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# Catalytic Hydrogenation of Carbon Dioxide

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Among several greenhouse gases such as water vapor, methane, ozone, and nitrous oxide, anthropogenic carbon dioxide contributes to global warming most significantly. Chemists have considered recycling carbon dioxide as a renewable and environmentally friendly source of carbon to reduce our dependence on petrochemicals. However, there are only a few industrial processes that utilize $CO_2$ because of its high kinetic and thermodynamic stability with high oxidation state of carbon.

The best way to overcome such difficulties could be transition metal-based catalysis. In recent years, many methods for catalytic conversion of $CO_2$ have been developed. Among them, hydrogenation of $CO_2$ to formic acid is an attractive approach, as formic acid serves as a versatile carbon source through many transformations in organic chemistry. Ru, Rh, Ir, and Fe complexes have been reported to be active for homogeneous catalytic hydrogenation of $CO_2$. A PNP pincer-type Ir (III) catalyst developed by Tanaka et al. exhibited the highest TON of 3,500,000 to date [1]. Despite this remarkable achievement, more economical and biorelevant metal-based catalytic systems are required. Fe-based $CO_2$ hydrogenation catalysts recently developed independently by Beller [2] and Milstein [3] were highly attractive, but TONs are in the range of 508~5104, which requires significant improvement.

More promising solution to global energy problem is the hydrogenation of $CO_2$ to produce methanol. Methanol is considered an excellent fuel for fuel cells and combustion engines [4]. Hydrogenation of $CO_2$ to methanol has favorable thermodynamics, but high activation energy barriers should be overcome by appropriate catalysts. Heterogeneous catalysts have been actively investigated with some success, but still the conditions are too harsh with the requirement of high temperature and high pressure of $CO_2$ and hydrogen. Homogeneous direct hydrogenation of $CO_2$ to methanol is less efficient than heterogeneous catalysis and has been pursued especially with Ru catalysts [5,6]. Recently developed indirect routes to methanol from carbonates, readily available from $CO_2$, are organic chemists' notable approaches to the problem [7,8].

In summary, hydrogenation of chemically stable carbon dioxide is a highly attractive solution to the recycling of the carbon source. New concepts and approaches for the development of highly efficient and economical $CO_2$ hydrogenation catalysts are long-awaited for the practical utilization of $CO_2$ as a renewable carbon source.

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