Catalysts for CO_2 Electroreduction to Hydrocarbons and Oxygenates

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Rising atmospheric carbon dioxide (CO_2) levels and the associated rise in global temperatures have been brought to light as major global concerns. In fact, annual atmospheric CO_2 emissions have risen from about 2 Gt to 10 Gt in the last 5 decades.[1] Electricity production (*via* fossil fuel, *etc*.) is a large contributor, accounting for 37% of total CO_2 emissions, and therefore scientist have turned to renewable energy as a mitigation strategy.[2,3] Another widely-studied approach has been to reduce CO_2 to value-added chemicals and fuels (carbon monoxide, ethanol, formic acid, *etc*.). Previous works have aimed at increasing the feasibility of the CO_2 electroreduction (CO_2RR). Being able to improve and control the selectivity of CO_2RR would greatly contribute to its industrial application.

Developing thermodynamically efficient and kinetically active catalysts is a key part of CO_2RR. Depending on the catalyst or operating conditions, a variety of products can be formed.[4] Hydrocarbons and oxygenates, such as ethanol and methanol, are attractive products because of their high-energy density and variability in application.[5] For example, methanol is a feedstock for the industrially mature methanol to gasoline (MTG) process, which has a 95% thermal energy conversion efficiency.[6] Although, some state of the art electrocatalysts for CO_2 electroreduction can produce CO and HCOOH at high selectivity (>80%) and energy efficiency (>60%), the selective production of higher hydrocarbons, especially oxygenates such as ethanol and methanol, is still lacking.[7]

In this talk, we will explore copper supported on metal oxides (Cu/M_xO_y), prepared *via* incipient wetness impregnation, as potential catalysts for the selective electroreduction of CO_2 to oxygenates and hydrocarbons using an alkaline flow electrolyzer at ambient conditions. The existing state of the art catalysts for the electroreduction of CO_2 to these desired C_1-C_2 products are copper-based catalysts.[4] Density functional theory calculations suggest that to form oxygenates *via* CO_2 electroreduction, a hydroxide intermediate must be present on the catalyst surface.[8] Metal oxide supports can be used to satisfy the required criterion. The catalysts tested were Cu/TiO_2 and Cu/CeO_2 because the metal oxide supports remain stable under the cathodic conditions of the flow electrolyzer (negative potential and alkaline electrolyte) unlike copper oxide.[9]

Initial results with 20% loading Cu/M_xO_y catalysts show that these catalysts depict selectivity toward C_1 hydrocarbons (FE~20% for CH_4 & CO) with low Faradaic efficiencies for ethylene and ethanol compared to copper nanoparticles. When the loading was increased to 30% for Cu/TiO_2, similar results were achieved, but traces of methanol (FE = 0.5%) were observed at more negative potentials. These data lead to the questions of how the presence of a metal oxide support effect the previously hypothesized carbon dimerization mechanism for C_2 product formation.[5,10] Presence of a metal oxide may cause hindrance between active copper nanoparticles. Moreover, the presence of the metal oxide supports may facilitate methanol production typically associated with copper oxide catalysts.[8]

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