Development of Homogeneous Hydrogenation of Carbon Dioxide to Formate Catalyzed by Copper Complexes

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Abstract

Carbon capture and utilization technologies have been investigated with a view to curbing the GHG emissions and producing value of carbon dioxide (CO₂). In particular, CO₂ has drawn much attention as an abundant, inexpensive and low-toxic carbon feedstock in chemical industry. The amount of CO₂ utilized annually in chemical manufacturing, including urea production, hovers around 120 million tons, in contrast to the 24,000 million tons of CO₂ released by anthropogenic emission.¹ This disparity indicates that CO₂ transformation is not highly utilized in the chemical industry. The catalytic hydrogenation of CO₂ is promising for the large-scale fixation of CO₂. Recently, the CO₂ hydrogenation and reverse water gas shift reaction have been applied to practical methanol, methane, or diesel synthesis in the combination of captured CO₂ with hydrogen (H₂) derived from surplus renewable energies in Iceland and Germany. In these hydrogenation plants, heterogeneous metal catalysts have been used to promote the hydrogenation at high temperature, however the severe conditions often cause limited selectivity of the products and low energy efficiency of the entire transformation process.

On the other hand, homogeneous catalysis which exploits transition metal complexes as catalysts has been commonly adopted to achieve selective transformations under relatively mild reaction conditions thanks to the appropriate design of the catalyst. Since the pioneering work by Inoue et al. in 1976,² the catalytic hydrogenation of CO₂ to formate has been mainly achieved by a range of homogeneous ruthenium, rhodium, and iridium complexes, because such hydrogenation can substitute conventional methods using carbon monoxide, and formate has possible application as a hydrogen energy carrier.³ Compared to precious metal catalysts, generally abundant and inexpensive first-row transition metals, especially manganese, iron, cobalt, nickel, and copper, are advantageous for large-scale chemical processes.⁴ In this context, several iron, cobalt, and nickel complexes bearing sophisticated ligands have emerged in the recent decade.

In this paper, we focused on the the catalytic ability of copper complexes for the hydrogenation of CO₂ prompted by broad contributions of copper chemistry in chemical synthesis.⁵ As shown in Scheme 1, we have found that the catalytic hydrogenation of CO₂ was promoted by using commercially available copper salts such as copper acetate, nitrate, and halides in the presence of strong organic bases including amidines and guanidines. In particular, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) proved to be the most effective base to produce its formate salt in ethereal solvents under the pressurized conditions (60 atm total) of a 1:1 mixture of H₂ and CO₂ at 100 °C. It is noteworthy that the Cu/DBU system requires no extra ligands which are generally found in other first-row transition metal catalysts, and the formate product can be easily isolated as precipitated granules from the reaction mixture at room temperature. Further
investigations suggested that DBU serves not only as a base but also as a ligand bonded to copper to promote the transformation. These results described here open up the availability of copper complexes for the homogeneous CO₂ hydrogenation, especially in the development of inexpensive catalyst system composed of commercially available materials with relatively mild reaction conditions.

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\text{CO}_2 + \text{H}_2 + \text{DBU} \xrightarrow{\text{Cu salt cat.}} 1,4\text{-dioxane} \rightarrow [\text{DBU-H}]^+\text{[HCO}_2]^-
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**Scheme 1**

References