Communication

Iridium(NHC)-Catalyzed Sustainable Transfer Hydrogenation of CO_2 and Inorganic Carbonates

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Abstract: Iridium(NHC)-catalyzed transfer hydrogenation (TH) of CO_2 and inorganic carbonates with glycerol were conducted, demonstrating excellent turnover numbers (TONs) and turnover frequencies (TOFs) for the formation of formate and lactate. Regardless of carbon sources, excellent TOFs of formate were observed (CO_2: 10,000 h^{-1} and K_2CO_3: 10,150 h^{-1}). Iridium catalysts modified with the triscarbene ligand showed excellent catalytic activity at 200 °C and are a suitable choice for this transformation which requires a high temperature for high TONs of formate. On the basis of the control experiments, the transfer hydrogenation mechanism of CO_2 was proposed.

Keywords: carbon dioxide; inorganic carbonate; transfer hydrogenation; iridium(NHC)

1. Introduction

The transition-metal-catalyzed hydrogenation of CO_2 has received great attention for its potential to contribute to the resolution of global warming by converting CO_2 to valuable chemicals, thus reducing the CO_2 concentration in the air [1–9]. The resulting hydrogenated CO_2 product, formate, is a sustainable and safe chemical for hydrogen gas storage. Since the pioneering work by Inoue et al. in 1976 [10], a variety of homogeneous catalysts have shown excellent catalytic activity for the hydrogenation of CO_2 to form formic acid/formate with high TONs and TOFs [11–18]. In parallel with the hydrogenation of CO_2, transfer hydrogenation using sustainable hydrogen sources has been used to further increase the environmental benefits of CO_2 utilization. Glycerol, a sustainable hydrogen source, increases the sustainability and economic value of the transfer hydrogenation of CO_2 because glycerol is the by-product of the biodiesel process, and glycerol provides hydrogen as well as useful C3 feedstocks, such as lactic acid in the transfer hydrogenation reaction [19–21]. The transfer hydrogenation of CO_2 and CO_2-derived inorganic carbonates with glycerol are relatively less well-studied compared to the glycerol-mediated transfer hydrogenation of aldehydes and ketones, largely due to the gaseous nature of CO_2 and the low reactivity of carbonates compared to aldehydes and ketones [22–27]. The transfer hydrogenation of CO_2 has also been studied using isopropanol as a hydrogen source [28–30], but advantages of glycerol such as sustainability and useful C3 product (lactic acid) generation increase the value of glycerol-mediated transfer hydrogenation of CO_2.

In recently reported transfer hydrogenation reactions of CO_2 with glycerol, including our work, iridium catalysts modified with carbene ligands formed formate and lactate with high TONs and TOFs [22–25]. The electron-donating property of NHC ligands in the iridium catalysts plays a key role along with the oxidation state of iridium ions and the coordination mode of NHC ligands (mono- or bidentate coordination) in the iridium catalyzed-transfer hydrogenation [31]. Based on our previous report, including theoretical calculations of the iridium-catalyzed transfer hydrogenation of carbonate in glycerol, the energy barrier of the reduction of CO_2 with Ir-H was much higher compared to other

steps, implying that more thermal energy is required to improve the CO_2 reduction [24]. Accordingly, multidentate carbene ligand-modified iridium catalysts showing stability at high temperatures (e.g., 200 °C) were considered to increase TONs and TOFs of the transfer hydrogenation of CO_2 and carbonate. Because we found that the triscarbene-modified iridium complexes exhibited excellent catalytic activities in the dehydrogenation of glycerol at high temperatures [32], we posit that triscarbene based-iridium catalysts are good candidates for the transfer hydrogenation of C1 sources, including CO_2 and carbonates at high temperatures. In this study, we present the highly efficient, sustainable, and versatile iridium(NHC)-catalyzed transfer hydrogenation of CO_2 and inorganic carbonates using biomass-derived glycerol, resulting in excellent TONs and TOFs (Scheme 1).
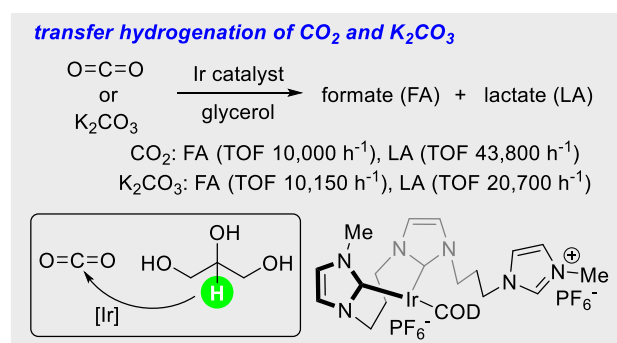
Scheme 1. Transfer hydrogenation of CO_2 and K_2CO_3.

2. Results and Discussion

The reaction optimization for the iridium(NHC)-catalyzed transfer hydrogenation of CO_2 is shown in Table 1. The iridium(NHC) catalysts used in this reaction are shown in Figure 1; their synthesis and characterization were reported in our previous publication [32]. The X-ray crystal structure of catalyst **3′** including dichloromethane is shown in Figure 2. A single crystal of **3′** was obtained by slow evaporation of a dichloromethane/hexane mixture at −20 °C. The reaction of CO_2 (5 bar) and KOH (20 mmol) with catalyst **1** (3.5×10^{-4} mol%) in glycerol (purchased from Aldrich) at 180 °C formed formate and lactate with TONs of 3360 and 3900 (TOFs of 168 and 195 h^{-1}), respectively (entry 1). Formate was formed by the reduction of CO_2 using Ir-H, and lactate was formed from dihydroxyacetone and glyceraldehyde which were derived from the dehydrogenation of glycerol [33]. When the gaseous CO_2 is added into the mixture, inorganic carbonates are immediately formed in the presence of KOH, and resulting carbonates participate in the transfer hydrogenation. This hypothesis is confirmed by the following observation and the NMR spectrum. The CO_2 pressure rapidly dropped from 5 to 1 bar, implying that gaseous CO_2 was converted to K_2CO_3 in the presence of KOH. Based on the ^{13}C NMR analysis of the reaction mixture after pressurizing CO_2, the formation of K_2CO_3 was confirmed (see Supporting Information, Figure S1). After running the reaction for 20 h, the residual gas analysis showed only hydrogen generated from the dehydrogenation of glycerol without residual CO_2 (see Supporting Information, Figure S2). Considering the balanced chemical equation of this reaction, 2 equivalents of bases are required. The addition of 40 mmol of KOH to the reaction resulted in slightly reduced TONs of formate but much higher TONs of lactate (entry 2). Because most transfer hydrogenations of CO_2 with glycerol are carried out at 150–180 °C [22–25], the iridium(NHC)-catalyzed transfer hydrogenation of CO_2 in glycerol began at 180 °C. As the reaction temperature was increased to 200 °C, TONs of formate and lactate were dramatically increased (entry 3). The effect of CO_2 pressure was evaluated (entries 4 and 5). Formate was formed with lower TONs under 1 bar of CO_2, which provided less carbon than the reaction of CO_2 at 5 bar (entry 3). Although higher CO_2 pressure (10 bar) provided more carbon, it also reduced the pH of the solution. The initial pHs of the solutions for entries 4 and 5 were 14.0 and 10.3, respectively. Because the transfer hydrogenation of CO_2 in glycerol favors basic media,

applying a higher CO_2 pressure is not favorable for the formation of both formate and lactate. Upon decreasing the catalyst loading (3.5×10^{-5} mol%), the TONs of formate and lactate were increased to 200,000 (10,000 h^{-1}) and 875,000 (43,800 h^{-1}), respectively (entry 6). Using the conditions of entry 6, mono and bimetallic iridium catalysts involving different types of ligands were employed (entries 7–11). The reactions using monometallic catalysts exhibited higher TONs and TOFs (entries 6, 8, and 10) than bimetallic complex-catalyzed reactions, which is attributed to the higher reactivity of bidentate NHC-coordinated iridium catalysts toward the CO_2 reduction.[24] The bimetallic complex **1′** possesses bidentate NHC-coordinated iridium ions (1.75×10^{-5} mol%) and monodentate NHC-coordinated iridium ions (1.75×10^{-5} mol%), whereas the monometallic complex **1** has only bidentate NHC-coordinated iridium ions (3.5×10^{-5} mol%). With catalyst **1**, formate and lactate were formed with the highest TOFs for formate (10,000 h^{-1}) and lactate (43,800 h^{-1}) to date (entry 6), and catalysts **2** and **3** also exhibited high TOFs for formate and lactate (entries 8 and 10). In the absence of base, the reaction did not proceed (entry 12). The reaction involving only KOH formed a small amount of formate and lactate (entry 13) [34,35]. The amounts of formate and lactate formed in entry 6 were 1.40 and 6.12 mmol, respectively, while 0.06 mmol of formate and 0.4 mmol of lactate were formed in the absence of catalysts (entry 13). In addition to glycerol, 1,2-propandiol was employed in the presence of catalyst **1**, exhibiting much lower TONs of formate (7800).

Table 1. Transfer hydrogenation of CO_2 in glycerol.

Entry	Catalyst (mol%)	CO_2 (bar)	KOH (mmol)	Temp (°C)	Formate (TON, TOF h^{-1})	Lactate (TON, TOF h^{-1})
1	**1** (3.5×10^{-4})	5	20	180	3360, 168	3900, 195
2	**1** (3.5×10^{-4})	5	40	180	1490, 74.5	23,800, 1190
3	**1** (3.5×10^{-4})	5	40	200	15,800, 790	73,900, 3700
4	**1** (3.5×10^{-4})	1	40	200	2110, 106	104,000, 5200
5	**1** (3.5×10^{-4})	10	40	200	12,700, 635	14,400, 720
6	**1** (3.5×10^{-5})	5	40	200	200,000, **10,000**	875,000, **43,800**
7	**1′** (1.75×10^{-5}) [a]	5	40	200	77,400, **3870**	534,000, **26,700**
8	**2** (3.5×10^{-5})	5	40	200	176,000, **8800**	753,000, **37,700**
9	**2′** (1.75×10^{-5}) [a]	5	40	200	70,400, **3520**	548,000, **27,400**
10	**3** (3.5×10^{-5})	5	40	200	174,000, **8700**	683,000, **34,200**
11	**3′** (1.75×10^{-5}) [a]	5	40	200	103,000, **5150**	414,000, **20,700**
12	**1** (3.5×10^{-5})	5	–	200	–	–
13	–	5	40	200	0.06 mmol	0.4 mmol

The mixture of catalysts, CO_2, KOH, and H_2O (1.0 ml) in glycerol (21.1 mmol) was heated at indicated temperature for 20 h. [a] Catalysts 1′, 2′ and 3′ have two iridium ions in the molecule.
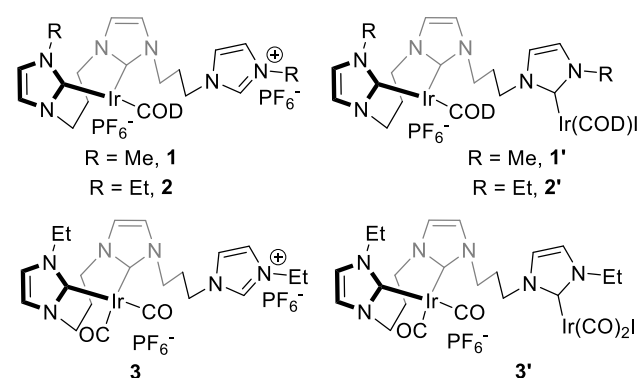

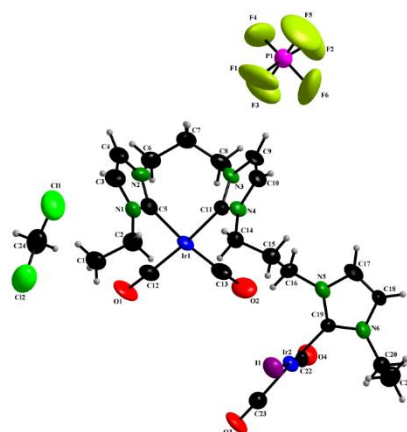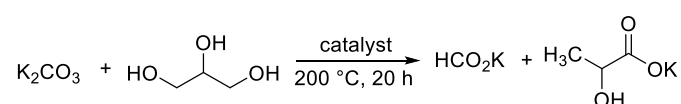**Figure 1.** Ir catalysts for the transfer hydrogenation of CO_2 and carbonates with glycerol.

Figure 2. X-ray crystal structure of catalyst **3′**.

For the transfer hydrogenation of K_2CO_3 with glycerol, a mixture of catalyst **1** (3.5×10^{-5} mol%), K_2CO_3 (40 mmol), and glycerol (42.3 mmol) was heated at 200 °C for 20 h, producing formate and lactate with TONs of 203,000 and 414,000, respectively (Table 2, entry 1). Catalysts **1′**, **2**, **2′**, **3**, and **3′** were employed under the conditions of entry 1; the highest TONs and TOFs were achieved with catalyst **1** (Table 2, entries 1–6). Compared to the result of CO_2 and KOH, the TONs of formate are similar and the TONs of lactate are lower with K_2CO_3 due to lesser basicity of K_2CO_3. The substituents at the carbene ligand or bi/monometallic structure of the catalysts did not make dramatic changes in TONs. The reaction of K_2CO_3 in 1,2-propandiol formed formate with TONs of 38,000, which is lower than the reactions of glycerol.

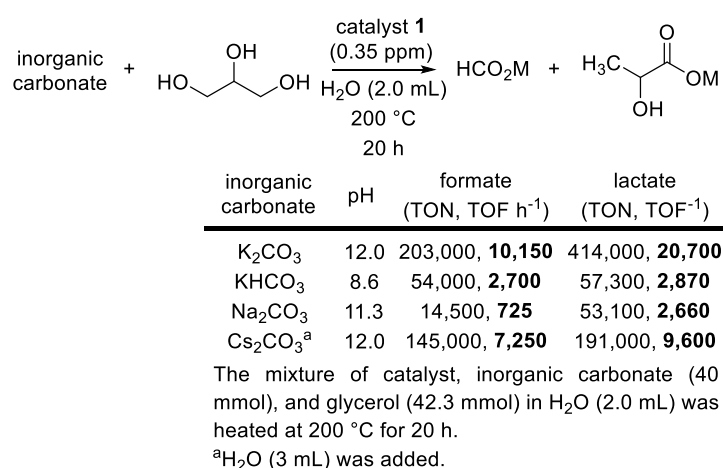**Table 2.** Transfer hydrogenation of K_2CO_3 in glycerol.

$$K_2CO_3 \; + \; HO\!\!\diagup\!\!\overset{OH}{\diagdown}\!\!\diagup\!\!OH \; \xrightarrow[\text{200 °C, 20 h}]{\text{catalyst}} \; HCO_2K \; + \; H_3C\!\!\overset{O}{\underset{OH}{\diagdown}}\!\!OK$$

Entry	Catalyst (mol%)	Formate (TON, TOF h^{-1})	Lactate (TON, TOF h^{-1})
1	**1** (3.5×10^{-5})	203,000, **10,150**	414,000, **20,700**
2	**1′** (1.75×10^{-5}) [a]	163,000, **8150**	357,000, **17,850**
3	**2** (3.5×10^{-5})	149,000, **7450**	315,000, **15,800**
4	**2′** (1.75×10^{-5}) [a]	178,000, **8900**	342,000, **17,100**
5	**3** (3.5×10^{-5})	164,000, **8200**	326,000, **16,300**
6	**3′** (1.75×10^{-5}) [a]	195,000, **9750**	400,000, **20,000**

The mixture of catalysts, K_2CO_3 (40 mmol), and glycerol (42.3 mmol) in H_2O (2 ml) was heated at 200 °C for 20 h. [a] Catalysts 1′, 2′ and 3′ have two iridium ions in the molecule.

To determine the effects of the solubility and basicity of inorganic carbonates in the transfer hydrogenation in glycerol [24,25], the reaction results of $KHCO_3$, Na_2CO_3, and Cs_2CO_3 were compared with that of K_2CO_3 (Scheme 2). The TONs and TOFs for formate formation with $KHCO_3$ were lower than those of K_2CO_3 due to the low basicity of bicarbonate ($KHCO_3$); the pH of the solution with $KHCO_3$ was 8.6. The reaction using Na_2CO_3 produced lower TONs and TOFs for formate formation because of the low solubility [24,25]. Although the pH of the solution including Cs_2CO_3 is the same as K_2CO_3, the TONs for the formation of formate and lactate were lower than those of K_2CO_3.
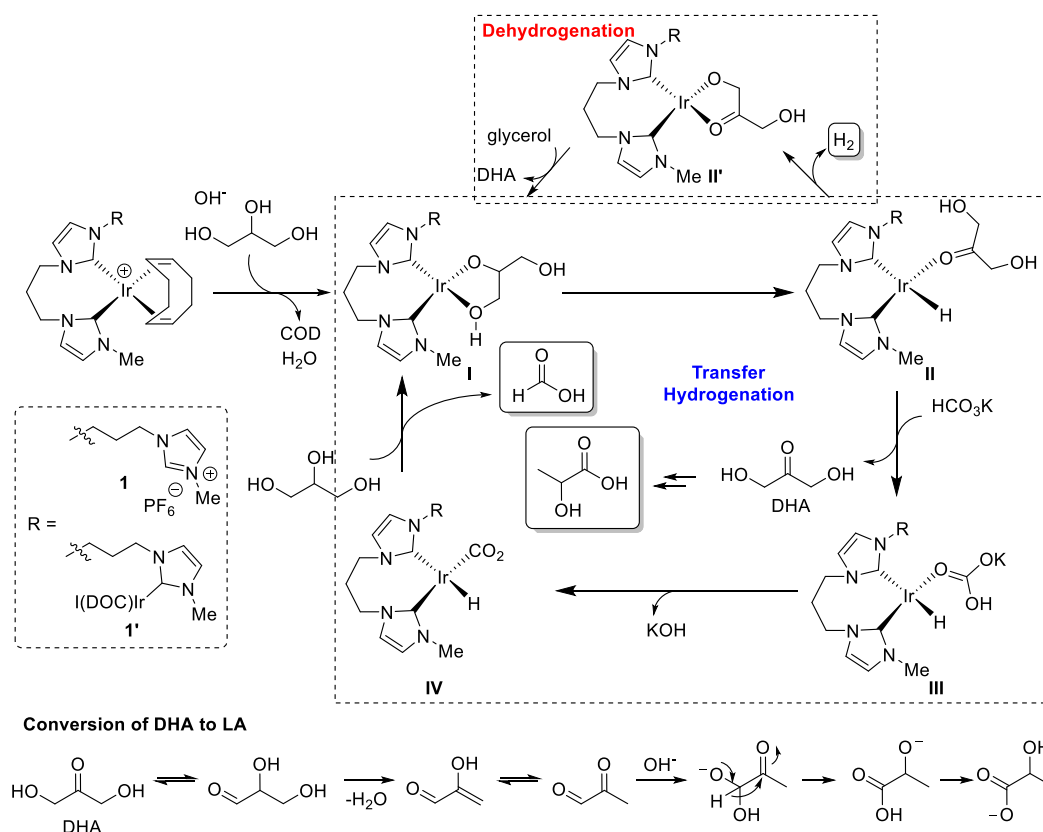
Scheme 2. Transfer hydrogenation of inorganic carbonate in glycerol.

The catalytic activities of previously reported catalysts in glycerol-mediated transfer hydrogenation of CO_2 (or K_2CO_3) are illustrated (Table 3). The ruthenium-NHC and iridium-abnormal NHC catalysts were employed for CO_2 transfer hydrogenation showing much lower TOFs (FA 44 and 90 h^{-1}, LA 70 h^{-1}) than this work (FA 10,000 h^{-1}, LA 43,800 h^{-1}) (entries 1, 3, and 6). The reactions of K_2CO_3 in glycerol were promoted by ruthenium-NHC and iridium-NHC (bidentate and monodentate) catalysts, exhibiting lower TOFs than current results (entries 2, 4, 5, and 7). Compared to previous work, our iridium-NHC catalysts showed high catalytic activities with extremely low concentrations and at high temperatures, resulting in the highest TOFs of formate and lactate.

Table 3. Previously reported catalysts for the transfer hydrogenation of CO_2 and inorganic carbonates with glycerol.

Entry	Catalyst	C1 Source	Temp (°C)	Formate (TOF h^{-1})	Lactate (TOF h^{-1})	Reference
1		CO_2 (26 bar)	180	44	70	[22]
2		K_2CO_3	150	179	2130	
3		CO_2 (1 bar)	150	90	–	[23]
4		K_2CO_3	180	840	1630	[24]
5		K_2CO_3	150	2170	3010	[25]
6		CO_2 (5 bar)	200	10,000	43,800	this work
7		K_2CO_3	200	10,150	20,700	

We proposed a catalytic cycle of iridium catalysts based on previous iridium-catalyzed TH reactions in Scheme 3 [24]. The catalysts **1** and **1'** undergo the dissociation of COD from the metal complex at the initial stage. After COD dissociation, deprotonated glycerol is added to form intermediate **I**, which undergoes β-hydrogen elimination. Replacing di-hydroxyacetone (DHA) with bicarbonate affords intermediate **III**. The released DHA is converted to lactic acid, illustrated at the bottom of the catalytic cycle [33]. The subsequent dehydroxylation and the reduction of CO_2 produced formic acid to complete the cycle (main cycle in Scheme 3). Since hydrogen was generated as a by-product, the outer cycle of Scheme 3 illustrates H_2 production by the protonation of Ir-H. Due to the presence of H_2 gas in the reaction vessel, this reaction may proceed via two separate steps composed of hydrogen generation from glycerol [36–39] and reduction of CO_2 with H_2 [3–18]. Tu's group published iridium catalysts having three NHC ligands for the dehydrogenation of alcohols, and we also reported triscarbene-modified iridium catalysts for the dehydrogenation of glycerol [32,36]. The reaction of CO_2 and H_2 was attempted in the presence of Ir(NHC) catalysts, resulting in small amounts of formate (see Supporting Information, Scheme S1). Therefore, the mechanism of the direct hydrogenation of CO_2 by H_2 can be ruled out.

Scheme 3. A proposed catalytic cycle.

In conclusion, we have evaluated iridium(NHC)-catalyzed transfer hydrogenation of CO_2 and K_2CO_3 in glycerol. The highest TOF values for the formate formation from CO_2 and K_2CO_3 are 10,000 and 10,150 h^{-1}, respectively. The observed TOFs of the transfer hydrogenation of CO_2 and carbonates are the highest values reported under conventional thermal conditions. The combination of high temperature and stable catalysts at such temperatures contributes to high TONs and TOFs of this transformation. We observe the hydrogen generation from glycerol during the reaction, but a reaction mechanism of the direct hydrogenation of CO_2 was excluded based on control experiments.

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