Communication

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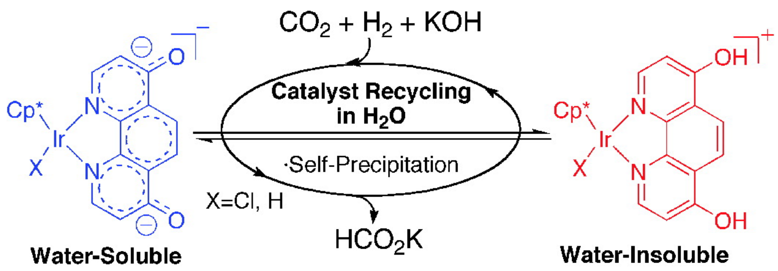

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Recyclable Catalyst for Conversion of Carbon Dioxide into Formate Attributable to an Oxyanion on the Catalyst Ligand

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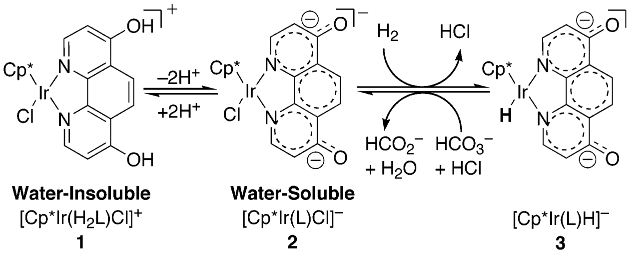
The development of efficient strategies for the recovery and recycling of homogeneous catalysts is now recognized as an important subject in catalysis research from an industrial point of view.[1−3] The conventional approaches are water/organic biphasic catalysis, based on the difference in polarity between water and organic solvents. However, to avoid the use of volatile organic chemicals (VOCs), the new separation strategies rely on the use of recently developed reaction media (e.g., supercritical fluids and ionic liquids) or filtration technology for polymer- and dendrimer-enlarged catalysts.[4] The re-immobilization of a catalyst by treatment with an acid or a base after reaction facilitated catalyst separation,[5] but the formation of salts as a waste is environmentally disadvantageous. More recently, the interesting finding reported by Bullock et al. is the fact that the catalyst for the solvent-free hydrosilylation of ketones precipitates spontaneously at the end of the reaction,[6] which is based on the difference in polarity between the substrate and product. Such a self-precipitation system helps to avoid the use of solvent and generation of a waste in the subsequent separation step.

The efficient utilization of CO_2 also remains the important issue and the long-term goal.[7] The formate salts generated in the homogeneous catalytic hydrogenation of CO_2 or bicarbonate are a valuable product used in leather tanning, etc. However, one of the problems, which must be solved, is catalyst recycling because highly active catalysts have presently been restricted to the complexes of precious metals, such as Pd, Rh, Ir, and Ru.[7,8]

In our previous report on the hydrogenation of bicarbonate,[9] we have revealed for the first time the significant roles of the oxyanion generated from the acidic phenolic hydroxyl on the catalyst ligand, in which its *electron-donating ability* and *polarity* lead to remarkable catalyst activation and water-solubility, respectively. As a result, the highest initial turnover frequency (TOF) and turnover number (TON) in the hydrogenation of bicarbonate in water was obtained by the use of 4,7-dihydroxy-1,10-phenanthroline (H_2L) complexes as catalyst precursors. At the same time, it was observed that some portion of the catalyst precursor is precipitated spontaneously at the end of the reaction. As shown in Scheme 1, it is suggested that the acidification by formate generation causes the transformation from the water-soluble deprotonated form into the water-insoluble monoprotonated [Cp*Ir(HL)Cl] and fully protonated form.[9a] This finding prompted us to examine the additional role played by an oxyanion, that is, the polarity change of the catalyst precursor by the acid−base equilibrium. Herein, we report the catalyst recycling by self-precipitation/filtration without waste generation in the CO_2 conversion.

The complex **1** shows the pH-dependent absorption spectral change, due to the acid−base equilibrium of two acidic protons[9,10] (see Supporting Information). However, besides the pH-dependent water-solubility of **1**, it should be noted that **1** is almost completely insoluble in acidic aqueous solutions. On the other hand, the pH of the reaction solution is affected by the pressure of CO_2 and the concentration of formate. First, the solubility of the catalyst during the reaction was visually observed by using a glass reactor containing 0.1 M KOH aqueous solution (50 mL) of [Cp*Ir(H_2L)Cl]Cl (**1**·Cl) (1.5 mg). The complex was completely soluble in CO_2-saturated KOH solution under 3 MPa of CO_2, in which CO_2 exists as bicarbonate. When the reactor was recharged with 3 MPa of H_2:CO_2 (1:1) at 60 °C, the clear pale yellow solution turned orange, which may indicate the formation of hydride complex **3**,[11] and then a yellow precipitate formed after 30 min. After 3 h of stirring, the pressure was slowly released. The resulting suspension was immediately filtered through a PTFE filter to give the clear pale yellow filtrate and the yellow precipitate. The filtrate (pH = 7.9) was found to contain 0.05 M formate (50% conversion) and 1.0 ppm of Ir (ca. 10% of the loaded Ir), as determined by HPLC and ICP-MS analysis, respectively. The precipitate was readily converted to a deprotonated form **2** by the addition of an aqueous base, as indicated by ^1H NMR.[9a] It was clarified that the catalyst precursor was precipitated with the generation of formate. The precipitation of the catalyst even under slightly basic conditions can be rationalized by the fact that the pH of an aqueous solution decreases under CO_2 pressure.[12]

Scheme 1. Proposed Mechanism for the Hydrogenation of Bicarbonate Catalyzed by the Iridium Complex with 4,7-Dihydroxy-1,10-phenanthroline



Then, we investigated the influence of the KOH concentration on the pH-dependent catalyst. Figure 1 shows the time course of the formate concentration within an initial period of 60 min at 6 MPa of H_2:CO_2 (1:1) at 60 °C in various KOH concentrations. The amount of formate generated during the initial 5 min was approximately the same for all the reactions. In other words, the catalyst exhibited the maximum ability (TOF = 5320 h^{-1}) at the beginning of the reaction under basic conditions. Subsequently, while the reaction rate in 1.0 M KOH solution was maintained high, those of the others decreased drastically after 5 min in 0.1 M solution and after 20 min in 0.5 M solution. After 24 h, the reaction rates in all cases significantly decreased with an increase in formate concentration. It can be seen that the pH decrease caused the catalyst precipitation by the protonation of water-soluble deprotonated form, which was activated by oxyanion, so that the reaction rate was decreased.

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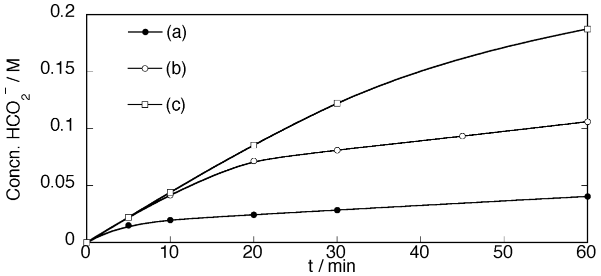
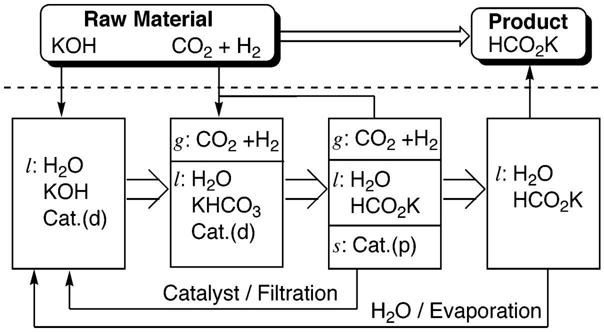


Figure 1. Time course of formate concentration for the hydrogenation of bicarbonate catalyzed by **1**·Cl (0.05 mM) at 6 MPa and 60 °C in (a) 0.1 M, (b) 0.5 M, and (c) 1.0 M aqueous KOH solutions.

Scheme 2. Recycling System of the Conversion of CO_2/H_2 and KOH into HCO_2K Using **1**·Cl in Water (*g*: Gas Phase, *l*: Liquid Phase, *s*: Solid Phase, Cat.(d): Deprotonated Form, Cat.(p): Protonated Form)



To promote the precipitation of the catalyst precursor by the pH decrease in the solution, the reaction in 0.1 M KOH solution was stirred for a prolonged period of time (20 h). By filtration of the obtained suspension, the catalyst precursor was recovered (vide infra). As expected, iridium leaching into the filtrate decreased drastically (0.11 ppm). The final concentration of formic acid (0.105 M) slightly exceeded the initial concentration of the added KOH, and the pH of the filtrate was found to be 5.5.[13,14] The evaporation of the filtrate and drying under vacuum at 100 °C gave pure potassium formate (≥98% pure).[15,16] It is interesting to note that the three components (i.e., catalyst, product (formate), and solvent (H_2O)) can be easily separated by conventional filtration and evaporation (Scheme 2). Sodium formate was also obtained by the same procedure from NaOH with efficient recovery and conversion. These results are indicative of the possibility of the catalyst recycling in the conversion of CO_2 into formate without waste generation.

Finally, the reusability of the catalyst was examined in the batchwise cycle. The above-mentioned recovered catalyst precursor was dissolved in a 0.1 M degassed aqueous KOH, in which ICP-MS analysis of the solution indicated that iridium could be efficiently recovered (93% recovery; the loss of iridium was due to sampling for assay (2%) and handling losses) (Table 1). While the recovered catalyst retained high catalytic activity for all four cycles, leaching increased and recovery decreased with an increased recycling of the catalyst. The batch experiments require the careful handling of reaction solutions containing air-sensitive active species, but some exposure to air cannot be excluded. However, this problem can be solved if a continuous closed system or an integrated membrane reactor would be used. The thermal degradation was also observed. When the reaction was carried out at 80 °C for 10 h, iridium leaching increased to 0.9 ppm and recovery decreased to 75%. It appears that the thermal stress and exposure to air lead to an increase in catalyst leaching.

Table 1. Batchwise Catalyst Recycling in the Conversion of CO_2 into Formate Using **1**·Cl

cycle	loaded/recovered [Ir] (ppm)[a]	recovery efficiency (%)	leaching [Ir] (ppm)[a]	final concn of formate (M)[b]
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

[a] The Ir concentration was measured by ICP-MS analysis. [b] For all four cycles, no bicarbonate was detected.

In conclusion, we have found that the CO_2 conversion using the complex **1** is an environmentally benign process whose significant features are as follows: (i) catalyst recycling by self-precipitation/filtration, (ii) waste-free process, (iii) the easy isolation of the product, (iv) high efficiency under relatively mild conditions, and (v) aqueous catalysis without the use of organic materials. Furthermore, we have demonstrated the third additional role of an oxyanion on the catalyst ligand, that is, the catalyst recovery by acid−base equilibrium, in addition to the water-solubility by its polarity and the catalyst activation by its electron-donating ability. The attractive features of an oxyanion on the catalyst ligand may hold significantly broader implications for the design of new homogeneous catalysts.

Supporting Information Available: Typical procedures for catalyst recycling and absorbance change as a function of pH for iridium complex **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Bicarbonate was not detected by ^{13}C NMR analysis, in which the spectral signal-to-noise (S/N) ratio was over 50.
(16) Formic acid may decompose during drying: mp 166−169 °C (Aldrich catalog gives 165−168 °C). Anal. Calcd for CHO_2K: C, 14.28; H, 1.20. Found: C, 14.25; H, 1.16.

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