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The perplexing pH and concentration-dependent hydrogen production from formic acid catalyzed by iridium complexes in aqueous solutions

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ABSTRACT

Iridium based catalysts exhibit promising potential for large-scaled hydrogen production from formic acid due to their high activity and stability in base-free aqueous solutions. However, the performance of many of them is highly pH and catalyst concentration dependent, diminishing substantially at high catalyst concentrations, imposing grand challenges for fundamental understanding and scaling up and practical applications at large volume densities. In this work, we conduct a kinetic analysis to quantitatively examine the correlations between the turnover frequency (TOF) of a typical Iridium-based catalyst and its pH and concentration. The study reveals the intrinsic mechanism for the long-standing perplexing pH and concentration dependences of hydrogen production rates. Inspired by the mechanism, a new catalyst is developed. The hydrogen production rate of this catalyst increases linearly with concentration, thereby facilitating successful scale-up of formic acid dehydrogenation. These results not only address difficulties in practical applications but also offer valuable insights for future catalyst design.

1. Introduction

Hydrogen has long been recognized as a promising clean energy source in future renewable energy technologies due to its unique property of producing water as the sole product during combustion [1-8]. However, challenges remain in many aspects of hydrogen storage, transportation, and handling. One promising approach to address these difficulties is chemical storage [9–11]. Formic acid (FA), known for its high volumetric hydrogen capacity (53g $H_2 L^{-1}$), non-toxic nature, and relative safety in handling, has emerged as a promising hydrogen chemical storage material, particularly in automotive applications [10-19]. Envisioning a secure and reliable energy storage and utilization system for the next generation of hydrogen-powered vehicles involves carrying FA in liquid form and releasing hydrogen through selective dehydrogenation of FA, followed by direct consumption of hydrogen via a PEM fuel cell [20–22]. As a result, recent research efforts have been directed toward developing efficient catalytic systems for the dehydrogenation of FA.

In recent years, a variety of homogeneous catalysts based on

Rhodium [15,23], Ruthenium [20,24–29], Iron [30–34] and Manganese [35,36] have been reported for the selective dehydrogenation of FA under variable conditions. Some of these catalysts must be dissolved in organic solvents, e.g. DMF, DMSO, to function efficiently, which may not be favorable for many applications, e.g. automobiles, due to concerns about cost, pollution and toxicity. Some require the presence of amines or other organic bases to achieve high efficiency. The amines and organic bases can poison the catalyst of hydrogen fuel cells. Therefore, a catalytic system that can operate in simple aqueous solutions without the need for organic base protection is highly desirable for practical applications.

Iridium-based complexes have been demonstrated to function effectively in base-free aqueous solutions [37–43]. Examples of high turnover frequencies (TOFs) and high turnover numbers (TONs) achieved by Iridium-centered catalysts have been reported [40,44,45]. In our previous work [43], we have conducted an extensive evaluation of Cp*Ir(N–N)Cl catalysts for formic acid dehydrogenation, analyzing the relationship between stability, activity, and structural features. In practical applications, a high production rate of hydrogen from a small

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volume of catalytic solution is highly desirable for high-power fuel cell electricity generators with high energy densities, necessitating a high catalyst loading in the formic acid dehydrogenation system. On the one hand, this practical consideration differs from routine laboratory practice where the catalytic performance is usually evaluated under low catalyst concentrations. On the other hand, the catalytic activities of many of these catalysts decrease substantially when the catalyst concentration is increased and vary significantly with pH [38,46]. These unexpected catalytic outcomes not only raise interesting and important questions about the fundamental mechanistic understanding of the reaction, but also impose serious challenges for the manufacturing of electricity generators of high power and high energy densities from the catalytic systems.

Herein, we conduct a comprehensive kinetic analysis of an effective Ir-based catalyst, employing both experimental and theoretical approaches. Our investigation quantitatively illustrates the impact of pH and catalyst concentration on the catalytic activity, and reveals that the coordination equilibrium of the anions present in the solution is the major limiting factor. Inspired by this mechanism, a new catalyst is successfully developed to facilitate a linear increase in hydrogen production rate with catalyst concentration.

2. Method

2.1. Experimental section

General. Unless otherwise noted, all the commercially available chemicals were used as received. NMR spectra were measured with a Bruker Avance III HD 600 MHz with a 5 mm DCH cryoprobe. The pH values were measured by an Asmik with a glass electrode after calibration with standard buffer solutions. The amount of released gases was measured by Alicat Whisper Series Mass flow meter (range from 0 to 500 sccm and 0–5000 sccm). The simultaneous automatic recording of temperatures, gas flow rates and pressures was performed with a Guava-TFP Reaction Monitoring System from Beijing Guava Science, Inc. (www

.qmztech.com). Water used in the reactions was HPLC grade. Syntheses of the catalysts and detailed experimental procedures were described in the supporting information.

2.2. Computational details

For catalytic mechanism calculations, the geometry optimization and frequency analysis of catalysts were calculated at the level of M06 [47]/Def2TZVP [48,49] with SMD solvation model (H₂O as solvent). Vibrational frequency calculations were also conducted to verify all optimized structures as minima (no imaginary frequency) or first-order saddle point (one imaginary frequency) and free energies were provided at 298.15 K. Transition states located were checked by performing intrinsic reaction coordinate (IRC) [50,51] calculations to confirm that each of them actually connects the two desired minima. DFT calculations were carried out with the Gaussian 16 [52] software package and the thermodynamic results were calculated by the Shermo [53] software package.

3. Result and discussion

3.1. TOF and hydrogen production rate diminish with the increase of catalytic concentration

A pentamethylcyclopentadienyl (Cp*) Iridium complex [41,54,55] with N,N bidentate ligands (cat-1) has been synthesized in this work (Fig. 1e), representing a typical and highly efficient catalyst for formic acid dehydrogenation. Displayed in Fig. 1a, the catalytic turnover frequency (TOF) decreases with increasing catalyst concentration within the same volume (20 mL water). The TOF drops to about 1/3 when the concentration increases for about twenty times. As a consequence, the total hydrogen production rate increases only for less than two times when the concertation increases for 4 times from the 5-mg load to the 20-mg load, as shown in Fig. 1b. It is even worse that the hydrogen production rate levels off at high concentrations, e.g. the rates are very



Fig. 1. (a) TOF at 80 °C versus mass of cat-1 in 20 mL DI water; (b) Hydrogen production rate V at 80 °C versus mass of cat-1 in 20 mL DI water. Pure formic acid is added into the catalyst aqueous solution and the pump rate of FA gradually increases until the TOF reaches its maximum value. (c) pH-dependent experiment of FA dehydrogenation at 80 °C. All experiments are conducted in a 1 M FA aqueous solution with different types of acidic and base additives to adjust the pH from 0.6 to 7. Comparison is made among different acidic additives in FA solution. (d) TOF at 80 °C versus concentration of FA in aqueous solution. (e) Structure of cat-1 catalyst.

similar at the 15 and 20-mg loads (Fig. 1b), which means that the volume density of producing hydrogen can't be increased by increasing the catalytic concentration at high concentrations. The results illustrates apparent decreases in the slopes of the curves for the hydrogen production rate and TOF with respect to the catalyst concentration. These findings highlight challenges within the catalytic system when scaling up for practical applications.

3.2. TOF is dependent on pH and FA concentration

To further explore the mechanism and elucidate the aforementioned phenomena, pH-dependent and FA concentration-dependent experiments were conducted on cat-1.

The dehydrogenation activity of cat-1 in a 1 M formic acid (FA) solution was initially investigated through pH-dependent experiments. The solution acidity was enhanced by introducing additional protons into the FA solution, adjusting the pH from 1.8 to 0.6. Furthermore, extra base (NaOH) was introduced into the 1 M FA solution, leading to pH changing from 1.8 to 7. To evaluate the possible effect of additional anions in the system, three types of acids (HCl, H₂SO₄, and H₃PO₄) were utilized and compared. Notably, a pH of 1.8 represents the pH value of a 1 M FA solution without the addition of any other acids. As evident from the plotted results (Fig. 1c), the addition of extra protons into the reaction system did not enhance the turnover frequency (TOF). On the contrary, the catalytic activity is diminished by the addition of acids. Reducing the proton concentration doesn't help either. As can be seen from the blue columns in Fig. 1c, the TOF is maximum at about pH = 1.8, and quickly decreases no matter the pH value increases or decreases. Additionally, anions have an apparent effect on TOF. Specifically, the addition of HCl has the most detrimental impact on the catalytic activity (gold columns in Fig. 1c), H₃PO₄ second (red columns in Fig. 1c), whereas the effect of H_2SO_4 is very slight (blue columns in Fig. 1c). This trend is consistent with the coordination ability of the anions to transition metal cations. The coordination ability of Cl- is strongest, and those of PO_4^{3-} and HPO_4^{2-} and $H_2PO_4^{-}$ are second. SO_4^{2-} and HSO_4^{-} can only weakly coordinate to transition metal cations, which is also supported by DFT calculations in Fig. 2c. The result suggests that the catalytic mechanism of cat-1 may involve the dissociation and association of Cl⁻ with the Ir cations. The presence of an excess of Cl⁻ in the system may shift the equilibrium to the non-catalytic Cl⁻-associated Ir and thus reduce the number of catalytic Cl⁻ free Ir cations. A comprehensive discussion of the proposed catalytic mechanism will be provided later in detail

We conducted a concentration-dependent experiment on cat-1 to determine the optimal formic acid (FA) concentration under the same condition. The TOF is calculated and compared across a range of FA concentrations, from commercially available concentrated FA (\geq 98 %) to 1 M FA solution (Fig. 1d). The results in Fig. 1d demonstrates that 5 M



Fig. 2. (a) Energy profiles of the catalytic reaction by cat-1. The numbers above the bar refer to the activation energies and reaction energies in kcal/mol at 353.15 K. The black line shows the reaction path from MH to TS2, whereas the green line shows the reaction path from MH to TS2-2. (b) The Arrhenius plot of TOF values of cat-1. The activation energy is calculated to be 15.6 kcal/mol. The reaction was carried out using 1 mg cat-1 dissolved in 20 mL of DI water. Pure FA was then adding using a syringe pump at a constant flow rate (from 0 to 0.12 mL/min). (c) Energy profiles of M with different ligands (Cl⁻, HSO⁻₄, H₂PO⁻₄, H₂O). The numbers above the bar refer to the reaction energies in kcal/mol at 353.15 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

is the optimal concentration. Both excessively concentrated and overly dilute FA solutions don't yield significant catalytic activity for cat-1.

3.3. A proposed reaction pathway

Based on the aforementioned findings and in consideration of research on other catalysts of similar structures [41,56,57], a tentative catalytic mechanism is proposed, as illustrated in Scheme 1. In summary, the dehydrogenation of formic acid (FA) using an Ir-based complex typically involves four sequential steps. The initial step entails the dissociation of Cl⁻ from the Iridium center, followed by formate coordination to the Iridium center as the second step. The third step involves the dehydrogenation of formate, along with the release of carbon dioxide to form an Ir-hydride complex intermediate. The final step encompasses the dehydrogenation from the catalytic center, leading to the release of hydrogen gas and the regeneration of the intermediate M. The formation of the Ir-H complex has been substantiated through NMR studies (Figs. S1-S3). Additionally, NMR investigations have underscored the significance of the presence of a proton solvent, indicating that the existence of free formate anion, rather than formic acid, is crucial for the generation of the Ir-H complex. This observations are consistent with the concentration/pH-dependent matrix experiments.

Density Functional Theory (DFT) calculations of the free-energy profiles for the catalytic reaction by cat-1 has supported the proposed mechanism (Fig. 2a). The calculation suggests that the rate-determining step is the dehydrogenation of formate by coordinating H to the metal center, consistent with previous kinetic isotope experiments [58]. The energy barrier between the transition state **TS1** and **MF** ($\Delta E = 13.2$ kcal/mol) happens to agree well with the experimental data from temperature-dependent experiment (Fig. 2b, Ea = 15.6 kcal/mol).

Furthermore, the free energy of the intermediate combining the ligand of water (M – H₂O) is 11.7 kcal/mol higher than that of the catalytic active intermediate M (Fig. 2c), and M – H₂O does not appear in ESI-MS spectra (Figs. S4 and S5), leading to its exclusion from the energy profiles depicted in Fig. 2a. Additionally, the coordination energies of Cl⁻, H₂PO₄, and HSO₄ combining with M are also calculated, with the observed trends consistent with the experimental results in Fig. 1c.

3.4. Kinetic model

Based on the mechanistic calculation, a kinetic model is developed to elucidate the outcomes observed in the pH-dependent and concentration-dependent experiments.

The catalytic cycle is simplified into five steps, as illustrated in Scheme 2. The first step involves the dissociation of formic acid, where K_a represents the equilibrium constant for the dissociation of proton (H⁺) and formate anion (F⁻). In the second step, Cl⁻ dissociates from the Iridium center (M), with K_{Cl} denoting the equilibrium constant for the conversion of Cl⁻ and the catalytic active center (M) to MCl (cat-1). The third step involves the equilibrium between F⁻, M, and the catalyst associated with the formate ligand (MF), where k_F represents the equilibrium constant for M and F⁻ converting to MF. The fourth step also the rate-determining step [58] involves the elimination of CO₂ from MF, leading to the formation of MH, where k_1 is the reaction rate constant from MF to MH. The final step entails the protonation of MH and production of hydrogen, where k_2 represents the rate constant for hydrogen production.

3.5. TOF vs pH values

Based on the kinetic model, K_a and the concentration of formic acid

$$FA \xrightarrow{K_a} H^+ + F^-$$
$$MC1 \xrightarrow{K_{C1}} M + C1^-$$

$$M + F^{-} \xrightarrow{k_{1}} MF \xrightarrow{k_{1}} MH \xrightarrow{k_{2}} M + P$$

Scheme 2. A proposed kinetic process for formic acid dehydrogenation by cat-1.



Scheme 1. A proposed catalytic cycle for dehydrogenation of formic acid by cat-1.

(c_{FA}) are expressed as follows:

$$K_a = \frac{[H^+][F^-]}{[FA]}$$
(1)

 $c_{FA} = [FA] + [F^-] \tag{2}$

The concentration of formate anion F^- can be derived from the combination of equations (1) and (2).

$$[F^{-}] = \frac{K_a c_{FA}}{[H^+] + K_a} \tag{3}$$

The coordination constants $K_{\text{F}},\ K_{\text{Cl}},$ and K_{A} can be expressed as follows:

$$K_F = \frac{[M][F^-]}{[MF]} \tag{4}$$

$$K_{Cl} = \frac{[M][Cl^-]}{[MCl]} \tag{5}$$

Thus the concentration of MF and MCl are derived from equations (4) and (5) as follows:

$$[MF] = \frac{[F^-]}{K_F} [M] \tag{6}$$

$$[MCl] = \frac{[Cl^{-}]}{K_{Cl}} [M]$$
⁽⁷⁾

When assuming MH in the steady state (the rate-determining step), we can set the derivative of the concentration of MH over time to be 0.

$$\frac{d[MH]}{dt} = k_1[MF] - k_2[H^+][MH] = 0$$
(8)

Thus the concentration of MH can be derived from the combination of equations (6) and (8):

$$[MH] = \frac{k_1}{k_2[H^+]} [MF] = \frac{k_1}{k_2[H^+]} \frac{[F^-]}{K_F} [M]$$
(9)

The concentration of catalysts (c_M) can be represented as the sum of the concentration of M, MF, MH, and MCl.

$$c_M = [M] + [MF] + [MH] + [MCl]$$
(10)

Therefore, the concentration of M can be derived from the combination of equations (6), (7), (9) and (10).

$$[M] = \frac{c_M}{1 + \frac{[Cl^-]}{K_{Cl}} + \frac{[F^-]}{K_F} + \frac{k_1}{k_2[H^+]} \frac{[F^-]}{K_F}}$$
(11)

Our DFT calculation reveals that the rate-determining step involves the transition of MF to MH, which implies that the reaction rate (r) is given in equation (12).

$$r = k_1 [MF] = k_1 \frac{[F^-]}{K_F} [M]$$
(12)

Furthermore, the reaction rate (r) and TOF can be derived from the combination of equations (3), (11) and (12) as follows:

$$r = \frac{k_1 c_M}{\left(1 + \frac{|Cl^-|}{K_{Cl}}\right) K_F \frac{|H^+| + K_a}{K_a c_{FA}} + 1 + \frac{k_1}{k_2 [H^+]}}$$
(13)

$$TOF = \frac{V_0 r}{n_M} = \frac{r}{c_M} = \frac{k_1}{\left(1 + \frac{|Cl^-|}{K_{Cl}}\right) K_F \frac{|H^+| + K_a}{K_a c_{FA}} + 1 + \frac{k_1}{k_2 |H^+|}}$$
(14)

Eqs. (13) and (14) suggest that an elevation in the concentration of Cl^- leads to a reduction in both the reaction rate and the turnover frequency (TOF), providing an explanation for the experimental results presented in Fig. 1c: the coordination equilibrium between Cl^- and the

catalytic center is the limiting factor for the [Cl-] dependences.

When adding strong acid like H_2SO_4 or H_3PO_4 to the catalytic solution, there is also an equilibrium of these acids with the catalytic active center M: [MA] \leftrightarrow [M]+[A], where K_A is the coordination constant of MA:

$$K_A = \frac{[M][A]}{[MA]} \tag{15}$$

Thus equation (10) is modified as follows:

$$c_M = [M] + [MF] + [MH] + [MCl] + [MA]$$
(16)

Consequently, TOF can also be determined by equations (16) and (14) as follows:

$$TOF = \frac{k_1}{\left(1 + \frac{|Cl^-|}{K_{Cl}} + \frac{|A|}{K_A}\right)\frac{K_F}{|F^-|} + 1 + \frac{k_1}{k_2|H^+|}}$$
(17)

The concentration of anion ([A]) such as HSO_4^- and $H_2PO_4^-$ can be derived from the relationship of charge conservation as follows:

$$[A] \approx [H^+] - [F^-] \tag{18}$$

Under such a situation, the catalytic activity (TOF) is expressed as follows:

$$TOF = \frac{k_1}{\left(1 + \frac{|Cl^-|}{K_{Cl}} + \frac{1}{K_A} \left([H^+] - \frac{K_a c_{FA}}{|H^+| + K_a}\right)\right) K_F \frac{|H^+| + K_a}{K_a c_{FA}} + 1 + \frac{k_1}{k_2 |H^+|}}$$
(19)

Equations (17) and (19) quantitatively correlates TOF with the concentration of proton. As shown in Fig. 2c, HSO₄ can only weakly coordinate to catalytic active center M, thereby we assume that the concentration of MA is too low to be included. Consequently, the calculation of TOF versus pH values based on eq. (17) is plotted in Fig. 3a as the red curve In contrast, $H_2PO_4^-$ exhibits a comparatively stronger coordination with M, reducing the TOF at equivalent pH levels. This relationship, based on Equation (19), is represented by the blue curve in Fig. 3a. The parameters used in these equations are provided in Table 1. The calculations (lines) in Fig. 3a describe the experimental data (dots) extremely well, suggesting that the pH dependence of TOF is the natural consequence of coordination equilibria described in Scheme 2. The calculations also demonstrate that k₁ (about 80) is significantly smaller than k₂ (about 15,000), as shown in Table 1. This is consistent with the DFT calculation results that the energy barrier to release CO₂ (the kinetic step described by k_1) is significantly higher than that to release H₂ from the metal center (the kinetic step described by k₂).

3.6. TOF vs catalyst concentration

In catalyst concentration-dependent experiments, the concentration of c_M in eq. (10) can be simplified as follows:

$$c_{M} = \left(1 + \frac{[F^{-}]}{K_{F}} + \frac{k_{1}}{k_{2}[H^{+}]} \frac{[F^{-}]}{K_{F}}\right) [M] + [MCl] = m[M] + [MCl]$$
(20)

Because of the stable concentrations of protons and formic acid in specific conditions, m is assumed to be a constant.

$$m = 1 + \frac{[F^-]}{K_F} + \frac{k_1}{k_2[H^+]} \frac{[F^-]}{K_F}$$
(21)

Based on the equilibrium of MCl, the concentration of MCl and Cl^- can be represented by the concentration of M:

$$[MCl] = c_M - m[M] \tag{22}$$

$$[Cl^{-}] = c_{M} + m[M] \tag{23}$$

Thus K_{Cl} is expressed as follows:



Fig. 3. (a) pH-dependent results of FA dehydrogenation at 80 °C (dots) and the calculations (the red and blue curves) of TOF (s⁻¹) vs pH values based on equations (17) and (19), respectively. (b) Plot of the reaction rate at 80 °C versus concentration of cat-1 (c_m) in 20 mL DI water (dots) and the calculation (the red curve) based on equation (26). (c) Plot of the TOF (s⁻¹) at 80 °C versus concentration of cat-1 (c_m) in 20 mL DI water (dots) and the calculation (the red curve) based on equation (27). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1

Farameters of the carculations in Fig. 5.					
Calculations	c _{FA}	k ₁ ^c	k ₂	K _A	m
Fig. 3a	1 M	$\textbf{76.2} \pm \textbf{3.1}$	14929 ± 2258	/	/
Eq. 17 Fig. 3a	1 M	$\textbf{83.8} \pm \textbf{2.1}$	14929 ^c	0.0898 ± 0.0159	/
Fig. 3b	5 M ^b	$\overline{62.0\pm1.4}$	$\overline{12062\pm272^e}$	/	4.16 ^d
Eq. 26 Fig. 3c	5 M ^b	66.5 ± 3.2	$12938\pm 623^{\text{e}}$	/	

 a K_a is calculated with the equation [59] pK_a = -57.528+2773.9/T+9.1232 ln T, when T = 353.15 K, K_a = 1.4E-4. According to the DFT calculations and experimental results, K_F, K_{Cl} and [Cl⁻] are assumed to be 0.01, 4.4E-4 and 3.5E-5 M, respectively.

^b The concentration of FA in Fig. 3b and c is assume to be 5 M, which is the best condition for FA dehydrogenation in Fig. 1d. Thus $[F^-]$ and $[H^+]$ assumed to be equal to 0.02646 M.

 $^{\rm c}\,$ k₂ in eq. (19) is assumed to be equal to that in the calculation of eq. (17).

 $^{\rm d}$ m is calculated with the parameters in Fig. 3a and eq. (17).

 $^{e}\,$ k_{2} in Fig. 3b & c are calculated by equation (21).

$$K_{Cl} = \frac{[M][Cl^{-}]}{[MCl]} = \frac{c_M[M] + m[M]^2}{c_M - m[M]}$$
(24)

The solution to the quadratic equation in terms of [M] can be obtained as follows:

$$[M] = \frac{-(c_M + mK_{Cl}) + \sqrt{(c_M + mK_{Cl})^2 + 4c_M mK_{Cl}}}{2m}$$
(25)

The reaction rate (r) and TOF with respect to the catalyst concentration (c_M) can be expressed as follows:

$$r = k_1 \frac{[F^-]}{K_F} [M] = k_1 \frac{[F^-]}{K_F} \times \frac{-(c_M + mK_{Cl}) + \sqrt{(c_M + mK_{Cl})^2 + 4c_M mK_{Cl}}}{2m}$$
(26)

$$TOF = \frac{r}{c_M} = k_1 \frac{[F^-]}{K_F} \times \frac{-(c_M + mK_{Cl}) + \sqrt{(c_M + mK_{Cl})^2 + 4c_M mK_{Cl}}}{2mc_M}$$
(27)

Eqs. (26) and (27) take into consideration of the metal center bound with Cl^- when the catalytic concentration is not small compared to that of water in the solution, resulting in the nonlinear dependences of hydrogen production rate and TOF on the catalytic concentration. A larger catalytic concentration results in a smaller TOF (eq. (27)). The predictions of eqs. (26) and (27) describe experimental observations very well. As displayed in Fig. 3b and c, the calculations for the reaction rate (r) and the turnover frequency (TOF) as functions of c_M based on eqs. (26) and (27) nicely reproduce the experimental results. Combining the calculations in Fig. 3, k_1 is in the range of 60~85, and k_2 is between 12,000 and 15,000.

3.7. Development of new catalyst

Comparing eq. (14) with eq. (27), it is clear that the TOF restricted by the catalytic concentration is because of the association of chloride ions with the Ir centers. Therefore, removing Cl^- from the catalytic system or replacing it with a much weaker ligand must be able to improve the situation. Based on such a reasoning, a new Iridium complex, cat-2 (Fig. 4a), lacking the Cl^- ligand, has been synthesized by treating cat-1 with silver sulfate.

Cat-2 is characterized by a unique N–N ligand structure, which notably lacks the γ -(N)H group present in the structure of cat-1. This structural difference is confirmed by FTIR and ESI-MS spectral analysis, as depicted in Fig. S6 and Fig. S4&S5, respectively. DFT calculations, presented in Fig. S7, demonstrate that the free energy of cat-2's catalytic active site (denoted as M') is approximately 29 kcal/mol higher than that of M. However, as shown in Fig. 4b – Fig. S4 &S5, M and M' are interchangeable, depending on the acidity of the solvent. During catalytic reactions in aqueous formic acid solution, the concentration of M increases. This suggests that the intermediate M remains a crucial contributor to the catalytic process of cat-2, rather than being supplanted by M'. Thus, we believe that the pH dependence of cat-2 is similar to that of cat-1, as both catalysts share the same catalytic active center, M.

TON measurements which reflect the stability of catalysts were conducted with cat-1 and cat-2. Both catalysts were dissolved in 200 mL DI water and preheated to 80 °C, then pure formic acid was added to the catalyst aqueous solution at a constant rate (from 0 to 0.12 mL/min). The TON was calculated by totalizing the overall gas generation volume. The TON versus time curves for the two catalysts are depicted in Fig. 4c. As observed, the TON for cat-2 is nearly identical to that of cat-1 (cat-1: 1,718,614 vs cat-2: 1,758,550). The slopes of the two curves before 5 h also indicate that the initial TOFs of the two catalysts are almost equal (cat-1: 145,563 h^{-1} vs cat-2: 131,480 h^{-1}). However, the TOF of cat-2 is slightly lower than that of cat-1 in the 5-10 h range, suggesting that cat-2 decomposes at a faster rate compared to cat-1. This can be explained by our previous work [43], which demonstrated the underlying cause of Ir catalyst degradation. Specifically, the catalytic center M is prone to decomposition within the catalytic cycle, particularly under hydrogen-poisoning conditions. For cat-1, the equilibrium between Cland MCl allows Cl- to provide a protective effect on the metal center during decomposition. In contrast, cat-2, represented by M', converts directly to M in the formic acid solution, lacking this protective mechanism. As a result, a slight difference in stability emerges between the



Fig. 4. (a) Structure of cat-2 catalyst sythesized from cat-1. (b) Structures of M and M'. They are interchangeable, depending on the acidity of the solvent. (c) Plot of the TON of cat-1 and cat-2 at 80 °C overtime (1 mg catalyst in 200 mL DI water). Pure formic acid was added to the catalyst aqueous solutions at a constant rate (from 0 to 0.12 mL/min). (d) Plot of the hydrogen production rates (the flow rate of CO_2+H_2 , $CO_2/H_2 = 1/1$) at 80 °C versus mass of cat-1 and cat-2 in 20 mL DI water and the linear fitting with results of cat-2. (e) Plot of the concentration of cat-1 (c_M) versus the degree of dissociation (α) from MCl to M, and the calculation (the red curve) based on equation (32). α is equal to TOF_{cat-1}/TOF_{cat-2}. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

two catalysts, especially within the 5–10 h range. During this period, the concentration of the active species M in cat-1 is marginally higher than in cat-2, leading to a higher TON for cat-1. This observation suggests that the absence of chloride ions has a relatively minor effect on the catalytic activity and lifespan of the two catalysts at low concentrations. Comparison between these catalysts with selected ones from literature can be found from our previous work [43].

Cat-2, in the absence of Cl⁻, demonstrates stable activity even at high catalyst concentrations, allowing the hydrogen production rate to maintain a linear relationship with the catalyst concentration. As shown in Fig. 4d, the hydrogen production rate of cat-2 (black) exhibits a nearly linear increase as the catalyst concentration rises, in contrast to the non-linear growth observed for cat-1 (red).

This linear behavior is further supported by our kinetic model, as depicted in Fig. 4e which illustrates the relationship between the catalyst concentration (c_M) and the degree of dissociation (α) for MCl. The degree of dissociation can be quantified by the ratio of TOF values for cat-1 to cat-2 as follows:

$$\alpha = \frac{TOF_{cat-1}}{TOF_{cat-2}}$$
(28)

The value of $c_M \alpha$ can be identified as the sum of concentration of all catalytic intermediates, excluding MCl. The concentration of Cl⁻ and MCl can also be expressed by $c_M \alpha$ as follows:

$$c_{M}\alpha = [M] + [MF] + [MH] = m[M]$$
(29)

$$[Cl^{-}] = c_M(1+\alpha) \tag{30}$$

$$[MCl] = c_M(1 - \alpha) \tag{31}$$

Therefore, combining eq. (24) and eqs. (29)–(31), we derive the relationship between the concentration of catalyst (c_M) and the degree of dissociation (α) as follows:

$$c_M = \frac{(1-\alpha)}{\alpha(1+\alpha)} m K_{Cl} \tag{32}$$

The calculated value of mK_{Cl} is 1.83E-3 \pm 1.38E-4, as determined

from eq. (32) depicted in Fig. 4e. This value exhibits an excellent fit with the results listed as $mK_{Cl} = 1.83E-3$ in Table 1, lending further credibility to our kinetic model.

The experimental results suggest that cat-2, following the removal of chloride ions, exhibits the potential for large-scale hydrogen production with a large volume density. At the concentration of 20 mg cat-2/20 mL water as shown in Fig. 4d, more than 85 L of H₂/minute can be produced from 1 L of the catalytic solution, which can generate about 5.5 KW electricity with a fuel cell. To date, we have achieved a rate of 22 m³ of H₂ per hour with 12 g of cat-2 in 18 L of water (1 mM). For a passenger car which typically consumes an average power lower than 20 KW (the average power of TESLA model S is about 17 KW at the average speed of about 100 km/h), less than 4 L of the catalytic solution is sufficient to provide the required power.

4. Conclusion

Iridium catalysts for formic acid dehydrogenation have demonstrated high catalytic activity and stability under low catalyst loading, but their performance at high catalyst concentrations significantly diminishes and vary significantly with pH. This limitation imposes a considerable constraint on the application of these catalysts for many large-scale hydrogen production systems that require large volume densities, e.g. automobiles. In this study, we conduct quantitative investigations using a typical Ir-Cl catalyst (cat-1) to elucidate the correlations between the turnover frequency (TOF) and the catalyst concentration, pH, temperature, and formic acid concentration. Additionally, we employ DFT calculations to explore the reaction mechanism. Our experimental results and theoretical studies indicate that the dissociation and coordination equilibria between Cl⁻ and proton and the Ir center limits the linear increase of hydrogen production rate with the concentration of catalysts. Based on this mechanism, we have developed a new enhanced Iridium catalyst (cat-2) without Cl-, which exhibits constant activity at high catalyst concentrations, enabling the hydrogen production rate to exhibit a linear correlation with the catalytic concentration. The kinetic model and catalyst design approach proposed in this work offer valuable insights for the application of iridium-based catalysts in scaled-up formic acid dehydrogenation systems in the future.

CRediT authorship contribution statement

Chuanqing Hao: Writing - review & editing, Writing - original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Chengzhen Shen: Visualization, Validation, Software, Resources, Investigation, Formal analysis, Data curation, Conceptualization. Yufan Zhang: Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Jitian Liu: Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation. Xin Chen: Validation, Supervision, Resources, Investigation, Formal analysis, Data curation, Conceptualization. Jianxin Guan: Writing - review & editing, Writing original draft, Visualization, Validation, Supervision, Resources, Methodology, Investigation, Formal analysis, Data curation. Zhihao Yu: Writing - original draft, Validation, Supervision, Software, Investigation, Formal analysis, Data curation. Junrong Zheng: Writing - review & editing, Writing - original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Junrong Zheng reports financial support was provided by the National Science Foundation of China (NSFC-21927901, 92261206, 21627805, 12174012, and 21821004). Junrong Zheng reports financial support was provided by Beijing Guava Science Inc. Junrong Zheng reports financial support was provided by MOST (special talent programs) of China. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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C. Hao et al.

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