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Direction to practical production of hydrogen by formic acid dehydrogenation with Cp*Ir complexes bearing imidazoline ligands[†]

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A Cp*Ir complex with a bidentate pyridyl-imidazoline ligand achieved the evolution of 1.02 m^3 of H_2/CO_2 gases by formic acid dehydrogenation without any additives or adjustments in the solution system. The pyridyl-imidazoline moieties provided the optimum pH to be 1.7, resulting in high activity and stability even at very acidic conditions.

Hydrogen (H₂) is considered as a clean energy source because it produces only water when it undergoes combustion.¹ However, due to the difficulties associated with the storage and transport of H₂ gas, simple and safe methods to handle it easily are desired. One such approach is the storage of H₂ gas by incorporating it into a liquid organic compound. Formic acid (FA) is viewed as one of the promising hydrogen storage materials because it can be interconverted with H₂/ CO_2 .^{2–6} Based on this idea, much recent attention has been focused on transition metal-catalysed interconversion between H₂/CO₂ and FA.

In 2008, two distinct studies on FA dehydrogenation under mild reaction conditions without CO contamination were reported independently by Beller and Laurenczy.^{7,8} After these discoveries, other catalysts for the dehydrogenation of FA have been studied extensively. Fe,^{9–11} Ru,^{12,13} and Ir^{14–17} complexes were shown to be effective catalysts in the presence of amines and/or organic solvents. However, for the amine system, control of FA concentration with periodic additions of FA to maintain the reaction rate was needed, since the reaction rate decreased with the change in FA to amine ratio because of FA consumption. Furthermore, due to the loss of volatile amines during the hydrogen release process, the turnover numbers (TONs) in the amine systems were limited.¹³ Catalysts that function in aqueous solutions without any base can avoid these problems, although their catalytic activities and durabilities are generally unsatisfactory.^{8,18}

Pentamethylcyclopentadienyl (Cp*) iridium complexes with aromatic N,N bidentate ligands (e.g., consisting of pyridine, pyrimidine, or azole moieties) have been found to show high catalytic activity for the dehydrogenation of FA in aqueous solutions.¹⁹⁻²³ Furthermore, previous studies have revealed that both hydrogenation of CO₂ and dehydrogenation of FA are catalytically activated by an increase in electron donating ability from the N,N bidentate ligand to the Ir centre. Recently, we have reported that electron-rich azole moieties such as imidazole are also very effective ligands for FA dehydrogenation.²¹ Similarly, Xiao et al. have reported FA dehydrogenation by a Cp*Ir complex with a phenylimidazoline derivative, which was the C-C saturated analogue of azole, in a FA-amine (5:2) azeotrope.¹⁴ Although the catalyst showed excellent activity for the dehydrogenation reaction in 10 s, with a turnover frequency (TOF) corresponding to 145 000 h⁻¹, the repeated addition of FA at short intervals was required for sustained FA dehydrogenation. We have also reported that an imidazoline derivative, dihydroxypyrimidylimidazoline, displayed high activity due to the presence of a pendant OH group as a proton donor site.²⁴ Very recently, Li reported that Cp*Ir complexes with imidazoline and tetrahydropyrimidine moieties were highly efficient in small-scale experiments under reaction conditions similar to ours.²⁵ Based on these reports, imidazoline moieties could be concluded to be promising ligands for FA dehydrogenation as well as CO₂ hydrogenation.²⁶

A significant challenge for FA dehydrogenation catalysts is to satisfy both high catalytic efficiency and durability requirements.^{10,12,13} In our previous report, 50 L of H_2 (total volume:

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100 L, TON of 2 050 000) was evolved from 200 ml of 6 M FA solution, although the reaction rate decreased gradually.²⁴ Further efforts in the development of efficient and robust catalysts for the supply of large amounts of H_2 are required to enable the use of FA dehydrogenation on a practical scale.

Herein, we report effective catalysts bearing imidazoline derivatives for the dehydrogenation of FA that can produce a large volume of H_2 and can sustain their activities for extended periods of time in water without any organic additives. Particularly effective and stable H_2 production at highly acidic conditions (*e.g.*, pH 1.7) was achieved by the incorporation of a bidentate ligand that combines an imidazoline and a pyridine moiety.

We have previously reported on FA dehydrogenation using imidazole complexes C1, C2,²² and imidazoline complex C3²⁴ (Scheme 1) in acidic aqueous solutions (Table 1, runs 1, 2 vs. 3). The results indicated that the non-aromatic imidazoline moiety could be more efficient than the aromatic imidazole ones. Based on this hypothesis, we recently prepared imidazoline complexes C4-C6, and demonstrated their high catalytic activity for CO₂ hydrogenation under basic conditions.²⁷ Firstly, the dehydrogenation of FA for H₂ evolution using C4-C6 is investigated at standard conditions (1 M aqueous FA solution at 60 °C). In comparing the TOF value of C1 with that of C4, the imidazoline moiety was concluded to be more effective than the imidazole moiety for FA dehydrogenation (Run 1 vs. 4). This result showed a similar trend as in the hydrogenation of CO2.27 Additionally, FA dehydrogenation by the N-methylated complex C5 (Run 5) was almost the same as that of C4. From this result, it can be concluded that the proton in the N-H functionality has little involvement in the dehydrogenation reaction.¹⁴ This conclusion is further supported by density functional theory (DFT) calculations of the free-energy profiles of the catalytic reactions (see the ESI[†]). A high TOF of the bisimidazoline complex C6 was observed, which is similar to the results of Li.²⁵ Previously, we have shown that it is necessary to increase the electron donation ability from the N atom of the ligand to the Ir centre in order to improve the catalytic activity for FA dehydrogenation.²⁰ Based on our recent papers,^{22,27} we suggested that an imidazoline moiety would show the highest activity compared to imidazole and pyridine. In fact, C6 with two imidazoline moieties was confirmed by activity studies at



Table 1 Dehydrogenation of FA in water^a

Run	Cat./ μ M	Time/h	$\mathrm{TOF}^{c}/\mathrm{h}^{-1}$	TON	Conv	Ref.
1	C1/500	4	800	2000	98	22
2	C2/100	5	4000	10000	100	22
3	C3/100	3	5500	10000	100	24
4	C4/50	2.5	13 300	20 000	100	This work
5	C5/50	2.5	15000	20 000	100	This work
6	C6/10	4	54700	100 000	100	This work
7	$C6/10^{b}$	4	81 900	784000	98	This work

^a The reaction was carried out in 1 M aqueous FA solution at 60 °C.
^b The reaction was carried out in 8 M aqueous FA solution. ^c Average TOF over the initial 10 min.

standard conditions to exhibit the highest TOF among all the employed catalysts (Table 1).

Next, we examined the pH-dependence of dehydrogenation with C4, adjusted by changing the ratio of FA and sodium formate (SF) to a total FA + SF concentration fixed at 1 M or by adding H₂SO₄ (Fig. 1). In our previous report, C3 showed maximum catalytic activity at pH 3.0, influenced by a pendant OH group on the pyrimidine moiety (Fig. 1, black solid line).²⁴ However, this result meant that a pH adjustment would be needed for maximum performance of C3. For practical use in a hydrogen storage system, complicated operations such as adding compounds for pH adjustment should be avoided. On the other hand, the reaction rate and conversion by C4 between pH 0.8 and 7.0 were found to be maximized at pH 1.7 (Fig. 1, blue solid line, Fig. S2(a),† and Table S1[†]). The maximum in the activity vs. pH profile of C4 is shifted to a lower pH than that of C6 (pH 2.2, Fig. 1, red solid line). Based on these results, we investigated the pHdependent rate-determining steps (RDSs) of C4 and C6 via kinetic isotope effect (KIE) studies (Tables S2 and S3⁺) and DFT calculations.^{21,24,25} FA dehydrogenation using a homogeneous catalyst generally proceeds through three steps: (i) formation of a formato complex; (ii) release of CO_2 by β -hydride elimination to generate a metal-hydride complex, [M]-H; and



Fig. 1 pH-dependence of FA dehydrogenation at 60 °C in 1 M FA/SF solution (pH 1.7–7.0) or 1 M FA containing H_2SO_4 (pH 0.8–1.6). The pH of the solution is adjusted by changing the ratio of FA and SF while keeping their total concentration constant. Black solid line, C3 (100 μ M); blue solid line, C4 (50 μ M); and red solid line, C6 (10 μ M).

(iii) production of H₂ from the reaction of [M]-H and a proton.²¹ This plausible mechanism for FA dehydrogenation using imidazoline-type catalysts was supported by NMR studies in which C4-C6 reacted with SF to generate the inferred Ir-H complex (Fig. S3-S5[†]). From the KIE studies, the formation of the [Ir]-H complex was found to be the RDS at low pH where activity is rising, switching to the formation of H₂ at higher pH for both C4 and C6 (Fig. 1 and S2[†]), where activity is decreasing. This switchover is further supported by the free-energy profiles generated by DFT calculations at the M06 level of theory²⁸ (Schemes S1-S14 and Table S3[†]). In our previous reports, we have demonstrated that the presence of proton responsive sites in the ortho-pyridinol moiety of a bidentate ligand and their associated pK_a values play a significant role in the switching of the RDS from β -hydride elimination to H₂ formation.²⁴ However, in the case of C4 and C6, there are no proton responsive sites in the associated pH range, and the change in the RDS occurs at more acidic pH values (1.7 for C4 and 2.2 for C6) compared to our previously reported catalysts (e.g., the switchover point for C3 is at pH \cong 3.0). As a consequence of this, C4 and C6 display their optimum activity at more acidic conditions rendering them more efficient catalysts for H₂ generation via FA dehydrogenation.

We also examined the temperature dependence of the dehydrogenation reaction by C4 (Fig. S6(a) and Table S4†). By analysing the Arrhenius plot (Fig. S6(b)†), the activation energy (E_a) was calculated to be 72.0 kJ mol⁻¹, which is almost the same as the value obtained using the bisimidazoline analogue C6.²⁵

The dependence on the concentration of FA in the range from 1 M to 20 M was investigated using C4 at 60 °C. The TOFs and the volumes of released gases are shown in Fig. 2a (detailed data in Table S5†). The time courses of the volumes of released gases are shown in Fig. 2b. In 8 M and 12 M FA solution, the gases were released at a constant rate by the end of the reaction. Interestingly, although the reaction rate was slow at the beginning of the reaction in the 20 M solution, it increased gradually due to the decrease in FA concentration and the solution becomes closer to the optimal pH. In all cases, FA was completely decomposed by the end of the reaction. Furthermore, the percentage of the components in the released gases measured by GC was about 1:1 of H₂:CO₂ during the reaction (Fig. S7[†]). On the other hand, although C6 showed excellent activity in the 1 M FA solution, 2% of the FA remained in the 8 M FA solution after 4 h (Table 1, run 6 vs. 7). In fact, C6 was clearly degraded in large-scale experiments, while the use of C4 led to complete conversion under the same conditions (Fig. S8[†]). Since high stability and activity of catalysts are prerequisites for practical use in hydrogen storage, C4 would be more useful than C6. In addition, a significant observation is that C4 showed the highest TOF at pH 1.7 in the presence of only FA in the reaction solution, which indicates that adjustment of the solution pH is not required to achieve optimum activity for C4. This indicates that although a pyridyl moiety does not further enhance catalytic activity, it gives much higher tolerance and provides more stability than an imidazoline moiety.

For the production of a larger volume of H₂, the dehydrogenation reaction catalysed by C4 was carried out in 1 L of 10 M FA solution at 50 °C (Fig. 3). After the reaction started, it maintained a very high average TOF value of 7340 h^{-1} . The total volume of the released gases reached about 0.4 m³ after 114 h. After the reaction rate became slow due to the decrease in substrate concentration, 10 mol of FA in 100 mL of H₂O was added to the reaction solution (Fig. 3). This second stage of reaction maintained high catalytic activity for a total of 363 h, and the average TOF value was 6250 h⁻¹. This means that the catalyst was still active in the second stage of the reaction. Overall, 1.02 m^3 of gases (H₂:CO₂ ratio of 1:1) was released from 20 mol of FA. HPLC analysis of the reaction solution showed that FA was completely converted to H₂ and CO₂ gases, and the final TON was 2000000. Although this epoch-making value was obtained only on the laboratory scale, C4 could be a promising catalyst for a future chemical hydrogen storage system. Furthermore, these reaction conditions (i.e., aqueous FA solution without any additives) can be assumed to be optimal because gas evolution was sustained as long as the FA concentration remained in a suitable range. For example, the addition of SF to the FA solution led to a



Fig. 2 (a) The plots of the TOF *versus* concentration of FA (solid line) and the volumes of released gases (dashed line) for the dehydrogenation of FA by C4 (50 μ M) at 60 °C. (b) The time courses of the volumes of the released gases in various FA concentrations at 60 °C by C4 in 8 M (red), 12 M (blue), and 20 M (black).



Fig. 3 The time courses of the volume and rate of released gases by FA dehydrogenation in 1 L of 10 M FA solution with C4 (10 μ M at the beginning of the reaction) at 50 °C (red: rate, black: volume of released gases).



Fig. 4 The time courses of the volume and rate of released gases, and the pressure of the vessel for FA dehydrogenation in 8 M FA solution (80 mL) at 60 °C by C4 (25 μ M). (red: rate of released gases, blue: pressure, black: volume of released gases, conditions: pressure gauge of the back pressure valve was set at 1 MPa).

significant decrease in the rate owing to the increase in pH caused by consumption of FA (Fig. S1†). Practical production of H_2 requires ease of handling (*e.g.*, no need for any additives) and control of the reaction system, both of which were achieved in FA dehydrogenation by C4.

We also investigated high pressure H_2 gas production in a closed vessel. The reaction was carried out using C4 at 60 °C in a glass autoclave with a back pressure valve set at 1 MPa (Fig. 4). After 47 min, the pressure reached 1 MPa and the gases started to be released through the back pressure valve. Even under high pressure conditions, no significant decrease in reaction rate was observed, and the average TOF was 17 700 h⁻¹, which was almost the same as that at atmospheric pressure (19700 h⁻¹, Table S5†). Compared to the results in Fig. 3, the reaction rate appeared to decrease earlier because a relatively small amount of FA (0.64 mol) was loaded.

After the gas evolution stopped, the residual FA concentration was only 0.4 mM (conversion yield, 99.995%). It is clear that the equilibrium between CO_2/H_2 and FA even under high pressure conditions favours gas evolution. It was confirmed by GC that the released gases were composed of only H_2 and CO_2 without CO (<1 ppm, Fig. S9†). This result could be very important for the supply of H_2 gas to devices such as fuel cells, which are easily degraded by a small amount of CO.

Conclusions

Effective catalysts for FA dehydrogenation for H_2 evolution were synthesized by the use of Cp*Ir catalysts with imidazoline derivatives. The C4 catalyst featuring a bidentate ligand with imidazoline and pyridine moieties displayed an improved stability and activity, especially in low pH solutions. C4 completed FA dehydrogenation with a fixed reaction rate even under higher FA concentration conditions, and as a consequence, 1.02 m³ of gas was produced and a TON of 2 000 000 was achieved using 20 mol of FA and 10 µmol of C4 in 363 h. In this experiment, complicated operations such as frequent additions of substrates or additives, or monitoring the solution system were not required. Furthermore, the gases could be released under high pressure conditions without any significant decrease in the reaction rate. An important feature of the C4 complex is that it displays optimum activity and high stability in acidic (pH 1.7) conditions. From the viewpoint of practical use in a hydrogen storage system, these results will contribute to the development of novel catalyst designs and the realization of a viable hydrogen storage system.

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