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Promotion of Iridium Complex Catalysts for HCOOH Dehydrogenation by Trace Oxygen[1]

Yulu Zhan[a, b], Yangbin Shen[b, c], Ying Du[a, b], Baohua Yue[a], and Xiaochun Zhou[b, d, *]

[a] *Department of Chemistry, College of Sciences, Shanghai University, 99 ShangDa Road, Shanghai, 200444 P.R. China*

[b] *Division of Advanced Nanomaterials, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou, 215125 P.R. China*

[c] *University of Chinese Academy of Sciences, Beijing, 100049 P.R. China*

[d] *Key Lab of Nanodevices and Applications, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou, 215123 P.R. China*

**e-mail: xczhou2013@sinano.ac.cn*

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Abstract—Ir complexes are important homogeneous catalysts for formic acid (FA) dehydrogenation. This paper reports that the activity of Ir complexes can be greatly improved through the activation by trace amounts of oxygen. After activation the activity of the heterodinuclear Ir–Ru catalyst increased 18-fold whereas for the mononuclear catalyst a 23-fold increase was observed. Oxygen is the key factor for the activation. But an excessive concentration of oxygen has a negative effect on the activity. There is an optimal concentration of H_2O_2 for the activation of Ir complex catalysts in HCOOH dehydrogenation. A very low concentration of oxygen (2.4×10^{-6} M) is needed for the activation of the heterodinuclear Ir–Ru catalyst while the mononuclear catalyst requires the presence of oxygen in a much higher concentration (290×10^{-6} M). From the results of the study it can be inferred that the activation of complex catalysts is due to the interplay of chemical and structural changes. These findings may be helpful in the attempts to improve the catalytic activity of homogeneous catalysts, which are widely used in formic acid dehydrogenation, CO_2 reduction and in other processes. In addition, this paper indicates that iridium complexes are excellent catalysts for the direct synthesis of H_2O_2 from the H_2 and O_2.

Keywords: formic acid dehydrogenation, iridium complex catalysts, oxygen, hydrogen peroxide, activation

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INTRODUCTION

Hydrogen is a renewable and environmentally friendly energy carrier for fuel cell applications because it possesses a high-energy content and gives water vapor as a clean exhaust product [1–3]. But current hydrogen storage technology is still far from meeting the application requirements [4–11]. Formic acid (**FA**) is a promising material for storage and production of hydrogen [12–14], since it can be produced by conversion of biomass or reduction of carbon dioxide [15–17]. In the presence of the catalyst, FA can be dehydrogenated to CO_2 and H_2 at mild conditions. Unlike the conventional methods used to generate hydrogen, the FA dehydrogenation can be performed at room temperature, and the produced hydrogen with low CO content can be directly used in proton exchange membrane fuel cell (**PEMFC**). Accordingly, the search for the catalysts for FA dehydrogenation has attracted considerable attention. The FA decomposition mainly follows two reaction pathways [12]:

$$HCOOH = CO_2 + H_2,\ \Delta G = -48.4\ \text{kJ mol}^{-1}, \quad \text{(I)}$$

$$HCOOH = CO + H_2O,\ \Delta G = -28.5\ \text{kJ mol}^{-1}. \quad \text{(II)}$$

The first pathway describes the desired FA dehydrogenation, while the second route is associated with an undesired side reaction, which generates CO poisoning to the proton exchange membrane fuel cell (PEMFC). Since the PEMFC needs high quality hydrogen with CO less than 100 ppm, a high selectivity for the first pathway in reaction (I) is required from the catalysts for FA dehydrogenation.

The catalysts for FA dehydrogenation can be mainly divided into two types: homogeneous [18–22] and heterogeneous systems [7, 23–29]. The heterogeneous catalysts are metal nanoparticles or nanoalloy [27, 30, 31], while a number of organic complexes are used as homogeneous catalysts. The homogeneous catalysts usually show very high selectivity for FA

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dehydrogenation and an adequate activity. However, the development of catalysts with an improved activity remains an important challenge, because an enhanced activity entails the reduction in the size of equipment, it also brings a lower cost, lower reaction temperatures and higher efficiency.

As important homogeneous catalysts for FA dehydrogenation, Ir complexes have many advantages, such as high activity, high selectivity, high stability and feasible synthesis procedure [32–37]. This paper reports that the activity of mononuclear Ir and heterodinuclear Ir–Ru complex catalysts can be improved by more than 10 times through a simple activation process.

EXPERIMENTAL

Synthesis of Ir–Phenanthroline Complex

$[Ir^{III}(Cp^*)Cl_2]_2$. Excess 1,2,3,4,5-pentamethylcyclopentadiene was added in H_2IrCl_6 methanol solution. The molar ratio of 1,2,3,4,5-pentamethylcyclopentadiene to H_2IrCl_6 was about 2.5 : 1. The mixture was stirred under reflux for 37 h, and then cooled to 0°C to yield a yellow brown product after filtration and washing with ether.

[(Cp*)Ir(phen)Cl]Cl. 1,10-phenanthroline and $[Ir^{III}(Cp^*)Cl_2]_2$ were mixed in the molar ratio of 2 : 1, $[Ir^{III}(Cp^*)Cl_2]_2$ (0.08 mmol) was added to dichloromethane (16 mL), two equivalents of the 1,10-phenanthroline was added to the above suspension. The mixture was stirred for 5 h at room temperature, until the color turned from orange to yellow-orange. The recrystallization was carried out on the reaction liquid using ice water, which gave the product a yellow powder in good yield [38].

Synthesis of Heterodinuclear Ir–Ru Complex

$[Ir^{III}(Cp^*)(H_2O)_3]SO_4$. The molar ratio of $[Ir(Cp^*)Cl_2]_2$ to Ag_2SO_4 was 1 : 2 in H_2O. The mixture was stirred at ambient temperature for 5 h in the dark, and then the solution was filtered with membrane filter. The filtrate was evaporated under reduced pressure to yield an orange powder of $[Ir^{III}(Cp^*)(H_2O)_3]SO_4$, which was dried in vacuum.

$[Ru^{II}(bpy)_2(H_2O)_2]SO_4$. The molar ratio of $[Ru^{II}(bpy)_2Cl_2] \cdot 2H_2O$ to Ag_2SO_4 was about 1 : 1. The mixture was stirred under reflux for 12 h, then the solution was filtered with membrane filter to form a red powder of $[Ru^{II}(bpy)_2(H_2O)_2]SO_4$.

$[Ru^{II}(bpy)_2(bpm)]SO_4$. The molar ratio of $[Ru^{II}(bpy)_2(H_2O)_2]SO_4$ to 2,2'-bipyrimidine was about 1 : 1 in H_2O, the mixture was stirred at ambient temperature for 5 h and chromatographed on a Sephadex G-10 column using H_2O as an eluent. The product was evaporated under reduced pressure to yield an orange powder of $[Ru^{II}(bpy)_2(bpm)]SO_4$.

$[Ir^{III}(Cp^*)(H_2O)(bpm)RuII(bpy)_2](SO_4)_2$. The molar ratio of $[Ir^{III}(Cp^*)(H_2O)_3]SO_4$ to $[Ru^{II}(bpy)_2(bpm)]SO_4$ was about 1 : 1. The mixture was stirred in H_2O for a few minutes. The product was evaporated under reduced pressure to quantitatively yield a green powder of $[Ir^{III}(Cp^*)(H_2O)(bpm)Ru^{II}(bpy)_2](SO_4)_2$ [39].

RESULTS AND DISCUSSION

Effect of Trace Oxygen on the Activation of the Catalysts

The heterodinuclear Ir–Ru complex catalyst $[Ir^{III}(Cp^*)(H_2O)(bpm)Ru^{II}(bpy)_2](SO_4)_2$ has a very high activity (TOF = 426 h^{-1}) for the hydrogen production from FA even at pH 3.8 and 298 K. We have found that activity of the heterodinuclear catalyst can be further improved by conducting an activation process (Fig. 1). The initial TOF of the heterodinuclear catalyst was 15 h^{-1} in the presence of air, but it reached a value of 337 h^{-1} after the activation. A 23-fold increase was therefore observed.

Since the concentration of FA is expected to decrease during FA decomposition, the reaction rate would be changed. In order to improve the measurement accuracy of reaction rate during FA decomposition, FA in a high concentration (5 M) was used to reduce the change of FA in our experiments. Moreover no formate sodium was added in the reaction mixture. It was found that the initial activity of the heterodinuclear catalyst is not as high as the TOF in literature.

During the activation process of the heterodinuclear catalyst, the volume of the gas produced ($V_{H_2+CO_2}$) slowly increases with time at the oxygen-free conditions (curve *1* in Fig. 1a). At the same time accelerated increase of the gas with time was recorded at the oxygen-containing conditions (curve *2* in Fig. 1a). Figure 1b shows that the heterodinuclear catalyst has a very slow reaction rate (r), i.e. activity, at the oxygen-free condition. On the other hand an increased activity at the oxygen-containing conditions is observed. An increase in activity with time at the oxygen-containing conditions indicates that oxygen can be directly associated with the activation of the heterodinuclear Ir–Ru complex catalyst $[Ir^{III}(Cp^*)(H_2O)(bpm)Ru^{II}(bpy)_2](SO_4)_2$. The activity of activated catalyst is 23 times higher than that of the inactivated system. It is worth noting that the use of oxygen in an excessive concentration (~290 × 10^{-6} M) could cause serious deactivation (not shown).

It appears that the activation process can be subdivided into three stages in Fig. 1b. In the interval from the beginning of reaction to the start time of activation

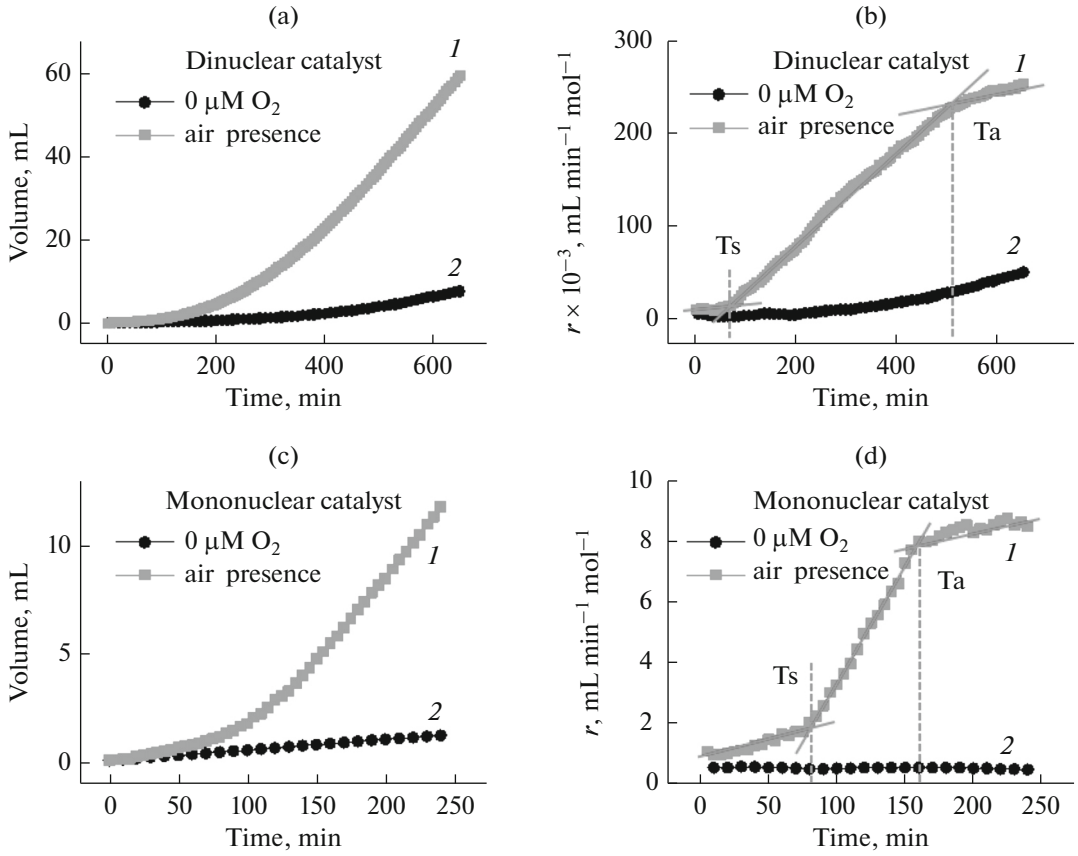


Fig. 1. Effects of promotion of two catalytic Ir complexes at the oxygen-containing conditions. Volume of the gases ($V_{H_2+CO_2}$) produced by FA dehydrogenation as a function of time for heterodinuclear (a) and mononuclear catalysts (c), and reaction rate (*r*) as a function of time for heterodinuclear (b) and mononuclear (d) catalysts, respectively. (*1*) The oxygen-free conditions, (*2*) the oxygen-containing conditions. The reaction was performed at 35°C with [FA] = 5 M. Ts—the start time of activation,Ta—the activation time.

(**Ts**), the heterodinuclear catalyst experiences a slow activation process (curve *2* in Fig. 1b). Then, the heterodinuclear catalyst undergoes a fast activation process that proceeds from Ts to **Ta** (activation time). Thereafter, the activation process comes to the end and the heterodinuclear catalyst reaches a steady activity. Accordingly, we could define Ts as the start time for fast activation, and define Ta as the activation time. The start time of activation is ~70 min, while the activation time (Ta) for heterodinuclear catalyst is as long as 520 min.

Figures 1c, 1d show that the mononuclear Ir complex catalyst [(Cp*)Ir(phen)Cl]Cl is subject to the similar activation process under an oxygen containing condition. After the activation process mononuclear Ir catalyst is ~18 times as active as the nonactivated system. The start time of activation (Ts) is ~70 min, while the activation time (Ta) for mononuclear catalyst is 160 min, which is much shorter than 520 min needed to activate the heterodinuclear catalyst. Note, that the activation of the mononuclear Ir complex requires the oxygen in much higher concentrations in the solution than that of the heterodinuclear Ir–Ru catalyst.

Since the heterodinuclear Ir–Ru complex catalyst $[Ir^{III}(Cp^*)(H_2O)(bpm)Ru^{II}(bpy)_2](SO_4)_2$ has two cores and many ligands, the study of its activation mechanism is fraught with difficulties. The mononuclear Ir complex catalyst [(Cp*)Ir(phen)Cl]Cl has the same Ir core as the heterodinuclear Ir–Ru complex catalyst. They also have some same ligands and similar structure. In order to simplify the research into the activation mechanism, priority in this paper would be given to the mononuclear catalyst.

Figure 2 shows the start time for fast activation (Ts) for the mononuclear catalyst [(Cp*)Ir(phen)Cl]Cl as a function of pH. With the increasing pH, the start time for fast activation (Ts) shows decreasing values. The start time could be zero when the pH value is higher than 3.0. Since the concentration of formate ($HCOO^-$) increases with pH value, the activation process can be associated with formate formation. Therefore, in addi-

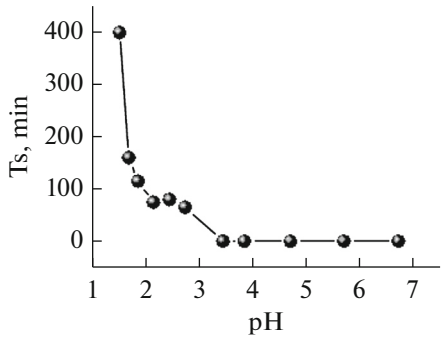


Fig. 2. Start time for fast activation (Ts) as a function of pH for mononuclear catalyst [(Cp*)Ir(phen)Cl]Cl.

tion to oxygen formiate may be another key factor for the activation of catalyst.

The Existence of Hydrogen Peroxide in the Reaction Solution

What role does oxygen play in the activation of the catalytic Ir complex? If oxygen is directly involved in the activation process, the activation rate (dr/dt) should be proportional to the oxygen concentration in solution. In this case the activation rate is expected to reach a maximum value at the start of the reaction, since at this time point the oxygen concentration attains its highest value. As a consequence the activation rate would decrease due to the consumption of oxygen. However, the activation rate (dr/dt) is very low at the beginning of the reaction and shows increasing values after a certain period of time (Ts, ~70 min for mononuclear and heterodinuclear catalysts). Therefore, some intermediates may play the key role in the activation process.

The oxygen and hydrogen can react with each other to directly generate hydrogen peroxide (H_2O_2) mediated by the catalyst [40, 41]. We can further speculate that hydrogen peroxide may be the only species directly participating in the activation process. To examine our speculation, it would be tempting to detect the existence of hydrogen peroxide in the reaction solution. However the detection procedure is very difficult since the solution include many components like HCOOH, catalyst and oxygen. Here, we utilized the specificity of enzyme to detect hydrogen peroxide. Horseradish peroxidase (HRP) can specifically convert non-fluorescent Amplex Red to highly fluorescent resorufin in hydrogen peroxide solution (Fig. 3a) [42, 43]. This method can overcome the negative effect of other species during hydrogen peroxide detection.

Figure 3b shows the in situ UV-Vis absorption spectra of quantitative conversion reaction of Amplex Red to resorufin by H_2O_2. As the reaction proceeds the absorbance bands of resorufin at ~571.5 nm increase in intensity, while that of Amplex Red at ~275 nm decreases, indicating the conversion of Amplex Red to resorufin. The time profile of absorbance at 571.5 nm shows the direct increase of resorufin production

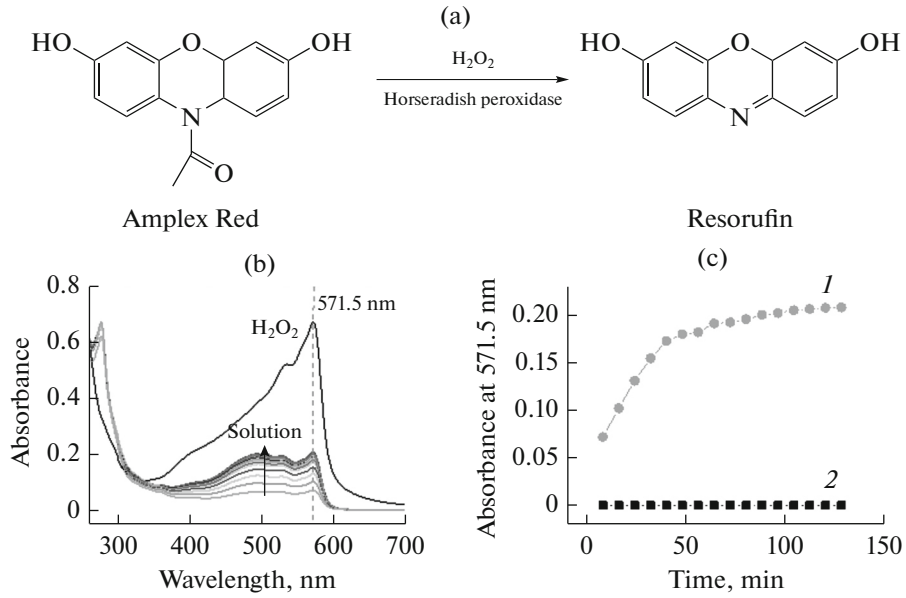


Fig. 3. Detection of hydrogen peroxide in reaction by horseradish peroxidase (HRP). Scheme showing conversion of nonfluorescent Amplex Red to highly fluorescent resorufin in hydrogen peroxide solution by HRP (a) in situ UV-Vis absorption spectra of quantitative conversion reaction; (b) spectra were taken at 8 min time intervals, time profile for the intensity of the peak at 571.5 nm corresponding to the absorbance of resorufin in the presence (*1*) and in the absence of HRP (*2*) (c).

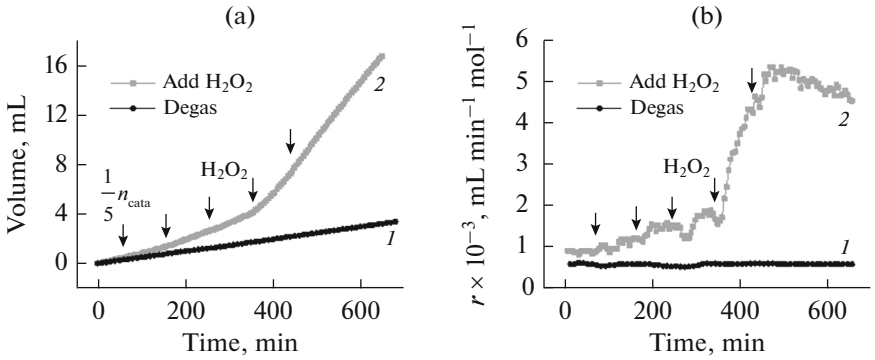


Fig. 4. Activation of mononuclear catalyst by direct additions of H_2O_2. $V_{H_2+CO_2}$ vs. time (a), reaction rate vs. time (b), (*1*) and (*2*) curve are for oxygen-free conditions and for the environment containing H_2O_2, respectively. The reaction solution contains 9.74×10^{-6} mol [(Cp*)Ir(phen)Cl]Cl. Every time, 4 μL 0.48 M H_2O_2 was added into the solution.

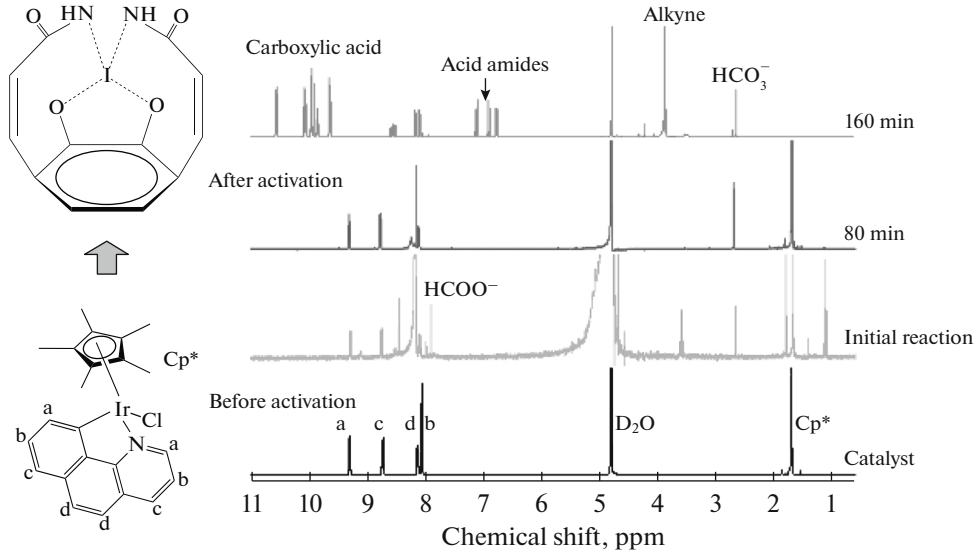


Fig. 5. ^{1}H–NMR spectra of the mononuclear catalyst and the reaction solution registered at different time intervals. D_2O is used as the solvent of the reaction solution. The NMR peak for $HCOO^-$ at 8.25 ppm decreases as the reaction proceeds, conforming the decomposition of formic acid [45, 46].

(curve *1* in Fig. 3c). In a control experiment we could not observe the formation of resorufin in the absence of HRP (curve *2* in Fig. 3c). Through these measurements, the concentration of H_2O_2 in the reaction solution was determined to be 99×10^{-6} M.

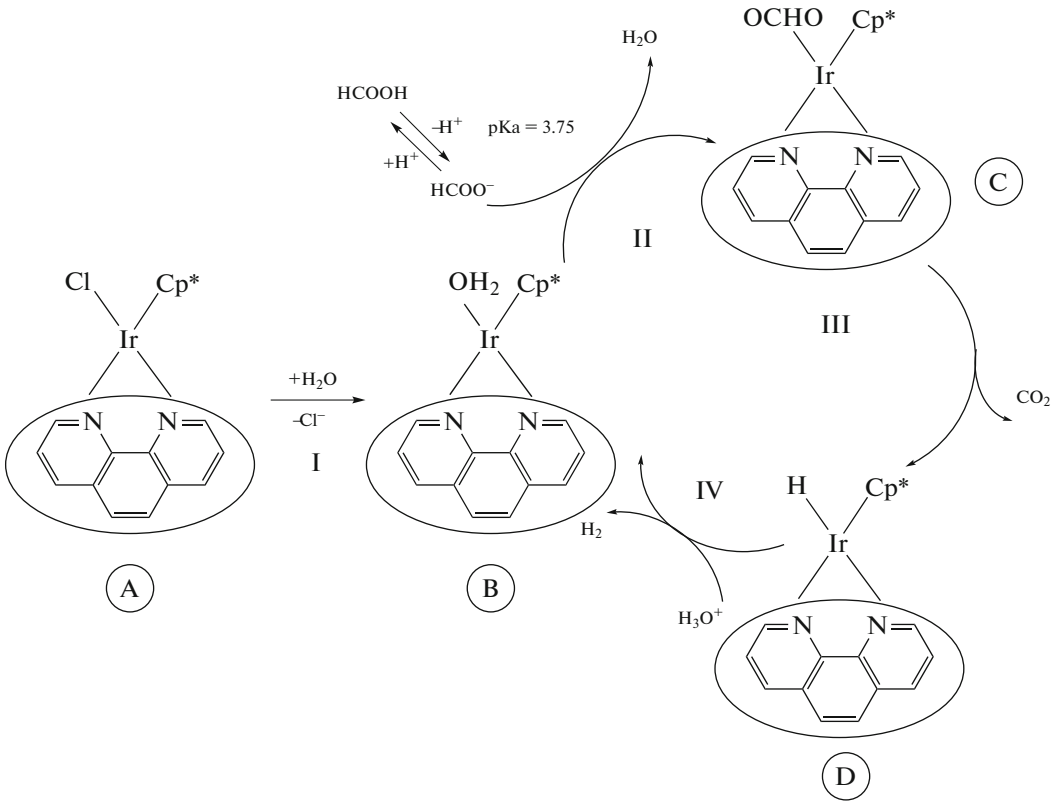
Hydrogen peroxide was then directly added into the reaction solution to validate its activation effect on the mononuclear catalyst. Figure 4a shows that the addition of hydrogen peroxide notably accelerates the reaction. As can also be seen on Fig. 4b, the addition of hydrogen peroxide causes a steady increase in the reaction rate values over the period of time, in which the first three portions were added. Interestingly, a sharp increase followed the fourth addition indicating a faster activation process. This result is consistent with data given in Figs. 1c, 1d. After the fifth addition, the reaction rate reaches a maximum value and then decreases. This observation suggests that excessive amounts of hydrogen peroxide could contribute to the catalyst deactivation.

Proposed Activation Mechanism

The spectra of ^{1}H–NMR (Fig. 5) show that the activation caused considerable changes in the chemical structure of the catalyst. Lower in Fig. 5 indicates five forms of hydrogen occuring on the mononuclear catalyst [(Cp*)Ir(phen)Cl]Cl, which can be attributed to 1,10-phenanthroline [44] and Cp* [45]. After total acti-

vation of 160 min, ^{1}H–NMR peak at 1.6 ppm which refers to Cp* and peaks between 8–9.5 ppm which represent 1,10-phenanthroline both disappear (Fig. 5). As a result, some new peaks between 6.5–11 ppm from 1,10-phenanthroline appear upper curve, which may be assigned to alkene, phenolic hydroxyl, acid amides and carboxylic acid. In addition, some new peaks possibly due to alkyne arose between 3–4.5. Since all these new peaks were invisible at the start time of fast activation (Ts), the fast activation may be a reason for the dramatic change of chemical structure of the catalyst.

The proposed mechanism for the decomposition of formic acid is presented in Scheme 1.



Scheme 1. The proposed mechanism for the decomposition of formic acid in the presence of [(Cp*)Ir(phen)Cl]Cl.

The substitution of aqua ligand in II 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 reaction of hydride species with H^+ can produce H_2. A strong electronic effect, similar to that described in previous reports, was observed in the reaction.

CONCLUSIONS

In summary, this research reveals that the activity of iridium complex catalysts for HCOOH dehydrogenation can be considerably increased through a simple activation process. After activation the activity of the heterodinuclear Ir–Ru catalyst increased 18-fold whereas for the mononuclear catalyst a 23-fold increase was recorded. Oxygen is the key factor for the activation. The results outlined above also indicate that the activation of the catalytic complex is caused by the chemical and structural changes in the ligands. These findings may be helpful in the attempts to improve the catalytic activity of homogeneous catalysts, which are widely used in formic acid dehydrogenation [47], CO_2 reduction [48] and in other reactions [49]. In addition, this paper reports that iridium complex catalysts are excellent catalysts for the direct synthesis of H_2O_2 from the H_2 and O_2. We note, however, that the reaction mechanism remains uncertain and that further efforts are needed to gain further understanding of the individual steps involved.

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