gas.[3–5]

Organic hydrogen storage systems have attracted considerable attention, because most organic materials are light and inexpensive. In this context, formic acid has an advantage over other substrates because it is less toxic and it can be easily handled and stored. Thus, International Civil Aviation Organization (ICAO) approved the use of formic acid for mobile applications in fuel cells (DGP/21-WP/30 Dangerous Goods Panel). Formic acid contains 4.4 wt% and 53 g/L of hydrogen at ambient conditions and produces only gaseous products (H_2/CO_2), thereby preventing the accumulation of by-products.[6,7] In industry, a significant amount of formic acid as a by-product is produced from CO during the synthesis of acetic acid. Recently, many efficient homogeneous catalysts that can be used to catalyse the formation of formic acid and formate by the hydrogenation of CO_2 and bicarbonate, respectively, have been found (eqn. 1 and 2).[8–12] However, the decomposition of formic acid in order to yield hydrogen is underdeveloped so far.[13–19] Currently, the efficient decomposition of formic acid generally demands harsh conditions, which is a limitation for mobile applications in fuel cells.

$$HCO_3^- + H_2 \rightleftharpoons HCO_2^- + H_2O \qquad (1)$$

$$CO_2 + H_2 \rightleftharpoons HCO_2H \qquad (2)$$

In 2004, we reported that the evolution of H_2 and CO_2 by the decomposition of formic acid (turnover frequency (TOF) = 238 h^{-1}) in H_2O at 40 °C was catalysed by a rhodium bipyridine complex ([Cp*Rh(bpy)Cl]Cl).[20] More recently, Beller and co-workers achieved a high TOF of 3630 h^{-1} (after 20 min) using a ruthenium-based catalyst generated in situ from $RuBr_3$ and PPh_3 in the presence of amines at 40 °C. The use of amines for the formation of formic acid as well as for its decomposition enables a closed cycle with CO_2 as a hydrogen carrier. Furthermore, they demonstrated that the CO-free gas generated by the decomposition of formic acid can be directly used in fuel cells.[21–23] Independently, Laurenczy and co-workers reported the decomposition of formic acid/sodium formate (9:1) in an aqueous solution. The noteworthy features are as follows: (i) no inhibition of hydrogen evolution under a pressure of 75 MPa, (ii) continuous evolution of hydrogen with constant formic acid addition, and (iii) near-complete decomposition of formic acid. Unfortunately, the efficient evolution of hydrogen requires a higher temperature (TOF = 460 h^{-1} at 120 °C).[24,25] In these studies, the authors discussed the possibility of CO_2 as a storage medium for hydrogen on the basis of the catalytic formation and decomposition of formic acid using different catalysts in each reaction.

Recently, we had reported a remarkable improvement in catalysts with a bipyridine ligand, in which the use of 4,4′-dihydroxy-2,2′-bipyridine (DHBP) and 4,7-dihydroxy-1,10-phenanthroline as ligands led to a remarkable catalytic activation and pH-dependent catalyst tuning.[8,20,26–28] In other words, highly efficient, waste-free and catalyst-recyclable conversion of CO_2 into a formate was achieved. This is attributed to the tuning of a pH-dependent catalyst between the pyridinol and pyridinolate form by an acid–base equilibrium of the hydroxyl groups on the ligand (Scheme 1). The above-mentioned results and the increasing demand for hydrogen economy prompted us to reinvestigate the decomposition of formic acid by DHBP catalysts. Herein, we report the highly efficient evolution of hydrogen by the decomposition of formic acid in H_2O catalysed by the

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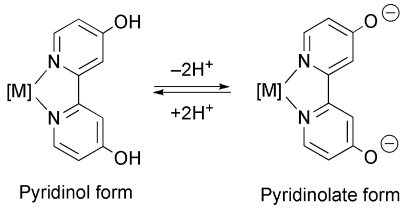


Scheme 1 Acid–base equilibrium of 4,4′-dihydroxy-2,2′-bipyridine (DHBP) complexes.

DHBP-iridium catalyst (TOF of up to 14000 h^{-1} at 90 °C). The evolution of the gas is CO-free and is controlled by the reaction temperature. Almost complete decomposition of formic acid was observed, even at elevated pressures. The combination of the decomposition of formic acid with the hydrogenation of bicarbonate will provide a promising cycle of CO_2 as a hydrogen carrier.

Results

Previously, we had reported that the decomposition of formic acid was achieved using the rhodium bipyridine complex ([Cp*Rh(bpy)Cl]Cl) as a catalyst in a HCO_2H/HCO_2Na solution at a pH of 3.5 and at 40 °C.[20] The volumes of evolution of H_2 and CO_2 increase linearly with time, and the TOFs for both are 238 h^{-1} (Fig. 1). Interestingly, CO was not detected in the gas mixture by gas chromatography (GC) and by using a gas sensor (Gastec 1LK: <5 ppm). The promising catalytic properties of the bipyridine complex prompted us to reinvestigate the decomposition of formic acid catalysed by more activated complexes with the DHBP ligand.

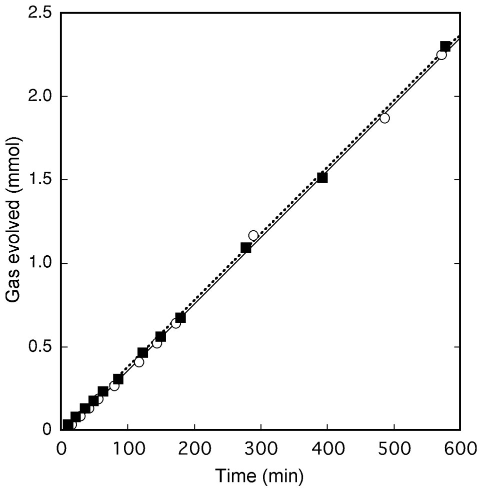


Fig. 1 Time course of the evolution of H_2 (closed squares) and CO_2 (open circles) by decomposition of formic acid using [Cp*Rh(bpy)Cl]Cl (1.0 μmol) in a HCO_2H/HCO_2Na solution at a pH of 3.5 and at 40 °C.[20]

The gas evolution was investigated using iridium-, rhodium-, and ruthenium-DHBP complexes (**1**–**3**·SO_4) in a 2 M aqueous formic acid solution (10 mL) at 60 °C (Chart 1). The rhodium catalyst **2**·SO_4 showed a moderate TOF of 510 h^{-1}. The TOF of the ruthenium analogue **3**·SO_4 was only 40 h^{-1}. On the other hand, the gas evolution using the iridium catalyst **1**·SO_4 was observed with a TOF of 2800 h^{-1}. The central metal effect was similar to that in previous results using DHBP catalysts.[27–29]

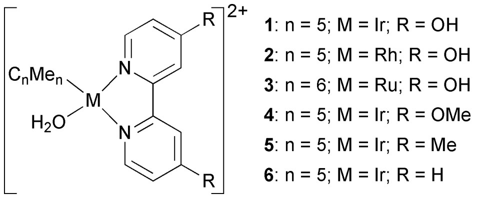


Chart 1

Fig. 2 shows the time course of gas evolution using **1**·SO_4 (2 μmol) in 2 M aqueous formic acid (10 mL) at 40–90 °C. A brief induction period was detected. In these reactions, CO was not detected by GC with a flame ionisation detector (FID) equipped with a methaniser (Fig. 3). The highest TOF of 14000 h^{-1} was obtained at 90 °C. It should be noted that an almost complete decomposition of formic acid was observed by HPLC analysis at the end of the reaction. The Arrhenius plot of the data shows an apparent activation energy of 76 kJ mol^{-1} at 40–70 °C. In previous studies, the apparent activation energies for the decomposition of formic acid were 87 and 40–60 kJ mol^{-1} for $[Cp^*Rh(bpy)(H_2O)]^{2+}$ and Pt dispersion, respectively.[30,31]

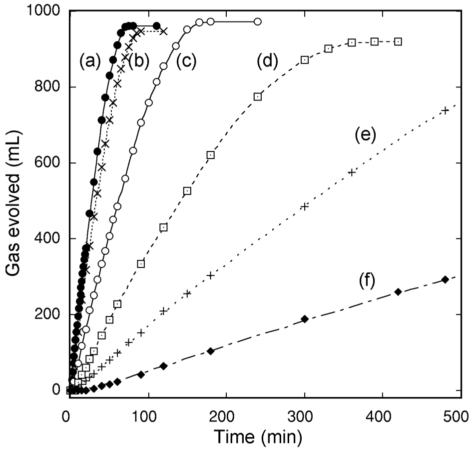


Fig. 2 Time course of gas evolution using **1**·SO_4 (2 μmol) in 2 M aqueous formic acid (10 mL) at (a) 90 °C (14000), (b) 80 °C (10000), (c) 70 °C (5950), (d) 60 °C (2800), (e) 50 °C (1240), and (f) 40 °C (450). The values in parenthesis are the initial TOFs (h^{-1}).

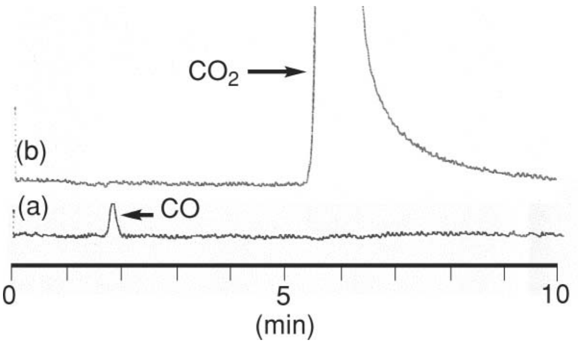


Fig. 3 Gas chromatogram using a methaniser and a FID of (a) 8 ppm CO (100 μL) and (b) the evolved gas (100 μL) using **1**·SO_4 (2 μmol) in 2 M aqueous formic acid (10 mL) at 80 °C.

The temperature dependence of catalyst **1** led to the control of the rate of gas evolution for 33 h (Fig. 4). Furthermore, **1** showed a high thermal stability. After 5 cycles of replenishing of formic acid, no significant degradation of the catalyst was observed even at 90 °C. The results indicated that the catalytic system could provide the desired amount of CO-free hydrogen gas for a long period.

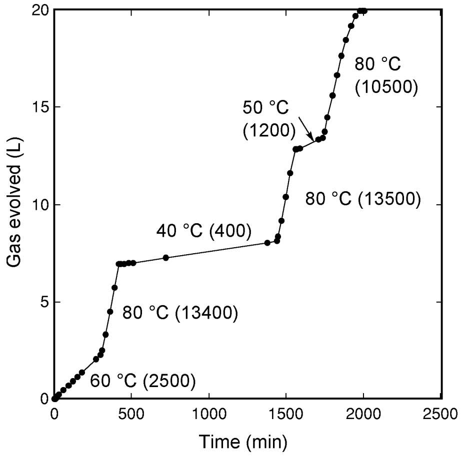


Fig. 4 Time course of gas evolution using $\mathbf{1}\cdot SO_4$ (4 μmol) in 8 M aqueous formic acid (50 mL) at 40–80 °C. The values in parenthesis are the average TOFs (h^{-1}).

Optimization of the pH of the reaction solution was carried out because **1** shows a strong dependence on the pH in aqueous catalysis.[28] The TOFs and the amount of gas evolved from a 1 M formate solution were measured at various pH values (Fig. 5). Maximum catalytic activity and complete consumption of formic acid was observed in the aqueous solution of formic acid without sodium formate. An increase in the pH caused a decrease in the TOFs and the amount of the evolved gas. Moreover, no gas evolution was detected above a pH of 4.5. It appeared that formate was not decomposed.[24,25] The trend in the pH-dependance of **1** was observed to be different from that of the rhodium analog $[Cp^*Rh(bpy)(H_2O)]\cdot SO_4$, in which the maximum activity was detected at a pH of 3.8.[30]

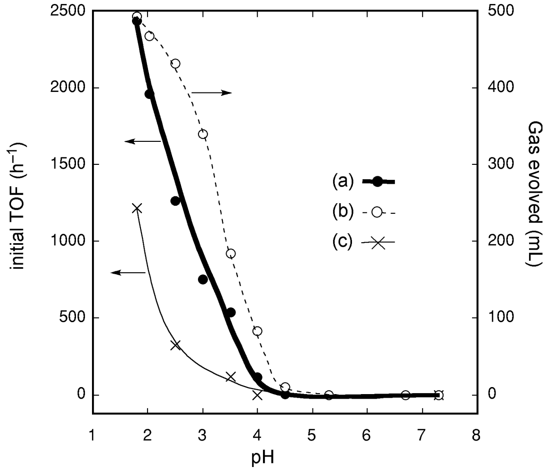


Fig. 5 pH-dependence of gas evolution at 60 °C in 1 M HCO_2H/HCO_2Na (10 mL) at various pH values. (a) Initial TOF, (b) amount of gas evolution using $\mathbf{1}\cdot SO_4$ (2.0 μmol), and (c) initial TOF using $\mathbf{4}\cdot SO_4$ (2.0 μmol).

The amount of evolved gas was proportional to the concentration of formic acid (Fig. 6). The initial TOFs were dependent on the concentration of formic acid: the highest TOF of 3100 h^{-1} was observed in a 4 M formic acid solution. However, the catalytic activity in 99% formic acid was significantly reduced (TOF = 760 h^{-1}). For efficient gas evolution, it is necessary to use formic acid diluted with H_2O.

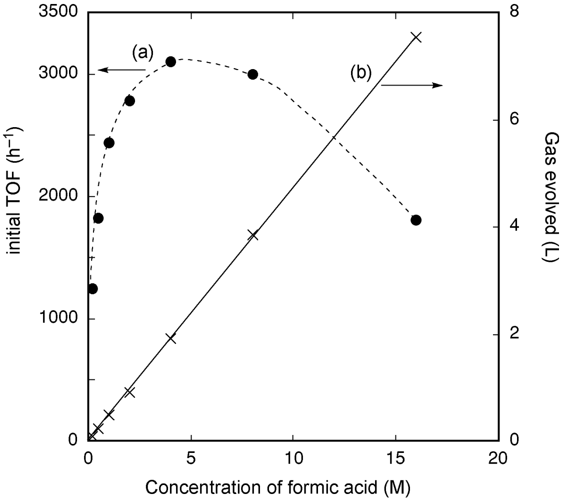


Fig. 6 Dependence of formic acid concentration (10 mL) on (a) initial TOF and (b) amount of gas evolution using $\mathbf{1}\cdot SO_4$ (2 μmol) at 60 °C.

The electronic substituent effect was investigated using a series of iridium complexes **1**, **4**–**6**. It was found that the initial TOF of **1** was approximately 90 times and 2 times that of the unsubstituted analogue **6** and the methoxy analogue **4**, respectively. Under acidic conditions, the electronic effect of the substituents in **1** behaves as a hydroxyl group ($\sigma_p^+ = -0.91$). Similar to that in previous studies on transfer hydrogenation,[8,27,28] the TOF values for a series of iridium complexes showed a good correlation with the Hammett substituent constants (σ_p^+) (Fig. 7). The

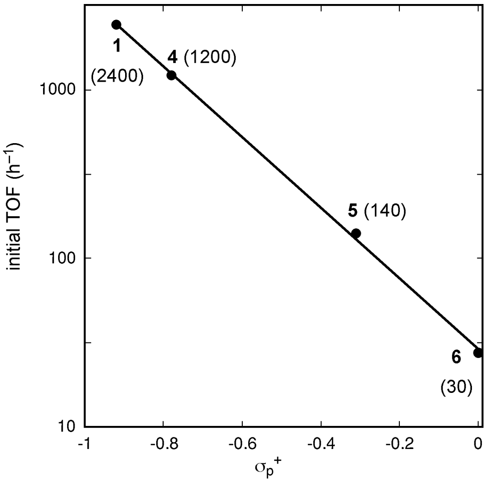


Fig. 7 Hammett plot of initial TOFs *vs.* σ_p^+ values of substituent (R) in the catalyst (2.0–20 μmol) at 60 °C in 1 M aqueous formic acid solution (10 mL). The values in parenthesis are the initial TOFs (h^{-1}).

pH-dependance of the methoxy analogue **4** was similar to that of **1** (Fig. 5c).

Catalytic decomposition of formic acid proceeded even at elevated pressures.[21] The gas evolution in a closed system proceeded smoothly and the pressure of the gas exceeded 4 MPa after 3 h (Fig. 8). It was noteworthy that only 7.5 mM of formic acid (0.4%) remained at the end of the reaction. It was found that the pressures in the system did not inhibit the reaction.

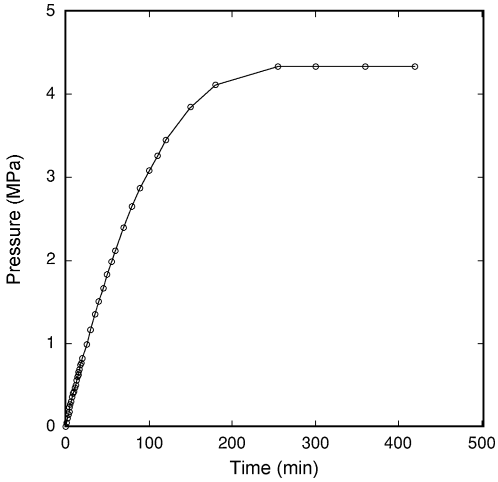
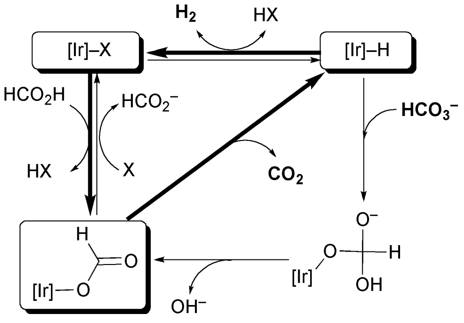


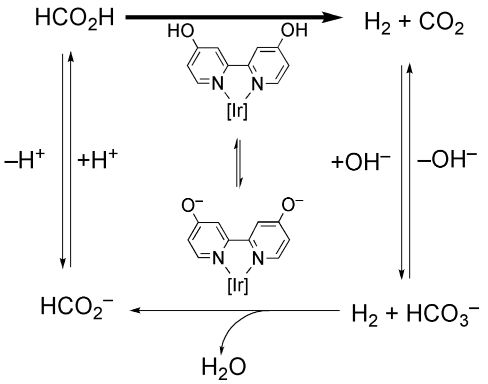
Fig. 8 Time course of pressure using $\mathbf{1}\cdot SO_4$ (1 μmol) at 80 °C in a 2 M formic acid solution (10 mL) in an autoclave.

The proposed mechanism for the decomposition of formic acid (bold arrows) is presented in Scheme 2.[30] The substitution of aqua ligand in **1** by formate produced the formate complex [Ir]-OC(=O)H as an intermediate. The hydride complex was generated through a β-hydrogen elimination accompanied by CO_2 evolution. The β-elimination may be a rate-determining step. The hydride species reacted with H^+ to produce H_2. A strong electronic effect, similar to that described in previous reports, was observed in the reaction.[8,27] The plain arrows in Scheme 2 indicate the proposed mechanism for the hydrogenation of bicarbonate under basic conditions.[8]



Scheme 2 Proposed mechanism for the decomposition of formic acid under acidic conditions (bold arrows) and the hydrogenation of bicarbonate under basic conditions (plain arrows).

Herein and in previous papers, we described that **1** serves as an effective catalyst for both the decomposition of formic acid (evolution of hydrogen) and the hydrogenation of bicarbonate (fixation of CO_2 and storage of H_2). The combination of these reactions will lead to a cycle of CO_2 as a hydrogen carrier (Scheme 3). To the best of our knowledge, the highest TOF values for both these reactions were obtained under aqueous conditions. Furthermore, hydrogen storage and evolution can be adjusted by changing the pH of the solution. Namely, the decomposition of formic acid under acidic conditions was catalysed by its pyridinol form, whereas the hydrogenation of bicarbonate under basic conditions was catalysed by its pyridinolate form.



Scheme 3 Cycle of CO_2 as a hydrogen carrier by means of CO_2 fixation and H_2 storage using the iridium-DHBP catalyst **1**.

Conclusions

We have demonstrated an efficient catalytic hydrogen evolution process by the decomposition of formic acid using the iridium-DHBP catalyst **1** in H_2O. The salient features of this reaction are as follows: (1) The highest catalytic activity (TOF of up to 14000 h^{-1} at 90 °C) was obtained. (2) The desired volume of CO-free hydrogen could be produced by controlling the temperature. (3) The added formic acid was completely and selectively converted to H_2 and CO_2. (4) The catalytic system yielded high pressured hydrogen. (5) The catalytic activities were strongly dependent on the pH and the electronic effect of the substituent in the bipyridine ligand. (6) Iridium-DHBP catalyst **1** showed a high thermal stability in aqueous solution.

The efficient evolution and storage of hydrogen, *i.e.*, the fixation of CO_2 and the decomposition of formic acid, has been reported for the first time; we used the same catalyst **1** by controlling the pH of the solution. The combination of these catalytic reactions will provide the possibility of the cycle of CO_2 as a hydrogen carrier. These results suggest that formic acid may find practical applications as a hydrogen storage medium in portable electric devices.

Experimental section

General procedure

All manipulations were carried out under argon atmosphere. All aqueous solutions were degassed prior to use. The gas samples, which were obtained at various intervals with a gastight syringe through a septum, were analyzed for H_2 with a TCD (thermal conductivity detector) using an activated carbon 60/80. In case of CO_2, the samples were analysed with an FID equipped with a methaniser using a Porapak Q 80/100 at 50 °C, on a GL

Science GC390 gas chromatograph. The formate concentrations were monitored by an HPLC on an anion-exclusion column (Tosoh TSK gel SCX(H^+)) with an aqueous phosphate solution (20 mM) as an eluent and a UV detector (λ = 210 nm). The complexes **1–5**·SO_4 were prepared according to the literature.[28]

Catalytic decomposition of formic acid. Typically, a 20 mM solution of **1**·SO_4 (100 μL, 2 μmol) was added to a deaerated aqueous formic acid solution, and the mixture was stirred at the desired temperature. The volume of gas evolution was determined by a gas meter (Shinagawa Corp., W-NK-05).

Decomposition of formic acid under pressured conditions. The experiments were performed in a 20 mL autoclave. A 10 mM solution of **1**·SO_4 (100 μL, 1 μmol) was added to deaerated aqueous 2 M formic acid solution (10 mL), and the mixture was stirred at 80 °C. The pressure in the reactor was measured by a digital pressure gauge (NAGANO KEIKI Co., LTD. GC64).

Acknowledgements

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