

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



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

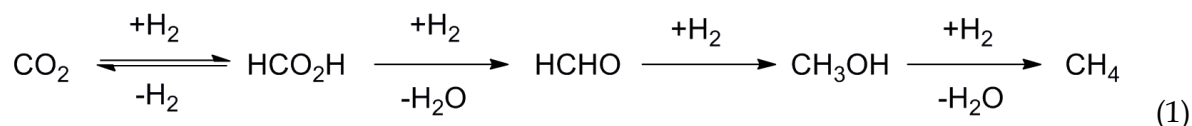
Wan-Hui Wang and Yuichiro Himeda

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/48658>

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 ($\Delta G^{\circ}_{298} = -394.36 \text{ kJ mol}^{-1}$). 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, step 1).



Complexes based on most of group VIII transition metals such as Pd, Ni, Rh, Ru, Ir et al. can be used to catalysis CO_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_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_2O . However, in the early years, water-insoluble phosphine ligands are generally employed. Due to the insolubility of the phosphorous complexes in water, the homogeneous hydrogenation of CO_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_2 is an effective solvent due to the enormous concentration of CO_2 and H_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_2 in organic solvent and supercritical CO_2 , the homogeneous hydrogenation of CO_2 to formic acid in the green solvent—water has recently achieved great success and attracted much more attention. Despite H_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_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_3 , Na_2CO_3 and amines, which can absorb the generated proton and make the reaction thermodynamically favourable (Scheme 1).

	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° ($\text{J mol}^{-1} \text{ K}^{-1}$)
$\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{HCO}_2\text{H}(\text{l})$	32.9	-31.2	-215
$\text{CO}_2(\text{aq}) + \text{H}_2(\text{aq}) \longrightarrow \text{HCO}_2\text{H}(\text{aq})$	-4	-	-
$\text{CO}_2(\text{aq}) + \text{H}_2(\text{aq}) + \text{NH}_3(\text{aq}) \longrightarrow \text{HCO}_2^-(\text{aq}) + \text{NH}_4^+(\text{aq})$	-9.5	-84.3	-250

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_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 ($\text{RhCl}(\text{PPh}_3)_3$) and the Ru analogue ($\text{RuCl}(\text{PPh}_3)_3$) 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 CO_2 . 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 CO_2 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 H_2/CO_2 (1/1). Using dimethylamine as an additive, the Rh complex $[\text{RhCl}(\text{tppts})_3]/\text{tppts}$ (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 NaHCO_3 and CaCO_3 instead of the organic amine as additive. (Joó et al., 1999) Among the different series of Ru and Rh catalysts, $[\text{RhCl}(\text{tppms})_3]$ (tppms = 3-sulfonatophenyldiphenylphosphine) exhibited the better activity than others, and gave a turnover frequency (TOF) of 262 h^{-1} . Based on the equilibrium of $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}^+$, they proposed that HCO_3^- may be the real substrate in the catalytic cycle. In 2000, Laurenczy et al. reported hydrogenation with moderate activity using $[\text{RuCl}_2(\text{PTA})_4]$ (PTA = 1,3,5-triaza-7-phosphaadamantane) in an aqueous solution at 25–80 °C under 20 bar CO_2 and 60 bar H_2 . In contrast to the other works, they found that slightly acidic and neutral conditions are preferable for the reaction rate. In case of 10% $\text{HCO}_3^-/90\% \text{CO}_2$, 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 $[\text{RuCl}_2(\text{tppms})_2]_2$ (tppms = sodium diphenylphosphinobenzene-3-sulfonate) at 50 °C and 10 bar H_2 , a TOF of 54 h^{-1} was obtained. (Elek et al., 2003) Their results suggest that bicarbonate is more reactive than hydrated CO_2 . Interestingly, in presence of 5 bar CO_2 the reaction was about 10% slower than that without CO_2 . This result is in contrast to the reaction with $[\text{RuCl}_2(\text{PTA})_4]$, which increased significantly with increasing of CO_2 pressure. Using this complex $[\text{RuCl}_2(\text{tppms})_2]_2$, they have achieved a TOF of 9600 h^{-1} , the highest rate in pure aqueous solutions at that time, at 80 °C under H_2/CO_2 (60/35 bar) in a 0.3 M NaHCO_3 solution.

Most recently, Beller et al. reported hydrogenation of bicarbonate in $\text{H}_2\text{O}/\text{THF}$ with in situ catalyst of $[\text{RuCl}_2(\text{C}_6\text{H}_6)]_2/\text{dppm}$ (dppm = 1,2-bis(diphenylphosphino)methane). (Boddien et al., 2011) In the presence of CO_2 , the reaction gave higher TON than that in the absence of CO_2 . 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 $[\text{RuCl}_2(\text{tppms})_2]_2/\text{tppms}$ 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 CO₂ in water with a series of 2,2'-bipyridine- and 1,10-phenanthroline-based Ru and Rh catalysts including [Cp*Rh(bpy)Cl]Cl (Cp* = pentamethylcyclopentadienyl; bpy = 2,2'-bipyridine), [Cp*Rh(4,4'-Me-bpy)Cl]Cl (4,4'-Me-bpy = 4,4'-dimethyl-2,2'-bipyridine), [(η⁶-C₆Me₆)Ru(phen)Cl]Cl (phen = 1,10-phenanthroline) etc. (Himeda et al., 2007a) Among these catalysts, complex **4** based on 4,7-dihydroxyl-1,10-phenanthroline (DHPT) exhibited high activity and reached a TON of 2400 in a 1 M KHCO₃ solution under 4 MPa H₂/CO₂ (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 [(η⁶-C₆Me₆)Ru^{II}(bpy)H](SO₄) from the reaction of an aqua complex [(η⁶-C₆Me₆)Ru^{II}(bpy)(OH₂)](SO₄) with NaBH₄ in water. (Hayashi et al., 2003) The hydride complex was found to be active in reaction with CO₂, but the reaction rate obtained by UV spectroscopy was demonstrated to be very slow. One year later, they achieved the hydrogenation of CO₂ to HCOOH in acidic solutions (pH 2.5-5.0) under H₂ (5.5 MPa) and CO₂ (2.5 MPa) at 40 °C with ruthenium complexes [(η⁶-C₆Me₆)Ru^{II}(bpy)(OH₂)](SO₄) and [(η⁶-C₆Me₆)Ru^{II}(4,4'-OMe-bpy)(OH₂)](SO₄) (4,4'-MeO-bpy = 4,4'-dimethoxyl-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 H₂/CO₂ (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 CO₂ with *i*PrOH 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 H₃Ir(PPh₃)₃ exhibited a lower activity than Rh and Ru analogues. About 20 years later, an iridium catalyst was again applied to CO₂ hydrogenation and similar result was observed. (Joó et al., 1999) Rhodium(I) and

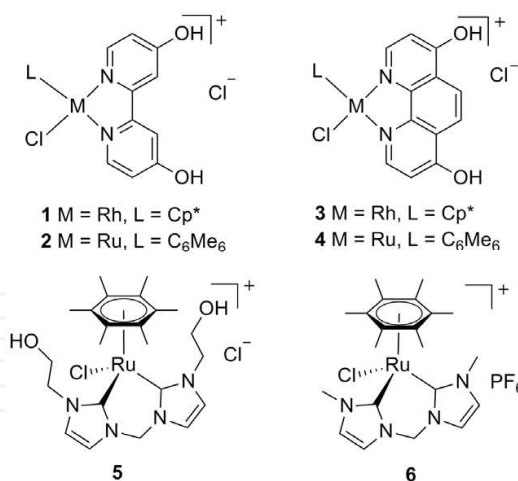


Figure 1. Ru and Rh catalysts with nitrogenous ligands.

Catalyst	Solvent	Additive	P(H ₂ /CO ₂) /MPa	T/°C	t/h	TOF ^a /h ⁻¹	TON
Ruthenium							
RuH ₂ (PPh ₃) ₄	C ₆ H ₆	NEt ₃ /H ₂ O	2.5/2.5	rt	20	4	87
RuH ₂ (PMe ₃) ₄	scCO ₂	NEt ₃	8.5/12	50	1	1400	1400
RuCl(OAc)(PMe ₃) ₄	scCO ₂	NEt ₃ /C ₆ F ₅ OH	7/12	50	0.3	95,000	32,000
RuCl ₂ (PTA)	H ₂ O	NaHCO ₃	6/0	80	-	(807)	-
[RuCl ₂ (tppms)] ₂	H ₂ O	NaHCO ₃	6/3.5	80	0.03	9600	320
[RuCl ₂ (C ₆ Me ₆)]/ dppm	H ₂ O	NaHCO ₃	0.2/0.8	50	1	50	1600
K[RuCl(EDTA-H)]	H ₂ O	-	5/0	130	2	800	-
2	H ₂ O	KOH	0.3/1.7	40	0.5	250	-
4	H ₂ O	KOH	3/3	120	8	(4400)	13,620
	H ₂ O	KOH	3/3	120	24	(3600)	15,400
Rhodium							
RhCl(tppts) ₃	H ₂ O	NHMe ₂	2/2	81	0.5	7300	-
1	H ₂ O	NHMe ₂	2/2	rt	12	287	3400
3	H ₂ O	KOH	2/2	80	12	(790)	1800
	H ₂ O	KOH	2/2	80	32	(270)	2400
Iridium							
8	H ₂ O	KOH	3/3	120	57	(42,000)	190,000
9	H ₂ O	KOH	3/3	120	48	(33,000)	222,000
9	H ₂ O	KOH	0.5/0.5	30	30	(3.5)	81
10	H ₂ O/THF	KOH	4/4	200	2	150,000	300,000
	H ₂ O/THF	KOH	4/4	120	48	73,000	3,500,000
15	H ₂ O	KOH	3/3	200	75	2500	190,000

Table 1. Hydrogenation of CO₂ to formic acid/formate. *a.* The data in parenthesis are initial TOF.

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, $[\text{IrCl}(\text{CO})(\text{tppms})_2]$, 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 analogous, (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.

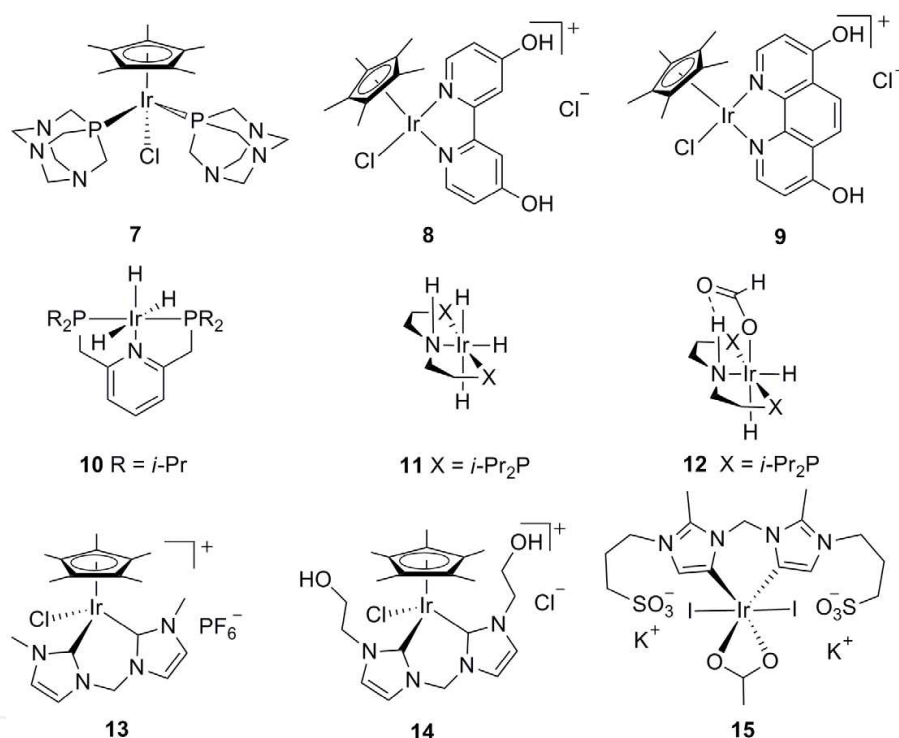


Figure 2. Representative iridium catalysts for the hydrogenation of CO_2 .

Himeda and co-workers achieved a highly efficient iridium catalyst for the hydrogenation of CO_2 in H_2O 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, $[\text{Cp}^*\text{Rh}(\text{bpy})\text{X}]^+$, 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 dihydroxybipyridine (DHBP) ligand was introduced. The acid-base equilibrium between the hydroxyl and oxanion 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).

Catalyst	Solvent	Additive	T/°C	Pressure /MPa	t/h	Initial TOF ^a /h ⁻¹	TON
7	H ₂ O	-	100	10	-	23	-
8	H ₂ O	KOH	120	6	57	42,000	190,000
8	H ₂ O	KOH	60	0.1	50	33	376
9	H ₂ O	KOH	60	0.1	50	32	444
9	H ₂ O	KOH	30	0.1	30	3.5	81
9	H ₂ O	KOH	120	6	48	33,000	222,000
10	H ₂ O/THF	KOH	200	5	2	(150,000)	300,000
10	H ₂ O/THF	KOH	120	6	48	(73,000)	3,500,000
12	H ₂ O	KOH	185	5.5	24	(14,500)	348,000
12	H ₂ O	KOH	185	5.5	1	(18,780)	18,780
13	H ₂ O	KOH	80	6	18	-	1600
14	H ₂ O	KOH	200	4	20	-	9500
15	H ₂ O	KOH	200	6	75	(2500)	190,000

Table 2. Hydrogenation of CO₂ to formic acid/formate using iridium catalysts. *a.* The data in parenthesis are average TOF.

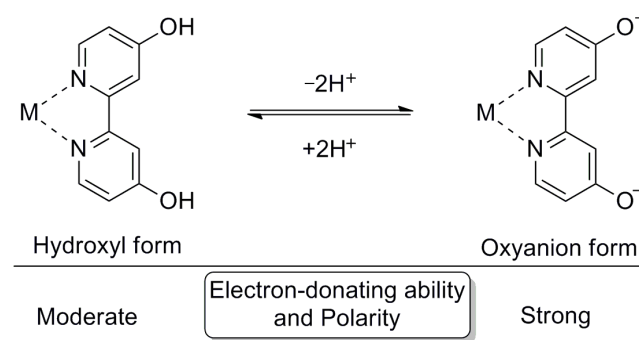


Figure 3. Acid-base equilibrium between hydroxyl and oxyanion forms.

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_nMe_n)M(L)Cl]⁺ (M = Rh, Ir, n = 5; M = Ru, n = 6), on the hydrogenation of CO₂. 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_nMe_n)M(4,4'-R₂-2,2'-bpy)Cl]⁺ (M = Ir, Rh, Ru; R = OH, OMe, Me, H). Note that under basic conditions the hydroxyl group (Hammett constant, σ_p⁺ = -0.92) was deprotonated to generate an oxyanion, which is a much stronger donor and has a σ_p⁺ of -2.30. The Hammett plots show a good correlation between the initial TOFs and the σ_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

apparent that the remarkable activation of the iridium DHBP catalyst can be attributed to the strong electron-donating ability of the oxyanion. 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 **8** 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.

Catalyst ^a	TON				
	L:	bpy	DHBP	phen	DHPT
Rh-L		216 ^b	1800	220	2300
Ru-L		68	4400	78 ^c	5100
Ir-L		105 ^c	5500	59	6100

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.

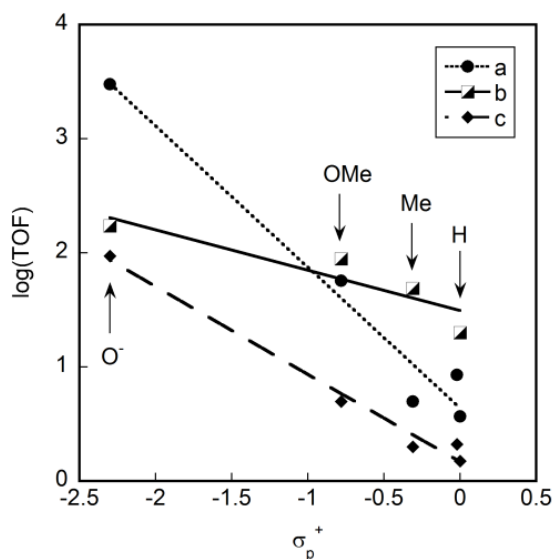


Figure 4. Correlation between initial TOFs and σ_p^+ values of substituents (R) for the hydrogenation of CO₂ catalyzed by [(C_nMe_n)M(4,4'-R₂-2,2'-bpy)Cl]Cl. *a.* M = Ir, *n* = 5; *b.* M = Rh, *n* = 5; *c.* M = Ru, *n* = 6; R = OH, OMe, Me, H. The reactions were carried out in an aqueous 1 M KOH solution under 4 MPa (CO₂:H₂ = 1:1) at 80 °C for 20 h.

In 2009, Nozaki and co-workers designed Ir(III) complexes **10** 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, **10**, showed the highest TON (3,500,000) and TOF (150,000 h⁻¹) to date. (Tanaka et al., 2009) In 2011, Hazari and co-workers investigated CO₂ insertion into PNP-Ir hydrides using a computational method. (Schmeier et al., 2011) 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

experimentally isolated air- and moisture-stable complex **12**. When **12** was used for the hydrogenation of CO₂, 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 CO₂. Most recently, Peris and co-workers reported a series of IrCp*(NHC) complexes. A bis-NHC Ir complex, **13**, showed modest activity (TON of 1600) for the hydrogenation of CO₂ 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 CO₂ to formate using *i*PrOH as a hydrogen donor.

4. Hydrogenation with other metal complexes

As mention above, the homogenous catalysts for hydrogenation of CO₂ 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 CO₂ to formate esters in alcohols with [HFe₃(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(η²-CO₂)(PMePh₂)₂. In addition, using the Pd complexes, PdCl₂L₂ (L = PMe₃; PMePh₂; PPh₃), they obtained formic acid in 12% yield in benzene/H₂O under 100 atm H₂/CO₂ (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 CO₂ in DMSO. (Tai et al., 2003) They found the combination of FeCl₃ and NiCl₂ with dcpe ligand (dcpe = Cy₂PCH₂CH₂PCy₂) 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 CO₂ and bicarbonate to formate in MeOH. The best iron catalyst, Fe(BF₄)₂/PP₃ (PP₃ =

$P(CH_2CH_2PPh_2)_3$, could reduce bicarbonate to formate in a TON of 610 which was comparable with that using $[RuCl_2(C_6H_6)_2]/PP_3$. It also could transform CO_2 and H_2 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 CO_2 with in situ generated cobalt catalyst. They obtained a high TON of 3877 using the $Co(BF_4)_2 \cdot 6H_2O$ and PP_3 in a sodium formate at $120^\circ C$ 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 $trans-[(tBu-PNP)Fe(H)_2(CO)]$ which showed similar activity to noble metal catalysts. (Langer et al., 2011) Hydrogenation of sodium bicarbonate to formate in H_2O/THF (10/1) have achieved a TON of 320 at $80^\circ C$ under 8.3 bar H_2 . Hydrogenation of CO_2 in a 2 M NaOH solution gave a TON of 788 and TOF of $156\ h^{-1}$ at total pressure of 10 bar ($H_2/CO_2 = 6.7/3.3$) for 5 h.

5. Mechanism of CO_2 hydrogenation

To understand the reaction process of CO_2 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 CO_2 hydrogenation, there are several aspects need to pay attention to, such as activation of dihydrogen and CO_2 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 CO_2 to facilitate CO_2 insertion (Figure 5A). Lau et al. found the reaction rate is enhanced by adding 20% water in THF by using $TpRu(PPh_3)(CH_3CN)H$ [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 CO_2 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.

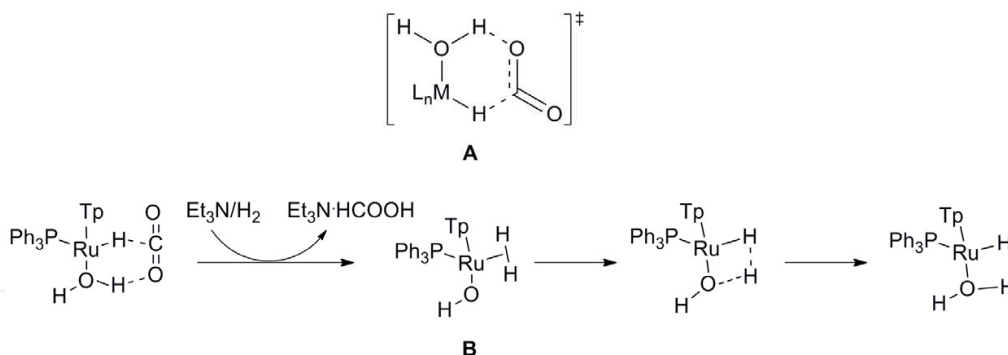


Figure 5. Water effect in the hydrogenation of CO₂.

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).

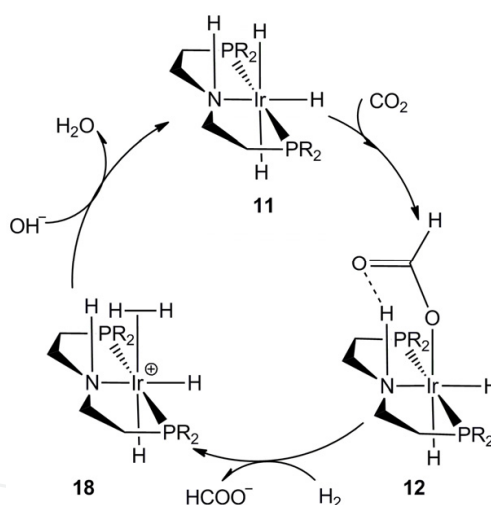


Figure 6. Reaction mechanism of CO₂ hydrogenation proposed by Hazari et al.

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

proposed a mechanism for the catalytic reaction (Figure 7): the insertion of CO_2 into **10** gives formate complex **16**, which undergoes dissociation of the formate 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**.

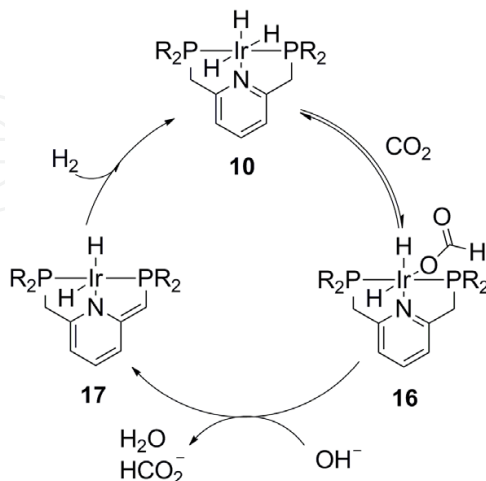


Figure 7. Catalytic mechanism for the hydrogenation of CO_2 proposed by Nozaki.

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 $(\text{PNP})\text{IrH}_3$ 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 .

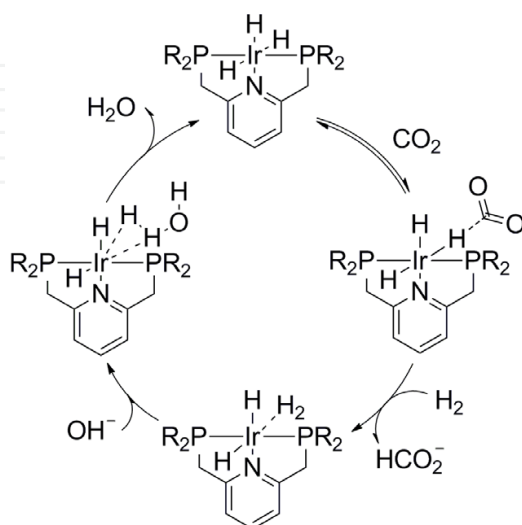


Figure 8. Catalytic mechanism of CO_2 hydrogenation proposed by Yang.

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 P_{H_2} and P_{CO_2} respectively. (Ogo et al., 2006) The rate-determining step of $[(\eta^6-C_6Me_6)Ru(bpy)(OH_2)](SO_4)$ and $[(\eta^6-C_6Me_6)Ru(4,4'-OMe-bpy)(OH_2)](SO_4)$ was suggested to be the reaction of aqua complexes with H_2 . In contrast, the Ir analogous was supposed to be the 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 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 carben species for hydrogenation of CO_2 . (Baffert et al., 2011) Using pyrrolidine as an additive, Ru_{cym} and $M-Ru_{cym}$ (Figure 9) showed low catalytic activity. By introducing basic phosphorous ligand PMe_3 , the activity of $M-RuP$ (Figure 9) is improved and showed comparable TON with the parent catalyst $[RuCl_2(PMe_3)_4]$. However, the supported catalyst are unstable due to the weak Ru-NHC linkage, 50% of Ru was found leached into reaction solution.

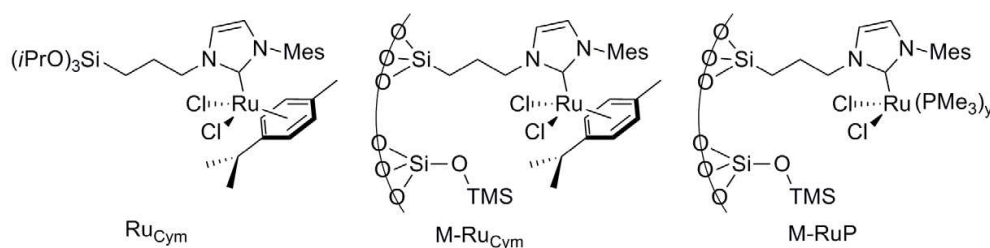


Figure 9. Silica supported Ru catalysts. (Mes: Mesityl; TMS: trimethylsilyl)

Zheng et al. have reported the ruthenium immobilized on functionalized silica could be used as catalyst precursor for hydrogenation of CO_2 in organic solvent with adding triphenylphosphine. (Zhang et al., 2004) In light of this result, in 2008, Han et al. prepared the silica supported catalyst " $Si-(CH_2)_3NH(CSCH_3)-[RuCl_3(PPh_3)]$ " and used it to the hydrogenation of CO_2 in a mixture solvent of H_2O and ionic liquid. The ionic liquid, 1-(N,N-dimethylaminoethyl)-2,3-dimethylimidazolium trifluoromethanesulfonate ($[mammim][TfO]$), 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 $110\text{ }^\circ C$ to remove the water and then heated to $130\text{ }^\circ C$ to separate the formic acid. Since the ionic liquid is non-volatile and stable below $220\text{ }^\circ C$, it can be separated and reused after the distillation. The catalyst and ionic liquid could be reused four times without decrease of TOF ($\sim 44\text{ h}^{-1}$). 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”-(CH₂)₃NH(CSCH₃)-[RuCl₃(PPh₃)], CO₂ 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⁻¹ was obtained at 80 °C under 18 MPa of H₂/CO₂ (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.

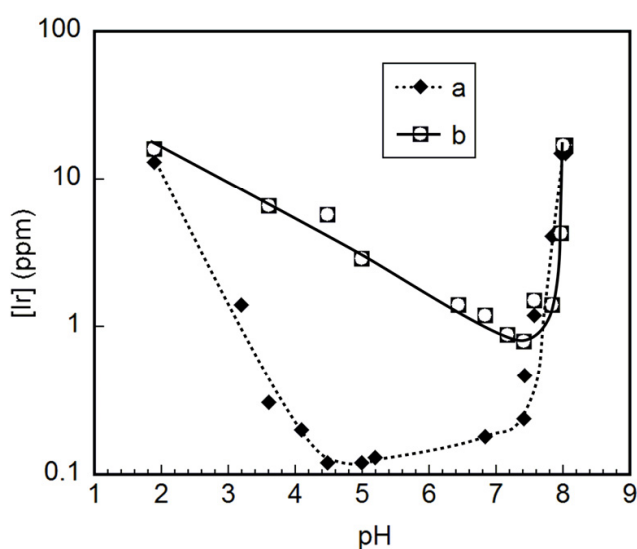


Figure 10. Solubility of a) DHBP catalyst **8** and b) DHPT catalyst **9** in a 1 M aqueous formate solution.

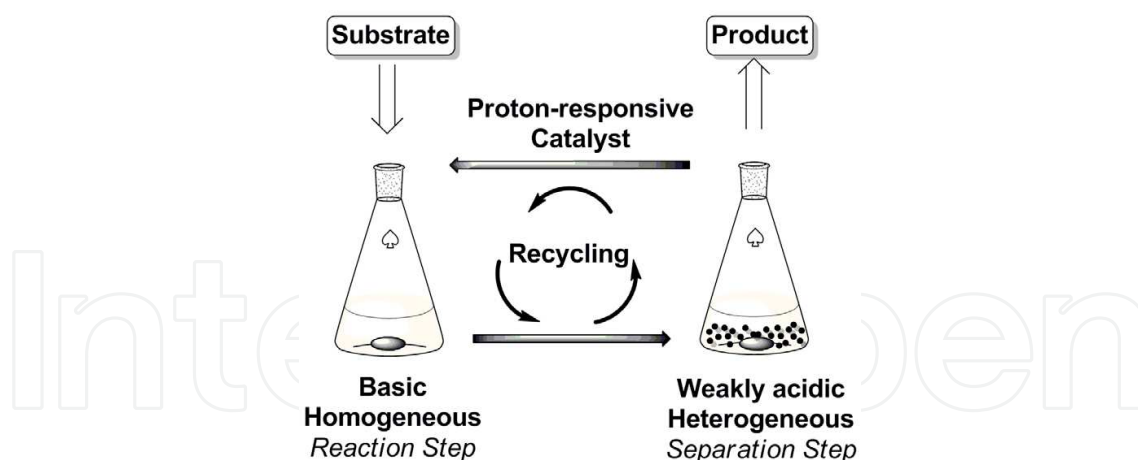


Figure 11. Recycling of proton-responsive catalyst with tunable solubility.

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.

Cycle	Loaded/recovered cat./ppm	Recovery efficiency/%	Leaching iridium ^a /ppm	Final conc. of formate/M
1	9.0	-	0.11	0.105
2	8.4	93	0.22	0.104
3	7.7	92	0.42	0.103
4	7.0	91	0.61	0.103

Table 4. Catalyst recycling studies for the conversion of CO₂ into formate using iridium-DHPT catalyst **9**. 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.

Author details

Wan-Hui Wang and Yuichiro Himeda

National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan

Acknowledgement

We thank the Japanese Ministry of Economy, Trade, and Industry for financial support.

8. References

- Ahlquist, M. S. G. (2010). Iridium catalyzed hydrogenation of CO₂ under basic conditions—Mechanistic insight from theory. *J. Mol. Catal. A: Chem.*, Vol.324, No.1-2, pp. 3-8, ISSN 13811169
- Azua, A.; Sanz, S. & Peris, E. (2011). Water-soluble IrIII N-heterocyclic carbene based catalysts for the reduction of CO₂ to formate by transfer hydrogenation and the deuteration of aryl amines in water. *Chem.-Eur. J.*, Vol.17, No.14, pp. 3963-3967, ISSN 1521-3765 (Electronic)
- Baffert, M.; Maishal, T. K.; Mathey, L.; Coperet, C. & Thieuleux, C. (2011). Tailored ruthenium-N-heterocyclic carbene hybrid catalytic materials for the hydrogenation of carbon dioxide in the presence of amine. *ChemSusChem*, Vol.4, No.12, pp. 1762-1765, ISSN 1864-564X (Electronic)
- Boddien, A.; Gärtner, F.; Federsel, C.; Sponholz, P.; Mellmann, D.; Jackstell, R.; Junge, H. & Beller, M. (2011). CO₂-“Neutral” Hydrogen Storage Based on Bicarbonates and Formates. *Angew. Chem. Int. Ed.*, Vol.50, No.28, pp. 6411-6414, ISSN 1521-3773
- Chu, H. S.; Lau, C. P.; Wong, K. Y. & Wong, W. T. (1998). Intramolecular N-H...H-Ru Proton-Hydride Interaction in Ruthenium Complexes with (2-(Dimethylamino)ethyl)cyclopentadienyl and (3-(Dimethylamino)propyl)cyclopentadienyl Ligands. Hydrogenation of CO₂ to Formic Acid via the N-H...H-Ru Hydrogen-Bonded Complexes. *Organometallics*, Vol.17, No.13, pp. 2768-2777, ISSN 0276-7333
- Elek, J.; Nadasdi, L.; Papp, G.; Laurenczy, G. & Joó, F. (2003). Homogeneous hydrogenation of carbon dioxide and bicarbonate in aqueous solution catalyzed by water-soluble

- ruthenium(II) phosphine complexes. *Appl. Catal. A-Gen.*, Vol.255, No.1, pp. 59-67, ISSN 0926-860X
- Erlandsson, M.; Landaeta, V. R.; Gonsalvi, L.; Peruzzini, M.; Phillips, A. D.; Dyson, P. J. & Laurenczy, G. (2008). (Pentamethylcyclopentadienyl)iridium-PTA (PTA = 1,3,5-Triaza-7-phosphaadamantane) Complexes and Their Application in Catalytic Water Phase Carbon Dioxide Hydrogenation. *Eur. J. Inorg. Chem.*, Vol.2008, No.4, pp. 620-627, ISSN 14341948
- Evans, G. O. & Newell, C. J. (1978). Conversion of CO₂, H₂, and alcohols into formate esters using anionic iron carbonyl hydrides. *Inorg. Chim. Acta*, Vol.31, pp. L387-L389, ISSN 0020-1693
- Federsel, C.; Boddien, A.; Jackstell, R.; Jennerjahn, R.; Dyson, P. J.; Scopelliti, R.; Laurenczy, G. & Beller, M. (2010a). A well-defined iron catalyst for the reduction of bicarbonates and carbon dioxide to formates, alkyl formates, and formamides. *Angew. Chem. Int. Ed.*, Vol.49, No.50, pp. 9777-9780, ISSN 1521-3773 (Electronic)
- Federsel, C.; Jackstell, R. & Beller, M. (2010b). State-of-the-art catalysts for hydrogenation of carbon dioxide. *Angew. Chem. Int. Ed.*, Vol.49, No.36, pp. 6254-6257, ISSN 1521-3773 (Electronic)
- Federsel, C.; Ziebart, C.; Jackstell, R.; Baumann, W. & Beller, M. (2012). Catalytic hydrogenation of carbon dioxide and bicarbonates with a well-defined cobalt dihydrogen complex. *Chem.-Eur. J.*, Vol.18, No.1, pp. 72-75, ISSN 1521-3765 (Electronic)
- Gassner, F. & Leitner, W. (1993). CO₂ Activation 3. Hydrogenation of Carbon Dioxide to Formic Acid Using Water-Soluble Rhodium Catalysts. *J. Chem. Soc.-Chem. Commun.*, No.19, pp. 1465-1466, ISSN 0022-4936
- Getty, A. D.; Tai, C.-C.; Linehan, J. C.; Jessop, P. G.; Olmstead, M. M. & Rheingold, A. L. (2009). Hydrogenation of Carbon Dioxide Catalyzed by Ruthenium Trimethylphosphine Complexes: A Mechanistic Investigation Using High-Pressure NMR Spectroscopy. *Organometallics*, Vol.28, No.18, pp. 5466-5477, ISSN 0276-7333
- Hayashi, H.; Ogo, S.; Abura, T. & Fukuzumi, S. (2003). Accelerating effect of a proton on the reduction of CO₂ dissolved in water under acidic conditions. Isolation, crystal structure, and reducing ability of a water-soluble ruthenium hydride complex. *J. Am. Chem. Soc.*, Vol.125, No.47, pp. 14266-14267, ISSN 0002-7863
- Hayashi, H.; Ogo, S. & Fukuzumi, S. (2004). Aqueous hydrogenation of carbon dioxide catalysed by water-soluble ruthenium aqua complexes under acidic conditions. *Chem. Commun.*, No.23, pp. 2714-2715, ISSN 1359-7345
- Himeda, Y. (2007). Conversion of CO₂ into formate by homogeneously catalyzed hydrogenation in water: Tuning catalytic activity and water solubility through the acid-base equilibrium of the ligand. *Eur. J. Inorg. Chem.*, No.25, pp. 3927-3941, ISSN 1434-1948
- Himeda, Y.; Miyazawa, S. & Hirose, T. (2011). Interconversion between Formic Acid and H₂/CO₂ using Rhodium and Ruthenium Catalysts for CO₂ Fixation and H₂ Storage. *ChemSusChem*, Vol.4, No.4, pp. 487-493, ISSN 1864-5631
- Himeda, Y.; Onozawa-Komatsuzaki, N.; Sugihara, H.; Arakawa, H. & Kasuga, K. (2003). Transfer hydrogenation of a variety of ketones catalyzed by rhodium complexes in

- aqueous solution and their application to asymmetric reduction using chiral Schiff base ligands. *J. Mol. Catal. A-Chem.*, Vol.195, No.1-2, pp. 95–100, ISSN 1381-1169
- Himeda, Y.; Onozawa-Komatsuzaki, N.; Sugihara, H.; Arakawa, H. & Kasuga, K. (2004). Half-sandwich complexes with 4,7-dihydroxy-1,10-phenanthroline: Water-soluble, highly efficient catalysts for hydrogenation of bicarbonate attributable to the generation of an oxyanion on the catalyst ligand. *Organometallics*, Vol.23, No.7, pp. 1480–1483, ISSN 0276-7333
- Himeda, Y.; Onozawa-Komatsuzaki, N.; Sugihara, H.; Arakawa, H. & Kasuga, K. Japan Patent 3968431 (filed on Jan. 21, 2003), 2007a.
- Himeda, Y.; Onozawa-Komatsuzaki, N.; Sugihara, H. & Kasuga, K. (2005). Recyclable catalyst for conversion of carbon dioxide into formate attributable to an oxyanion on the catalyst ligand. *J. Am. Chem. Soc.*, Vol.127, No.38, pp. 13118–13119, ISSN 0002-7863
- Himeda, Y.; Onozawa-Komatsuzaki, N.; Sugihara, H. & Kasuga, K. (2006). Highly efficient conversion of carbon dioxide catalyzed by half-sandwich complexes with pyridinol ligand: The electronic effect of oxyanion. *J. Photochem. Photobiol. A-Chem.*, Vol.182, No.3, pp. 306–309, ISSN 1010-6030
- Himeda, Y.; Onozawa-Komatsuzaki, N.; Sugihara, H. & Kasuga, K. (2007b). Simultaneous tuning of activity and water solubility of complex catalysts by acid-base equilibrium of ligands for conversion of carbon dioxide. *Organometallics*, Vol.26, No.3, pp. 702–712, ISSN 0276-7333
- Horváth, H.; Laurenczy, G. & Kathó, Á. (2004). Water-soluble (η^6 -arene)ruthenium(II)-phosphine complexes and their catalytic activity in the hydrogenation of bicarbonate in aqueous solution. *J. Organomet. Chem.*, Vol.689, No.6, pp. 1036-1045, ISSN 0022328X
- Hutschka, F.; Dedieu, A.; Eichberger, M.; Fornika, R. & Leitner, W. (1997). Mechanistic aspects of the rhodium-catalyzed hydrogenation of CO₂ to formic acid - A theoretical and kinetic study. *J. Am. Chem. Soc.*, Vol.119, No.19, pp. 4432-4443, ISSN 0002-7863
- Inoue, Y.; Izumida, H.; Sasaki, Y. & Hashimoto, H. (1976). Catalytic fixation of carbon dioxide to formic acid by transition-metal complexes under mild conditions. *Chem. Lett.*, pp. 863-864, ISSN
- Jessop, P. G., Homogeneous hydrogenation of carbon dioxide. In *Handbook of Homogeneous Hydrogenation*, De Vries, J. G.; Elsevier, C. J., Eds. Wiley-VCH: Weinheim, 2007; Vol. 1, pp 489-511.
- Jessop, P. G.; Hsiao, Y.; Ikariya, T. & Noyori, R. (1996). Homogeneous catalysis in supercritical fluids: Hydrogenation of supercritical carbon dioxide to formic acid, alkyl formates, and formamides. *J. Am. Chem. Soc.*, Vol.118, No.2, pp. 344-355, ISSN 0002-7863
- Jessop, P. G.; Ikariya, T. & Noyori, R. (1994). Homogeneous Catalytic-Hydrogenation of Supercritical Carbon-Dioxide. *Nature*, Vol.368, No.6468, pp. 231-233, ISSN 0028-0836
- Jessop, P. G.; Joó, F. & Tai, C.-C. (2004). Recent advances in the homogeneous hydrogenation of carbon dioxide. *Coord. Chem. Rev.*, Vol.248, No.21-24, pp. 2425-2442, ISSN 00108545
- Joó, F.; Laurenczy, G.; Nadasdi, L. & Elek, J. (1999). Homogeneous hydrogenation of aqueous hydrogen carbonate to formate under exceedingly mild conditions - a novel possibility of carbon dioxide activation. *Chem. Commun.*, No.11, pp. 971-972, ISSN 1359-7345

- Langer, R.; Diskin-Posner, Y.; Leitun, G.; Shimon, L. J.; Ben-David, Y. & Milstein, D. (2011). Low-Pressure Hydrogenation of Carbon Dioxide Catalyzed by an Iron Pincer Complex Exhibiting Noble Metal Activity. *Angew. Chem. Int. Ed.*, pp. 9948-9952, ISSN 1521-3773 (Electronic)
- Laurenczy, G.; Joó, F. & Nadasdi, L. (2000). Formation and characterization of water-soluble hydrido-ruthenium(II) complexes of 1,3,5-triaza-7-phosphaadamantane and their catalytic activity in hydrogenation of CO₂ and HCO₃⁻ in aqueous solution. *Inorg. Chem.*, Vol.39, No.22, pp. 5083-5088, ISSN 0020-1669
- Leitner, W.; Dinjus, E. & Gassner, F. (1994). Activation of Carbon Dioxide 4. Rhodium-Catalyzes Hydrogenation of Carbon Dioxide to Formic Acid. *J. Organomet. Chem.*, Vol.475, No.1-2, pp. 257-266, ISSN 0022-328X
- Leitner, W.; Dinjus, E. & Gassner, F., In *Aqueous-Phase Organometallic Catalysis, Concepts and Applications*, Cornils, B.; Herrmann, W. A., Eds. Wiley-VCH: Weinheim, 1998; pp 486-498.
- Munshi, P.; Main, A. D.; Linehan, J. C.; Tai, C. C. & Jessop, P. G. (2002). Hydrogenation of carbon dioxide catalyzed by ruthenium trimethylphosphine complexes: The accelerating effect of certain alcohols and amines. *J. Am. Chem. Soc.*, Vol.124, No.27, pp. 7963-7971, ISSN 0002-7863
- Ng, S. M.; Yin, C. Q.; Yeung, C. H.; Chan, T. C. & Lau, C. P. (2004). Ruthenium-catalyzed hydrogenation of carbon dioxide to formic acid in alcohols. *Eur. J. Inorg. Chem.*, No.9, pp. 1788-1793, ISSN 1434-1948
- Ogo, S.; Kabe, R.; Hayashi, H.; Harada, R. & Fukuzumi, S. (2006). Mechanistic investigation of CO₂ hydrogenation by Ru(II) and Ir(III) aqua complexes under acidic conditions: two catalytic systems differing in the nature of the rate determining step. *Dalton Trans.*, No.39, pp. 4657-4663, ISSN 1477-9226 (Print)
- Ohnishi, Y. Y.; Matsunaga, T.; Nakao, Y.; Sato, H. & Sakaki, S. (2005). Ruthenium(II)-catalyzed hydrogenation of carbon dioxide to formic acid. theoretical study of real catalyst, ligand effects, and solvation effects. *J. Am. Chem. Soc.*, Vol.127, No.11, pp. 4021-4032, ISSN 0002-7863
- Papp, G.; Csorba, J.; Laurenczy, G. & Joó, F. (2011). A Charge/Discharge Device for Chemical Hydrogen Storage and Generation. *Angew. Chem. Int. Ed.*, Vol.50, No.44, pp. 10433-10435, ISSN 1521-3773
- Sakamoto, M.; Shimizu, I. & Yamamoto, A. (1994). Synthesis of the first carbon dioxide coordinated palladium(0) complex, Pd(η^2 -CO₂)(PMePh₂)₂. *Organometallics*, Vol.13, No.2, pp. 407-409, ISSN 0276-7333
- Sanz, S.; Azua, A. & Peris, E. (2010a). '(η^6 -arene)Ru(bis-NHC)' complexes for the reduction of CO₂ to formate with hydrogen and by transfer hydrogenation with *i*PrOH. *Dalton Trans.*, Vol.39, No.27, pp. 6339-6343, ISSN 1477-9234 (Electronic)
- Sanz, S.; Benítez, M. & Peris, E. (2010b). A New Approach to the Reduction of Carbon Dioxide: CO₂ Reduction to Formate by Transfer Hydrogenation in *i*PrOH. *Organometallics*, Vol.29, No.1, pp. 275-277, ISSN 0276-7333
- Schmeier, T. J.; Dobereiner, G. E.; Crabtree, R. H. & Hazari, N. (2011). Secondary coordination sphere interactions facilitate the insertion step in an iridium(III) CO₂

- reduction catalyst. *J. Am. Chem. Soc.*, Vol.133, No.24, pp. 9274-9277, ISSN 1520-5126 (Electronic)
- Tai, C. C.; Chang, T.; Roller, B. & Jessop, P. G. (2003). High-pressure combinatorial screening of homogeneous catalysts: Hydrogenation of carbon dioxide. *Inorg. Chem.*, Vol.42, No.23, pp. 7340-7341, ISSN 0020-1669
- Tai, C. C.; Pitts, J.; Linehan, J. C.; Main, A. D.; Munshi, P. & Jessop, P. G. (2002). In situ formation of ruthenium catalysts for the homogeneous hydrogenation of carbon dioxide. *Inorg. Chem.*, Vol.41, No.6, pp. 1606-1614, ISSN 0020-1669
- Tanaka, R.; Yamashita, M. & Nozaki, K. (2009). Catalytic hydrogenation of carbon dioxide using Ir(III)-pincer complexes. *J. Am. Chem. Soc.*, Vol.131, No.40, pp. 14168-14169, ISSN 1520-5126 (Electronic)
- Tsai, J. C. & Nicholas, K. M. (1992). Rhodium-Catalyzed Hydrogenation of Carbon-Dioxide to Formic-Acid. *J. Am. Chem. Soc.*, Vol.114, No.13, pp. 5117-5124, ISSN 0002-7863
- Wang, W.; Wang, S.; Ma, X. & Gong, J. (2011). Recent advances in catalytic hydrogenation of carbon dioxide. *Chem. Soc. Rev.*, Vol.40, No.7, pp. 3703-3727, ISSN 1460-4744 (Electronic)
- Yang, X. (2011). Hydrogenation of Carbon Dioxide Catalyzed by PNP Pincer Iridium, Iron, and Cobalt Complexes: A Computational Design of Base Metal Catalysts. *ACS Catal.*, Vol.1, No.8, pp. 849-854, ISSN 2155-5435
- Yin, C.; Xu, Z.; Yang, S.-Y.; Ng, S. M.; Wong, K. Y.; Lin, Z. & Lau, C. P. (2001). Promoting Effect of Water in Ruthenium-Catalyzed Hydrogenation of Carbon Dioxide to Formic Acid. *Organometallics*, Vol.20, No.6, pp. 1216-1222, ISSN 0276-7333
- Zhang, Y.; Fei, J.; Yu, Y. & Zheng, X. (2004). Silica immobilized ruthenium catalyst used for carbon dioxide hydrogenation to formic acid (I): the effect of functionalizing group and additive on the catalyst performance. *Catal. Commun.*, Vol.5, No.10, pp. 643-646, ISSN 1566-7367
- Zhang, Z.; Hu, S.; Song, J.; Li, W.; Yang, G. & Han, B. (2009). Hydrogenation of CO₂ to formic acid promoted by a diamine-functionalized ionic liquid. *ChemSusChem*, Vol.2, No.3, pp. 234-238, ISSN 1864-564X (Electronic)
- Zhang, Z.; Xie, Y.; Li, W.; Hu, S.; Song, J.; Jiang, T. & Han, B. (2008). Hydrogenation of carbon dioxide is promoted by a task-specific ionic liquid. *Angew. Chem. Int. Ed.*, Vol.47, No.6, pp. 1127-1129, ISSN 1521-3773 (Electronic)