Formation of Formic Acid via CO₂ Hydrogenation with Silica-Supported Transition Metal Pincer Complexes

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Over the past decades, the hydrogenation of CO_2 to more valuable products such as formic acid or methanol has been highly emphasized in the academic field because of the continuous increase of CO_2 in the earth's atmosphere. The challenge of converting CO_2 results mainly from its considerable Gibbs free energy ($\Delta G^\circ = -394.4$ kJ/mol). Therefore active co-reactants and/or catalysts are usually needed. Formic acid, one of the CO_2 hydrogenation derivatives, is an efficient hydrogen carrier and has great potential to be applied in fuel cells. Nowadays various efficient homogeneous catalytic systems have been developed to convert CO_2 to formic acid, such as the iridium complexes with PNP pincer-type^{1,2} and bipyridine-type ligands³ or⁴ ruthenium complexes with N-heterocyclic carbenes.⁴ However, the above-mentioned homogeneous catalysts were only applied in batch reactors, which are less favored in industrial continuous processes, and efficient well-defined immobilized catalysts are still sparse in CO_2 hydrogenation. Here, we aim at synthesizing new immobilized catalysts, which are supported on well-defined silica-based hybrid materials or synthetic polymers, and applying them in a continuous CO_2 hydrogenation process.

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