

Introduction to Advanced Materials and Catalysts

The development and advancement of materials is an overarching need in systems that extract, distribute, store or use energy. The performance of these systems depends on the properties of the materials: plastics, coatings, alloys and catalysts are some of the broad classes of materials used in current energy devices. Advancements in these materials optimize energy conversion processes, improve system efficiency, extend lifetime, and reduce CO₂ emissions. Although initially developed for a specific application, material properties may cross-cut to other energy technologies or industries.

The two studies listed below are all materials intensive investigations in the advanced materials and catalysts area.

Professors Norskov, Jaramillo, Bent, and Nilsson began a project in 2014 entitled “Sustainable Fuel Production from CO₂ and CO: Higher Alcohol Synthesis on Transition Metal Catalysts”. The production of higher oxygenates from syngas offers one pathway for the conversion of CO and CO₂ to useful fuels and chemicals; however, current catalysts known for this process have proved insufficient. This work sought to improve the performance of catalysts for higher oxygenate production through promoters and strengthen our understanding of how these promoters interact with the metal surfaces. By combining catalyst surface modification and DFT calculations, these researchers have gained a better understanding of the active sites for production of higher oxygenates. Such understanding can help improve the design of catalysts for converting CO into value added chemicals and transportation fuels. These researchers developed a tandem catalytic system for the direct conversion of syngas to ethanol or acetic acid using catalysts that are robust, contain earth-abundant metals, and are commercially available at large scales. This efficient multi-step tandem catalytic process is highly selective for conversion of CO and CO₂ towards C₂ oxygenates. This work has revealed the fundamental mechanistic aspects of CO reduction on metallic surfaces at the ultrafast time-scale. So far this work has led to five publications and five in preparation.

Professors Kanan and Martinez lead a project entitled “Carbonate-catalyzed CO₂ Hydrogenation to Multi-carbon Products” that began in September 2015. Using renewable energy to drive the synthesis of organic compounds from CO₂ and H₂O could provide a sustainable source of fuels and chemicals with no net CO₂ emissions. The key technical challenge is to efficiently transform CO₂ into multi-carbon compounds and CO₂ hydrogenation is a key step to obtaining these. Currently available CO₂ hydrogenation methods are only useful for synthesizing methane, CO, or methanol. These methods use metal or metal oxide surfaces as catalysts. The absence of efficient multi-carbon product synthesis in this paradigm is understandable given the enormous challenges of designing a single surface that activates H₂ and CO₂ and mediates C–C bond formation in a controlled manner. The goal of this project is to develop a completely new approach to CO₂ hydrogenation that can directly produce multi-carbon products. The innovative aspect is to use simple carbonate salts (M₂CO₃ or MCO₃) as catalysts instead of transition metals or metal oxides. The target products include oxalate, acetate, ethylene, and ethanol. This research project is a highly synergistic collaboration between experimental studies

in the Kanan lab and theory in the Martinez lab to elucidate the chemical principles of carbonate-catalyzed CO₂ hydrogenations and use these insights to optimize reactions. This work has shown that hydrated alkali carbonates salts promote a very rapid CO₂ hydrogenation, to multi-carbon carboxylates, formate and oxalate, at intermediate temperature and pressure. It has also yielded insights into the mechanisms involved in carbonate-promoted CO₂ hydrogenation and C-H carboxylation. This sets the groundwork for future work to investigate ways to convert cesium oxalate into dimethyl oxalate and regenerate cesium carbonate, using CO₂ and propanol. If this proves to be efficient, the carbonate-promoted hydrogenation could be combined with Cu-catalyzed dimethyl oxalate hydrogenation for selective synthesis of ethylene glycol or ethanol from CO₂ and H₂. This work has led to two publications and a third currently under submission.