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Recent Advances in Transition Metal-Catalysed Homogeneous Hydrogenation of Carbon Dioxide in Aqueous Media

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1. Introduction

The excessive combustion of fossil fuels leads to enormous emissions of carbon dioxide which is the major greenhouse gases and significantly contributes to global warming. Since the middle of 20th century, the atmospheric concentration of CO₂ has risen remarkably. With the development of human society and increase in energy demand, emissions of CO₂ are increasing dramatically. To reduce the server environmental impact, scientists have paid considerable effort to prohibiting the increase of atmospheric CO₂ concentration. CO₂ is an attractive C1 resource because it is non-toxic, nonflammable, and abundant. Transforming of carbon dioxide to useful chemicals, fuels, and materials have attracted increasing attention because it could reduce the dependence on diminishing fossil oil as well as mitigate CO₂ increase. However, utilizing carbon dioxide is still a challenge research field due to its high stability ($\Delta G^{\circ} = -394.36$ kJ mol$^{-1}$). In the last decades, the homogeneous catalytic hydrogenation of CO₂ has been widely studied. There are some reviews related to this subject. (Leitner et al., 1998; Jessop et al., 2004; Himeda, 2007; Jessop, 2007; Federsel et al., 2010b; Wang et al., 2011) Besides formic acid, theoretically, CO₂ can be hydrogenated to multiple compounds such as, formamides, formaldehyde, methanol, and methane (Eq 1). However, generation of these compounds typically require harsher conditions which make most homogeneous catalysts deactivating, increase the energy cost and make these reductions economically unfavourable. In this chapter, we will focus on the hydrogenation of CO₂ to formic acid or formate which is relatively easy to achieve. Especially, formic acid has recently been recognized as a feasible hydrogen vector. Hydrogenation of CO₂ to formic acid, combined with the reverse reaction (ie. decomposition of formic acid) is considered as one promising method of hydrogen storage (Eq 1).
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Complexes based on most of group VIII transition metals such as Pd, Ni, Rh, Ru, Ir et al. can be used to catalyze CO\textsubscript{2} hydrogenation. Among these catalysts, Rh, Ru, and most recently Ir complexes were found to be most effective. Besides transition-metal catalyst, solvent is also important for optimizing the reaction rate. The homogeneously catalytic hydrogenation of CO\textsubscript{2} to formic acid was firstly reported in 1976 by Inoue et al. (Inoue et al., 1976) They found the reaction was accelerated by adding small amounts of H\textsubscript{2}O. However, in the early years, water-insoluble phosphine ligands are generally employed. Due to the insolvability of the phosphorous complexes in water, the homogeneous hydrogenation of CO\textsubscript{2} generally proceeded in organic solvents, such as DMSO, with water less than 20%. Until 1993, Leitner et al. reported the first water soluble rhodium catalysts which achieve the high turnover number (TON) of 3440 under relatively mild conditions. (Gassner & Leitner, 1993) Noyori and Jessop et al. have demonstrated supercritical CO\textsubscript{2} is an effective solvent due to the enormous concentration of CO\textsubscript{2} and H\textsubscript{2} and obtained highest catalytic performance at that time. (Jessop et al., 1994; Jessop et al., 1996; Munshi et al., 2002) Compared to reduction of CO\textsubscript{2} in organic solvent and supercritical CO\textsubscript{2}, the homogeneous hydrogenation of CO\textsubscript{2} to formic acid in the green solvent—water has recently achieved great success and attracted much more attention. Despite H\textsubscript{2} is less soluble in water, it is still considered to be a preferred solvent because water is abundant, inexpensive, and eco-friendly. More importantly, hydrogenation of CO\textsubscript{2} in water is considerably favoured (\(\Delta G^\circ = -4 \text{ kJ mol}^{-1}\)) compared to the reaction in gas phase (\(\Delta G^\circ = +32.9 \text{ kJ mol}^{-1}\)). In addition, excellent activity usually requires basic additives, such as NaOH, NaHCO\textsubscript{3}, Na\textsubscript{2}CO\textsubscript{3} and amines, which can absorb the generated proton and make the reaction thermodynamically favourable (Scheme 1).

Scheme 1. The thermodynamics of hydrogenation of carbon dioxide to formic acid/formate.

In this chapter, we review the state-of-the-art in homogeneous CO\textsubscript{2} hydrogenation to formic acid or formate in water; discuss the design and synthesis of highly effective water soluble complexes, as well as the catalytic mechanism. We also present the latest strategy for recycle and reuse of homogenous catalyst.
2. Hydrogenation with Ru and Rh complexes

In the pioneering work of Inoue et al., the famous Wilkinson catalyst (RhCl(PPh₃)₃) and the Ru analogue (RuCl(PPh₃)₃) were used and showed much better results than other catalysts of Pd, Ni, and Ir. (Inoue et al., 1976) Following this work, a variety of Rh and Ru catalyst based on various phosphorus ligands were developed and applied in the hydrogenation of CO₂. Recently, N-based ligands have been also investigated for this purpose and achieved great success. Most of the highly efficient Ru and Rh catalysts as well as some Ir complexes and their performance are listed in Table 1.

2.1. Phosphorous ligands

In 1993, Leitner et al. reported the first homogenous hydrogenation of CO₂ with water soluble rhodium–phosphane complexes in aqueous solutions. (Gassner & Leitner, 1993) The reaction was carried out in an aqueous solution of amine at room temperature under 40 atm of H₂/CO₂ (1/1). Using dimethylamine as an additive, the Rh complex [RhCl(tppts)]/tppts (tppts = tris(3-sulfonatophenyl)phosphine) can provide 1.76 M of formic acid with TON of 3440 which is the highest at that time. In 1999, Joó et al. have reported the hydrogenation using inorganic base such as NaHCO₃ and CaCO₃ instead of the organic amine as additive. (Joó et al., 1999) Among the different series of Ru and Rh catalysts, [RhCl(tppms)] (tppms = 3-sulfonatophenyldiphenylphosphine) exhibited the better activity than others, and gave a turnover frequency (TOF) of 262 h⁻¹. Based on the equilibrium of CO₂ + H₂O → HCO₃⁻ + H⁺, they proposed that HCO₃⁻ may be the real substrate in the catalytic cycle. In 2000, Laurenczy et al. reported hydrogenation with moderate activity using [RuCl₂(PTA)] (PTA = 1,3,5-triaza-7-phosphaadamante) in an aqueous solution at 25-80 °C under 20 bar CO₂ and 60 bar H₂. In contrast to the other works, they found that slightly acidic and neutral conditions are preferable for the reaction rate. In case of 10%HCO₃⁻/90%CO₂, they obtained the maximum TOF of 807 h⁻¹ and they suggested that the real substrate of hydrogenation in this system is the bicarbonate anion. (Laurenczy et al., 2000)

In 2003, Joó et al. reported the hydrogenation of bicarbonate with [RuCl₂(tppms)]; (tppms = sodium diphenylphosphinobenzene-3-sulfonate) at 50 °C and 10 bar H₂, a TOF of 54 h⁻¹ was obtained. (Elek et al., 2003) Their results suggest that bicarbonate is more reactive than hydrated CO₂. Interestingly, in presence of 5 bar CO₂ the reaction was about 10% slower than that without CO₂. This result is in contrast to the reaction with [RuCl₂(PTA)];, which increased significantly with increasing of CO₂ pressure. Using this complex [RuCl₂(tppms)];, they have achieve a TOF of 9600 h⁻¹, the highest rate in pure aqueous solutions at that time, at 80 °C under H₂/CO₂ (60/35 bar) in a 0.3 M NaHCO₃ solution.

Most recently, Beller et al. reported hydrogenation of bicarbonate in H₂O/THF with in situ catalyst of [RuCl₂(C₆H₆)];/dppm (dppm = 1,2-bis(diphenylphosphino)methane). (Boddien et al., 2011) In the presence of CO₂, the reaction gave higher TON than that in the absence of CO₂. In addition, the catalyst can also catalyse the dehydrogenation of formate. Consequently, they pronounced the first hydrogen storage based on interconversion of formate and bicarbonate. Soon after that, Joó et al. used [RuCl₂(tppms)];/tppms to catalyse
the hydrogenation of bicarbonate as well as the dehydrogenation of formate, and constructed a simple, rechargeable hydrogen storage device. (Papp et al., 2011) Similar with the system reported by Beller et al., but Joó’s system is in pure aqueous solutions and require no organic solvent.

2.2. Nitrogenous ligands

In 2003, Himeda et al. announced the homogenous hydrogenation of CO\(_2\) in water with a series of 2,2’-bipyridine- and 1,10-phenathroline-based Ru and Rh catalysts including \([\text{Cp}^\ast\text{Rh(bpy)}\text{Cl}]\text{Cl} (\text{Cp}^\ast = \text{pentamethylcyclopentadiyl;} \text{bpy} = 2,2’-\text{bipyridine}), [\text{Cp}^\ast\text{Rh(4,4’-Me-bpy)}\text{Cl}]\text{Cl} (4,4’-\text{Me-bpy} = 4,4’-\text{dimethyl-2,2’-bipyridine}), [(\eta^6-\text{C}_{12}\text{Mes})\text{Ru(phen)}\text{Cl}]\text{Cl} (\text{phen} = 1,10-\text{phenanthroline})\text{etc.} (\text{Himeda et al., 2007a})\) Among these catalysts, complex 4 based on 4,7-dihydroxy-1,10-phenanthroline (DHPT) exhibited high activity and reached a TON of 2400 in a 1 M KHCO\(_3\) solution under 4 MPa H\(_2\)/CO\(_2\) (1/1) at 80 °C after 21 h. Soon after that, Ogo et al. reported a mechanistic study of the hydrogenation with similar complexes under acidic conditions. They synthesized a water-soluble ruthenium hydride complex \([\eta^6-\text{C}_{12}\text{Mes})\text{Ru^{II}(bpy)H}]\text{(SO}_4\text{)}\) from the reaction of an aqua complex \([\eta^6-\text{C}_{12}\text{Mes})\text{Ru^{II}(bpy)(OH}_2\text{)](SO}_4\text{)}\) with NaBH\(_4\) in water. (Hayashi et al., 2003) The hydride complex was found to be active in reaction with CO\(_2\), but the reaction rate obtained by UV spectroscopy was demonstrated to be very slow. One year later, they achieved the hydrogenation of CO\(_2\) to HCOOH in acidic solutions (pH 2.5-5.0) under H\(_2\) (5.5 MPa) and CO\(_2\) (2.5 MPa) at 40 °C with ruthenium complexes \([(\eta^6-\text{C}_{12}\text{Mes})\text{Ru^{II}(4,4’-OMe-bpy)(OH}_2\text{)](SO}_4\text{)}\) (4,4’-MeO-bpy = 4,4’-dimethoxy-2,2’-bipyridine). (Hayashi et al., 2004) The TON was over 50 after 70 h. The reaction rate reached a maximum value at 40 °C and decreased with further increasing of temperature due to the decomposition of HCOOH at higher temperature. In contrast to the inactivity of this kind of complexes, Himeda et al. achieved significantly higher activity with 1-4 (Figure 1 and Table 1) by introducing two strong electron-donating groups into the bipyridine ligands. (Himeda et al., 2004, 2006, 2011) More interestingly, much higher activity was obtained with the iridium analogue (vide infra).

In 2010, Peris et al. used strong electron-donating bis-NHCs ligand (5 and 6) to mimic the bipyridine ligand and achieved a high TON of 23,000 with complex 6 at 40 atm H\(_2\)/CO\(_2\) (1/1) and 200 °C in a 1 M KOH solution for 75 h. (Sanz et al., 2010a) It is worth note that they also achieved transfer hydrogenation of CO\(_2\) with iPrOH using the Ru complex 6, and obtained the highest TON of 874 so far reported for this type of reaction.

3. Hydrogenation with Ir complexes

Although research into iridium catalysts dates back to 1976 (Inoue et al., 1976), the promising catalytic activity of iridium complexes has only recently been discovered. In the pathbreaking work of Inoue et al., the iridium complex H\(_3\)Ir(PPh\(_3\)) exhibited a lower activity than Rh and Ru analogues. About 20 years later, an iridium catalyst was again applied to CO\(_2\) hydrogenation and similar result was observed. (Joó et al., 1999) Rhodium(I) and
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Figure 1. Ru and Rh catalysts with nitrogenous ligands.

Table 1. Hydrogenation of CO\(_2\) to formic acid/formate.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>Additive</th>
<th>P(H(_2)/CO(_2)) (MPa)</th>
<th>T/°C</th>
<th>t/h</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ruthenium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru(II)(PPh(_3))</td>
<td>Cd(_6)</td>
<td>NEt(_3)/H(_2)O</td>
<td>2.5/2.5</td>
<td>rt</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>Ru(II)(PMe(_3))</td>
<td>sCCl</td>
<td>NEt(_3)</td>
<td>8.5/12</td>
<td>50</td>
<td>1</td>
<td>1400</td>
</tr>
<tr>
<td>RuCl(_2)(DAH)(PMe(_3))</td>
<td>sCCl</td>
<td>NEt(_3)/C(_6)F(_5)OH</td>
<td>7/12</td>
<td>50</td>
<td>0.3</td>
<td>95,000</td>
</tr>
<tr>
<td>RuCl(_2)(PATA)</td>
<td>H(_2)O</td>
<td>NaHCO(_3)</td>
<td>6/0</td>
<td>80</td>
<td>-</td>
<td>(907)</td>
</tr>
<tr>
<td>[RuCl(_2)(tppma)](_2)</td>
<td>H(_2)O</td>
<td>NaHCO(_3)</td>
<td>6/0.3</td>
<td>80</td>
<td>0.03</td>
<td>9600</td>
</tr>
<tr>
<td>[RuCl(_2)(4-Me-C(_6))(_2)/dppm</td>
<td>H(_2)O</td>
<td>NaHCO(_3)</td>
<td>0.2/0.8</td>
<td>50</td>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>K[RuCl(_2)(EDTA-H(_2))]</td>
<td>H(_2)O</td>
<td>NaHCO(_3)</td>
<td>5/0</td>
<td>130</td>
<td>2</td>
<td>800</td>
</tr>
<tr>
<td><strong>Rhodium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RhCl(ppy)$_2$</td>
<td>H(_2)O</td>
<td>NHMe</td>
<td>2/2</td>
<td>81</td>
<td>0.5</td>
<td>7300</td>
</tr>
<tr>
<td>RhCl(ppy)$_2$</td>
<td>H(_2)O</td>
<td>NHMe</td>
<td>2/2</td>
<td>rt</td>
<td>12</td>
<td>287</td>
</tr>
<tr>
<td></td>
<td>H(_2)O</td>
<td>KOH</td>
<td>2/2</td>
<td>80</td>
<td>12</td>
<td>(750)</td>
</tr>
<tr>
<td></td>
<td>H(_2)O</td>
<td>KOH</td>
<td>2/2</td>
<td>80</td>
<td>12</td>
<td>(270)</td>
</tr>
<tr>
<td><strong>Iridium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>H(_2)O</td>
<td>KOH</td>
<td>3/3</td>
<td>120</td>
<td>57</td>
<td>(62,000)</td>
</tr>
<tr>
<td>9</td>
<td>H(_2)O</td>
<td>KOH</td>
<td>3/3</td>
<td>120</td>
<td>48</td>
<td>(33,000)</td>
</tr>
<tr>
<td>10</td>
<td>H(_2)O</td>
<td>KOH</td>
<td>0.5/0.5</td>
<td>30</td>
<td>30</td>
<td>(5.5)</td>
</tr>
<tr>
<td>11</td>
<td>H(_2)O</td>
<td>THF</td>
<td>KOH</td>
<td>4/4</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>H(_2)O</td>
<td>THF</td>
<td>KOH</td>
<td>4/4</td>
<td>120</td>
<td>48</td>
</tr>
<tr>
<td>13</td>
<td>H(_2)O</td>
<td>KOH</td>
<td>2/2</td>
<td>200</td>
<td>75</td>
<td>2500</td>
</tr>
</tbody>
</table>

*The data in parenthesis are initial TOF.*
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ruthenium(II) complexes with a water-soluble phosphine ligand, tppms, showed a TOF up to 262 h\(^{-1}\) in an aqueous solution under mild conditions. However, the iridium complex, [IrCl(CO)(tppms)], gave no formate product under the same conditions. In 2008, Gonsalvi and Laurenczy et al. reported a half-sandwich iridium complex, 7, bearing a water-soluble phosphine ligand PTA. (Erlandsson et al., 2008) Compared to the ruthenium and rhodium analogs, (Horváth et al., 2004) it gave a much lower TOF of 22.6 h\(^{-1}\) at 100 °C. These preliminary studies implied that iridium complexes only provide low catalytic activity for the hydrogenation of CO\(_2\). However, recent research made a breakthrough and the high catalytic ability of iridium complexes was demonstrated resulting in renewed attention on iridium complexes. The representative iridium catalysts, 7–15, are presented in Figure 2 and the catalytic results are listed in Table 2.

![Figure 2. Representative iridium catalysts for the hydrogenation of CO\(_2\).](image)

Himeda and co-workers achieved a highly efficient iridium catalyst for the hydrogenation of CO\(_2\) in H\(_2\)O through sophisticated ligand design. (Himeda et al., 2004, 2005, 2006, 2007b; Himeda, 2007) At first, they focused on a half-sandwich bipyridine (bpy) rhodium complex, [Cp*Rh(bpy)X]\(^{+}\), as a prototype catalyst. (Himeda et al., 2003) Preliminary studies showed that this catalyst successfully hydrogenated CO\(_2\) in water but in low rate. Based on the rationale that electron-donating ligands should improve the catalytic activity of the complex, a tunable dihydroxylbipyridine (DHPBP) ligand was introduced. The acid-base equilibrium between the hydroxyl and oxyanion forms enabled switching of the polarity and electron-donating ability of the ligand thus affecting the catalytic activity and water-solubility of the complex (Figure 3).
Table 2. Hydrogenation of CO$_2$ to formic acid/formate using iridium catalysts. *a* The data in parenthesis are average TOF.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>Additive</th>
<th>T/°C</th>
<th>Pressure /MPa</th>
<th>t/h</th>
<th>Initial TOF$^a$/h$^{-1}$</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>H$_2$O</td>
<td></td>
<td>100</td>
<td>10</td>
<td>23</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>H$_2$O</td>
<td>KOH</td>
<td>120</td>
<td>6</td>
<td>57</td>
<td>42,000</td>
<td>190,000</td>
</tr>
<tr>
<td>9</td>
<td>H$_2$O</td>
<td>KOH</td>
<td>60</td>
<td>0.1</td>
<td>30</td>
<td>33</td>
<td>376</td>
</tr>
<tr>
<td>9</td>
<td>H$_2$O</td>
<td>KOH</td>
<td>60</td>
<td>0.1</td>
<td>30</td>
<td>32</td>
<td>444</td>
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<tr>
<td>9</td>
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<td>KOH</td>
<td>30</td>
<td>0.1</td>
<td>30</td>
<td>3.5</td>
<td>81</td>
</tr>
<tr>
<td>10</td>
<td>H$_2$O</td>
<td>KOH</td>
<td>120</td>
<td>6</td>
<td>48</td>
<td>33,000</td>
<td>222,000</td>
</tr>
<tr>
<td>10</td>
<td>H$_2$O/THF</td>
<td>KOH</td>
<td>200</td>
<td>5</td>
<td>2</td>
<td>(150,000)</td>
<td>300,000</td>
</tr>
<tr>
<td>10</td>
<td>H$_2$O/THF</td>
<td>KOH</td>
<td>120</td>
<td>6</td>
<td>48</td>
<td>(73,000)</td>
<td>3,500,000</td>
</tr>
<tr>
<td>12</td>
<td>H$_2$O</td>
<td>KOH</td>
<td>185</td>
<td>5.5</td>
<td>24</td>
<td>(14,500)</td>
<td>348,000</td>
</tr>
<tr>
<td>12</td>
<td>H$_2$O</td>
<td>KOH</td>
<td>185</td>
<td>5.5</td>
<td>1</td>
<td>(18,780)</td>
<td>18,780</td>
</tr>
<tr>
<td>13</td>
<td>H$_2$O</td>
<td>KOH</td>
<td>80</td>
<td>6</td>
<td>18</td>
<td>-</td>
<td>1600</td>
</tr>
<tr>
<td>14</td>
<td>H$_2$O</td>
<td>KOH</td>
<td>200</td>
<td>4</td>
<td>20</td>
<td>-</td>
<td>9500</td>
</tr>
<tr>
<td>15</td>
<td>H$_2$O</td>
<td>KOH</td>
<td>200</td>
<td>6</td>
<td>75</td>
<td>(2500)</td>
<td>190,000</td>
</tr>
</tbody>
</table>

Figure 3. Acid-base equilibrium between hydroxyl and oxyanion forms.

Under basic conditions, the hydroxyl group can be deprotonated to generate an oxyanion, which is a much stronger electron donor. Therefore, high catalytic activity was achieved by introducing two electron-donating hydroxyl groups onto the bipyridine ligand. Table 3 shows the effect of the hydroxyl group in the half-sandwich bipyridine catalyst, [(C$_n$Me$_n$)M(L)Cl]$^+$ (M = Rh, Ir, n = 5; M = Ru, n = 6), on the hydrogenation of CO$_2$. Significant activation of the catalysts was observed. The TONs of the iridium catalysts with hydroxyl groups were 52–103 times greater than those of the unsubstituted catalysts. The electronic substituent effect was investigated using [(C$_n$Me$_n$)M(4,4'-R$_2$-2,2'-bpy)Cl]$^+$ (M = Ir, Rh, Ru; R = OH, OMe, Me, H). Note that under basic conditions the hydroxyl group (Hammett constant, $\sigma_p' = -0.92$) was deprotonated to generate an oxyanion, which is a much stronger donor and has a $\sigma_p'$ of -2.30. The Hammett plots show a good correlation between the initial TOFs and the $\sigma_p'$ values which indicate their electron donating ability (Figure 4). This result suggests that strong donating ability of the substituents lead to high activity of the complexes. On the other hand, the substituent effects on the rhodium and ruthenium complexes, 1 and 2, were moderate compared to the effect on iridium complex 8 (Figure 4). (Himeda et al., 2011) It is
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apparent that the remarkable activation of the iridium DHBP catalyst can be attributed to the strong electron-donating ability of the oxoanion. The maximal catalytic activity (TOF = 42,000 h⁻¹, TON = 190,000) of the iridium DHBP catalyst was obtained at 6 MPa and 120 °C. Moreover, the catalyst allowed the reaction proceeding at atmospheric pressure. These results indicate that the corresponding hydride complex can easily be generated as an active species at atmospheric pressure.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TON</th>
<th>L:</th>
<th>DHBP</th>
<th>phen</th>
<th>DHPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-L</td>
<td>216</td>
<td>bpy</td>
<td>1800</td>
<td>220</td>
<td>2300</td>
</tr>
<tr>
<td>Ru-L</td>
<td>68</td>
<td>4400</td>
<td>78</td>
<td>5100</td>
<td></td>
</tr>
<tr>
<td>Ir-L</td>
<td>105</td>
<td>5500</td>
<td>59</td>
<td>6100</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Substituent effect of the ligand on the TON for hydrogenation of CO₂. The reaction was carried out with the catalyst (0.1 mM) in a 1 M KOH solution under 4 MPa (CO₂/H₂ = 1:1) at 80 °C for 20 h. a. Rh-L = [Cp*Rh(L)Cl]Cl, Ru-L = [(C₆Me₆)Ru(L)Cl]Cl, Ir-L = [Cp*Ir(L)Cl]Cl. b. [Catalyst] = 0.2 mM.

In 2009, Nozaki and co-workers designed Ir(III) complexes in which alkylphosphine-based pincer ligands were employed as efficient electron donors. These complexes were used for the hydrogenation of CO₂ in H₂O/THF. The PNP-Ir trihydride complex, showed the highest TON (3,500,000) and TOF (150,000 h⁻¹) to date. In 2011, Hazari and co-workers investigated CO₂ insertion into PNP-Ir hydrides using a computational method. They evaluated the nucleophilicity of the hydride through its calculated NBO charge and found a strong correlation between the NBO charge of the hydride and the thermodynamics of CO₂ insertion. Using this simple model, they predicted that complex 11 is favorable for CO₂ insertion. Furthermore, they
exponentially isolated air- and moisture-stable complex 12. When 12 was used for the hydrogenation of CO$_2$, maximum TON of 348,000 and TOF of 18,780 h$^{-1}$ were obtained, which is comparable to the best system reported by Nozaki.

N-Heterocyclic carbenes (NHCs), which have a high electron-donating ability, have also been introduced as ligands in iridium complexes for the hydrogenation of CO$_2$. Most recently, Peris and co-workers reported a series of IrCp*($^\text{NHC}$) complexes. A bis-NHC Ir complex, 13, showed modest activity (TON of 1600) for the hydrogenation of CO$_2$ to HCOOK. (Sanz et al., 2010b) To improve the water solubility of the complex, hydroxyl groups were introduced to the side carbon chains. Consequently, complex 14 gave a higher TON of 9500 under optimized conditions. (Sanz et al., 2010a) Furthermore, blocking the C2-position of imidazole with a methyl group and coordinating to the C5 position led to a higher electron-donating ability of the ligand. In addition, the introduction of sulfonate groups into the bis-NHC ligand increased the water solubility of the complex. As a result, a TON of 190,000 was achieved with complex 15. (Azua et al., 2011) Interestingly, these complexes also succeeded in the transfer hydrogenation of CO$_2$ to formate using iPrOH as a hydrogen donor.

4. Hydrogenation with other metal complexes

As mentioned above, the homogenous catalysts for hydrogenation of CO$_2$ into formic acid are typically restricted to complexes of the precious or platinum-group metals Rh, Ru and Ir. Other metals are less investigated due to the low efficiency. Hence the development of nonprecious metal based homogeneous catalyst is limited. Most catalysis using this kind of complexes were carried out in organic solvent and only few examples were in aqueous media, but not pure water. In the original work of Inoue, a non-platinum-group metal catalyst, Ni(dppe)$_2$: (dppe = 1,2-bis(diphenylphosphino)ethane), have been studied. It was proved to be inefficient with only a low TON of 7. Two year later, Evans and Newell studied the homogeneous catalytic reduction of CO$_2$ to formate esters in alcohols with [HFe(CO)$_{11}$]$^-$, but only obtained a low TOF (0.06 h$^{-1}$) and TON (< 6). (Evans & Newell, 1978) In 1994, Yamamoto et al. have studied the Pd based complex. They have synthesized and characterized the first carbon dioxide coordinated palladium(0) complex, Pd($\eta^2$-CO$_2$)(PMePh$_2$)$_2$. In addition, using the Pd complexes, PdCl$_2$(L = PMe$_3$; PMePh$_2$; PPh$_3$), they obtained formic acid in 12% yield in benzene/H$_2$O under 100 atm H$_2$/CO$_2$ (1/1) at room temperature. (Sakamoto et al., 1994)

Nonprecious metal was almost not concerned in the following years until 2003. Jessop and co-workers investigated a number of inexpensive metals such as Cu, Fe, Mn, Mo, Ni, and Zn with a high-throughput screening method in the hydrogenation of CO$_2$ in DMSO. (Tai et al., 2003) They found the combination of FeCl$_3$ and NiCl$_2$ with dcp ligand (dcp = Cy$_2$PCH$_2$CH$_2$PCy$_2$) gave better results (TON up to 117, TOF up to 15.6 h$^{-1}$) than other metals. In 2010, Beller and Laurenczy et al. have reported different iron precursors and various nitrogen- and phosphine-ligands for the homogeneous hydrogenation of CO$_2$ and bicarbonate to formate in MeOH. The best iron catalyst, Fe(BF$_4$)$_2$/PP$_3$ (PP$_3$ =
P(CH₂CH₂PPh₂)₃), could reduce bicarbonate to formate in a TON of 610 which was comparable with that using [RuCl₂(C₆H₅)₂]₂PP₃. It also could transform CO₂ and H₂ to formate esters and formamide in the presence of the corresponding alcohols and amines with TON up to 292 and 727, respectively.(Federsel et al., 2010a) Very recently, Beller et al. reported hydrogenation of sodium bicarbonate and CO₂ with in situ generated cobalt catalyst. They obtained a high TON of 3877 using the Co(BF₄)₂·6H₂O and PP₃ in a sodium formate at 120 °C for 20 h. This catalytic productivity is six times as high as the TON for the iron catalyst. They also found other phosphine ligands, such as triphenylphosphine, xantphos, 1,2-bisdiphenylphosphinoethane, and 1,1,1-tris(diphenylphosphinomethyl) ethane, showed no activity.(Federsel et al., 2012)

Inspired by the iridium pincer complexes, in 2011, Milstein et al. reported the most active iron(II) pincer complex trans-[(fBu-PNP)Fe(H₂)(CO)] which showed similar activity to noble metal catalysts.(Langer et al., 2011) Hydrogenation of sodium bicarbonate to formate in H₂O/THF (10/1) have achieved a TON of 320 at 80 °C under 8.3 bar H₂. Hydrogenation of CO₂ in a 2 M NaOH solution gave a TON of 788 and TOF of 156 h⁻¹ at total pressure of 10 bar (H₂/CO₂ = 6.7/3.3) for 5 h.

5. Mechanism of CO₂ hydrogenation

To understand the reaction process of CO₂ hydrogenation and design better catalyst, the study of the mechanism has always been the focus for chemists.(Hutschka et al., 1997; Getty et al., 2009) In the CO₂ hydrogenation, there are several aspects need to pay attention to, such as activation of dihydrogen and CO₂ involving ligand and metal, as well as the important effect of solvent and additive.

Along with the development of reaction in water, the exploration of the water effect has been on-going. The accelerating effect of small amounts of added water in organic solvents has been observed in active Pd(Inoue et al., 1976), Rh(Tsai & Nicholas, 1992) and Ru(Jessop et al., 1996) etc. systems. Note that in some case adding small amount of water to organic solvent could not improve the performance of the reaction system, even showed prohibit effect due to the deactivation of the hydrophobic catalyst.(Leitner et al., 1994) Therefore understanding the mechanism and then developing appropriate catalyst that can be applied in water is essential to high effective catalytic system. Nicholas et al. (Tsai & Nicholas, 1992) have proposed that water acts as an ancillary ligand and form hydrogen bond with oxygen of the CO₂ to facilitate CO₂ insertion (Figure 5A). Lau et al. found the reaction rate is enhanced by adding 20% water in THF by using TpRu(PPh₃)(CH₃CN)H [Tp = hydrotris[pyrazolyl]borate] as a catalyst.(Ng et al., 2004) They also have studied the promoting effect of water with the same Ru catalyst and proposed a mechanism to illustrate the water effect (Figure 5B). As suggested by their calculation, the incorporation of water could activate the CO₂ molecule and significantly reduce the reaction barrier.(Yin et al., 2001) In the most recent work of Nozaki et al. they investigated the reaction mechanism by density functional theory (DFT) calculation. They found that adding one or two water molecules the reaction barrier is markedly lowered compared to that in gas phase.
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Lau et al. have demonstrated the intramolecular N-H--H-Ru hydrogen bond in the Ru complexes catalysed hydrogenation. (Chu et al., 1998) Although the reaction rate was very slow, their research gave insight into the mechanism of hydrogen activation: intramolecular heterolytic cleavage of the dihydrogen was aided by the pendant amino group. The design principle has been employed by Hazari et al. in the designing of PNP Ir(III) catalyst and demonstrated the feasibility of such activation method. (Schmeier et al., 2011) With DFT calculations, they demonstrated that the intramolecular hydrogen bond in complex 12 facilitates CO₂ insertion (Figure 6).

Sasaki’s theoretical calculation (Ohnishi et al., 2005) and Jessop’s experimental results (Tai et al., 2002) have demonstrated the strong electron-donating power of the ligand resulting in high activity of the complexes. The following design of complexes generally applied this principle. As abovementioned, Himeda et al. developed DHBP catalyst by introducing the hydroxyl group to bpy; Nozaki et al. designed the complex with PNP-based pincer ligand as a strong donor; Peris et al. used the NHC as a strong electron-donating ligand for new catalyst design. All the examples have verified the importance of the donor powder of the ligand in activating the complex.

In 2009, Nozaki et al. reported the PNP pincer ligated Ir(III) complexes, 10, and achieved the highest TON (3,500,000) and TOF (150,000 h⁻¹) to date. (Tanaka et al., 2009) They also...

Figure 5. Water effect in the hydrogenation of CO₂.

Figure 6. Reaction mechanism of CO₂ hydrogenation proposed by Hazari et al.
proposed a mechanism for the catalytic reaction (Figure 7): the insertion of CO$_2$ into 10 gives formato complex 16, which undergoes dissociation of the formato ligand under basic conditions. Simultaneously, deprotonative dearomatization of the PNP ligand by OH$^-$ leads to intermediate 17, which is hydrogenated to regenerate the trihydride complex 10.

Figure 7. Catalytic mechanism for the hydrogenation of CO$_2$ proposed by Nozaki.

After Nozaki and co-workers reported the excellent PNP Ir(III) complexes, several groups have investigated the mechanism of CO$_2$ hydrogenation with these catalysts. Ahlquist et al. used a simple (PNP)IrH$_3$ structure to study the mechanism with DFT calculation. (Ahlquist, 2010) Their research suggested that the deprotonation by the hydroxide is the rate-limiting step (Figure 7). This calculation agreed with the experimental observation that higher basicity leads to a higher rate. Most recently, Yang reinvestigated this mechanism using the DFT method and proposed a different reaction pathway (Figure 8). (Yang, 2011) He suggested that direct H$_2$ cleavage by OH$^-$ is more favourable than the Nozaki-postulated H$_2$ cleavage model. Using this new reaction pathway, the calculation gave a low overall enthalpy barrier of 77.8 kJ mol$^{-1}$ for the formation of HCOOH from H$_2$ and CO$_2$.

Figure 8. Catalytic mechanism of CO$_2$ hydrogenation proposed by Yang.
The catalytic hydrogenation mechanism of nitrogen-based complexes has been less investigated. In 2006, Ogo et al. determined that the different rate-determining step for bpy-based Ru and Ir complexes by the observation of the saturation behaviour of the TON with increasing \( \text{Pt} \) and \( \text{PCO} \), respectively. (Ogo et al., 2006) The rate-determining step of \( [(\eta^6-\text{C}_6\text{Me}_6)\text{Ru(bpy)(OH}_2])\text{(SO}_4]) \) and \( [(\eta^6-\text{C}_6\text{Me}_6)\text{Ru(4,4'-OMe-bpy)(OH}_2])\text{(SO}_4]) \) was suggested to be the reaction of aqua complexes with \( \text{H}_2 \). In contrast, the Ir analogous was supposed to be the \( \text{CO}_2 \) insertion into the iridium hydride complexes which were isolated and characterized by NMR, ESI-MS, and IR. The different mechanism of Ru and Ir complexes may help to understand the excellent performance of other iridium complexes.

6. Catalyst immobilization and recycle

Homogeneous catalyst has exhibited high catalytic activity in the hydrogenation of \( \text{CO}_2 \). For further practical application, the recycle and reuse of the catalyst is an important issue that needs to be resolved because most of the catalysts contain noble metal.

In 2011, Baffert et al. reported a series of silica supported ruthenium-N-heterocyclic carbene species for hydrogenation of \( \text{CO}_2 \). (Baffert et al., 2011) Using pyrrolidine as an additive, \( \text{Ru} \text{cym} \) and \( \text{M-Ru}_{\text{cym}} \) (Figure 9) showed low catalytic activity. By introducing basic phosphorous ligand \( \text{PMe}_3 \), the activity of \( \text{M-RuP} \) (Figure 9) is improved and showed comparable TON with the parent catalyst \( \text{[RuCl}_2(\text{PMe}_3)_4 \) ]. However, the supported catalyst are unstable due to the weak Ru-NHC linkage, 50% of Ru was found leached into reaction solution.

Zheng et al. have reported the ruthenium immobilized on functionalized silica could be used as catalyst precursor for hydrogenation of \( \text{CO}_2 \) in organic solvent with adding triphenyl phosphine. (Zhang et al., 2004) In light of this result, in 2008, Han et al. prepared the silica supported catalyst “Si”-(CH\(_2\)).NH(CSCH\(_3\)].[RuCl(PPh\(_3\))] and used it to the hydrogenation of \( \text{CO}_2 \) in a mixture solvent of H\(_2\)O and ionic liquid. The ionic liquid, 1-(N,N-dimethylaminoethyl)-2,3-dimethylimidazolium trifluoromethanesulfonate ([mamin][TfO]), has a tertiary amino group which makes it can acts as a basic additive as well as a solvent. After the reaction, the immobilized catalyst could be simply recycled by filtration. The filtrate was first warmed to 110 °C to remove the water and then heated to 130 °C to separate the formic acid. Since the ionic liquid is non-volatile and stable below 220 °C, it can be separated and reused after the distillation. The catalyst and ionic liquid could be reused four times without decrease of TOF (~44 h\(^{-1}\)). With ICP-AES analysis, they found no significant loss of Ru during the recycling process. (Zhang et al., 2008)
Soon after that, they report another type of ionic liquid, 1,3-di(N,N-dimethylaminoethyl)-2-methylimidazolium trifluoromethanesulfonate ([DAMI][TfO]), which has two tertiary amino groups on the side chain of the cation. Using the silica supported Ru catalyst, “Si”-(CH\textsubscript{2})\textsubscript{3}NH(CSCH\textsubscript{3})-[RuCl\textsubscript{3}(PPh\textsubscript{3})], CO\textsubscript{2} was hydrogenated to formic acid in the presence of water and [DAMI][TfO]. They found TOF increased with increasing the amount of water added, and a weight ratio of water to ionic liquid is suitable between 1 and 2.5. Under the optimal conditions, a TON of 1840 and a TOF of 920 h\textsuperscript{-1} was obtained at 80 °C under 18 MPa of H\textsubscript{2}/CO\textsubscript{2} (1/1) for 2h. The ionic liquid and catalyst can be reused at least over four cycles without significant decrease of TOF. (Zhang et al., 2009)

The catalyst recycle usually require a solid supporter, and suffer from loss of catalytic activity due to the insolubility of the catalyst in the reaction solution. Himeda et al. reported an interesting method for catalyst recycling without a supporter. It was realized by utilising the tunable solubility of the complex along with changing pH of the reaction solution. The catalyst 9 based on DHPT showed a similar TOF and a slightly improved TON (Himeda et al., 2005) than DHBP catalyst 8 (Table 2). The abovementioned acid-base equilibrium not only changes the electronic properties of the complex but also affects its polarity and thus its water solubility. As shown in Figure 10, DHPT catalyst 9 exhibited negligible solubility (ca. 100 ppb) in a weakly acidic formate solution. Therefore, recycling of 9 was investigated in batch-wise cycles based on the concept shown in Figure 11. When the added KOH was completely consumed, the catalyst precursor spontaneously precipitated due to its decreased water solubility as a result of the lower pH value. Thus, the reaction was terminated and formed a heterogeneous system that could be filtered to recover the precipitated catalyst. The iridium complex remaining in the filtrate was found to be less than 2% of the catalyst loading (0.11 ppm). Since the catalytic action was “turned off”, the reverse reaction (i.e., the decomposition of formic acid) was prevented in the separation step. Additionally, the pure product (i.e., the formate salt) could be isolated simply by evaporating the filtrate.

![Figure 10. Solubility of a) DHBP catalyst 8 and b) DHPT catalyst 9 in a 1 M aqueous formate solution.](image-url)
The recovered catalyst retained a high catalytic activity across four cycles, as shown in Table 4. It is clear that the three components (i.e., catalyst, product, and solvent) can be easily separated without significant waste. The sophisticated design of the catalyst provided a proton-responsive catalyst with pH-tunable catalytic activity and water solubility. These results suggest that by carefully considering reaction profiles, the design and use of innovative homogeneous catalytic systems such as tailor-made catalysts can overcome the disadvantages of homogeneous catalysis.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Loaded/recovered cat./ppm</th>
<th>Recovery efficiency/%</th>
<th>Leaching iridium/ppm</th>
<th>Final conc. of formate/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.0</td>
<td>-</td>
<td>0.11</td>
<td>0.105</td>
</tr>
<tr>
<td>2</td>
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<td>93</td>
<td>0.22</td>
<td>0.104</td>
</tr>
<tr>
<td>3</td>
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<td>92</td>
<td>0.42</td>
<td>0.103</td>
</tr>
<tr>
<td>4</td>
<td>7.0</td>
<td>91</td>
<td>0.61</td>
<td>0.103</td>
</tr>
</tbody>
</table>

Table 4. Catalyst recycling studies for the conversion of CO₂ into formate using iridium-DHPT catalyst. Reaction conditions: DHPT catalyst (2.5 μmol), 6 MPa of H₂/CO₂ (1:1), 0.1 M KOH solution (50 mL), 60 °C for 2 h. a. Determined by ICP-MS analysis.

7. Conclusion

After decades of research, chemists have achieved great success in homogeneous hydrogenation of carbon dioxide. With appropriate catalysts and optimum conditions, some of the results are close to commercialization. However, to hydrogenate carbon dioxide efficiently, economically, and eco-friendly, several critical problems remain to be solved. The first is the high activity of the catalyst, which is generally required in order to lower the overall energy barrier for the conversion of thermodynamically stable CO₂. Present catalysts usually need high temperature and pressure to achieve high activity. Consequently, the energy cost is increased. The highly efficient catalyst that can work under mild conditions is highly requisite. Therefore, further research and understanding the mechanism and delicate design of the catalyst with multi-functional ligand are necessary. The second is the
prevention of waste generation (e.g., organic solvents and additives) during the reaction. The third is the recycle and reuse of the catalyst, which is important to increase the cost efficiency. The research of the catalyst recycling is still in the preliminary stage and suffers from a lot of problems. Better performance can be expected with the development of new immobilizing method, such as using ionic liquid.

Since much more effort has been paid to homogeneous hydrogenation of carbon dioxide over the last decade, we can expect more exciting results in the near future. We also believe transformation and utilization of carbon dioxide, especially for fuels production, will decrease its emission and reduce the reliance on fossil sources.

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