

Motivation/Introduction: Methanol is one of the most important chemical intermediates. It is currently produced by the catalytic hydrogenation of CO and CO₂ mixtures. The use of CO₂ as feedstock specifically has the potential to achieve a circular carbon economy and mitigate greenhouse gas emissions. The reaction, however, suffers thermodynamic constraints: the formation of methanol is favorable at low temperatures but CO₂ bond dissociation requires elevated temperatures. At higher temperatures, hydrogenation is also outcompeted by the thermodynamically favorable reverse water-gas shift (RWGS) reaction, producing CO^[1]. As such, experimental yields have remained limited by the thermodynamic equilibrium^[1] despite the wide range of catalysts that have been tested for this reaction. To overcome this barrier, I propose that the CO₂ hydrogenation process can be improved by utilizing methanol *in situ* by a secondary, promoting reaction (**Figure 1**). Specifically, transesterification by methanolysis (**2**) is a process that depolymerizes polyethylene terephthalate (PET) into DMT monomer and value-added ethylene glycol (EG). When coupled with CO₂ hydrogenation (**1**), degradation of PET by methanol can shift **1** forward (Le Chatelier's Principle), promoting methanol synthesis while also enhancing PET depolymerization. Excess hydrogen from **1** is then utilized in DMT hydrogenation (**3**), forming value-added products, and simultaneously promoting **1** and **2**. To achieve this, designing a single catalyst that is selective and dual-functional for CO₂ hydrogenation and PET methanolysis is a needed area of research.

Metal-organic frameworks (MOFs) are advantageous compared to other heterogeneous material for catalysis, owing to highly designable structures, metal active sites and large internal surface areas^[1]. MOFs are a type of coordination polymer with metal nodes linked by organic linkers and are the most porous materials in the world. Within their porous frameworks, MOFs can also act as supports for nanoparticles (NPs), adding more tunable catalysis design. In general, ZnO NPs have been effectively used as catalysts for PET methanolysis and Cu/ZnO NPs on Al₂O₃ for CO₂ hydrogenation^{[1][2]}. I hypothesize that by using a Cu/ZnO-NP supported on a MOF catalyst, reaction **1** coupled with **2** can synergistically promote both reactions concurrently, exceeding the thermodynamic limitations of **1** alone.

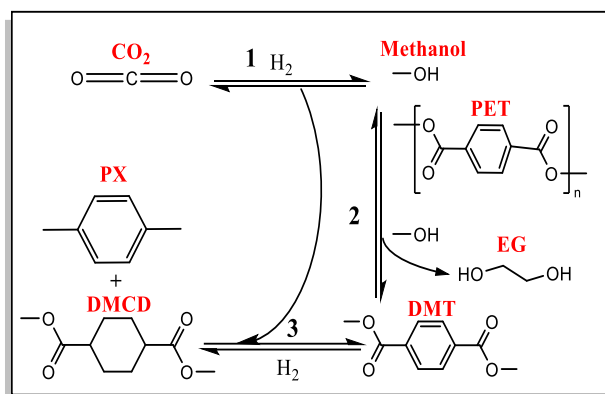


Figure 1. Proposed mechanism for dual-promotion reactions. CO₂ hydrogenation **1** is promoted by PET methanolysis **2**. Excess hydrogen then promotes DMT hydrogenation **3** to produce value-added products.

Research Plan

Synthesis and Characterization: NP-MOF composites will be prepared using various synthetic techniques. I propose using the polyol method to synthesize Cu/ZnO-NPs. Commercially available metal precursors and polyvinyl pyrrolidone polymer as a capping agent will be used to control the size of the NPs. The MOF support I will choose will be based on a Zr-MOF, based on traditional solvothermal synthesis--copper-zirconium interfaces are a strategy for selective hydrogenation over the RWGS reaction^[3]. Organic linkers will be chosen based on their hydrophobic character, enhancing selectivity of CO₂ in catalyst active sites over water, a common challenge in humid environments. To test the impact of nanoarchitecture for catalytic activity, Cu/ZnO-NPs will be allocated interior and exterior of the MOF via encapsulation during synthesis and sonication of NPs, respectively. Characterization will include crystal XRD for structure, TGA for thermal stability at high temperatures required for reaction and BET for available catalytic surface area within the pores. Transmission electron microscopy (TEM) will ascertain the size distribution of free NPs as well as the NP-MOF composite.

Thermodynamic Testing: Catalysis experiments will take place in a 100mL autoclave reactor. A commercially available standard Cu/ZnO/Al₂O₃ catalyst will be used as control for these experiments. Evidence of increased methanol yield for **1** coupled with **2** will indicate the thermodynamic equilibrium limit of methanol synthesis has exceeded that of **1** alone. The production of EG (as shown by NMR) will

directly quantify the degradation of PET powder and consumption of methanol (**Figure 1**, reaction **2**). Similarly, the yield of methanol from **1** will be determined through NMR using an internal standard. Complete species quantification for these experiments will be challenging; anticipated residual products resulting from PET polymer and its respective monomers can quickly complicate an NMR spectra. Creating control NMRs will help with recognition but alternatively, GC-MS is a time-consuming instrument capable of more sensitive, selective identification of products.

Catalytic Trials: If thermodynamic equilibrium can be exceeded from **1** coupled with **2**, the impact of nanoparticles on Zr-MOF will then be tested for these reactions, otherwise only for pure hydrogenation. The conversion and selectivity to desired products will first be tried with Zr-MOF without NPs for reference. Temperature, pressure, and catalyst to PET eq will then be optimized. Methanol yield for Cu/ZnO-NPs supported on Zr-MOF will be tested against the reference for evidence of improved activity. If shown, I will compare the turnover frequencies (TOF) of encapsulation vs. immobilization of NPs to weigh the impact of nanoarchitecture for the degradation of PET and formation of methanol. I hypothesize encapsulation of NPs within Zr-MOF will be more catalytically active than immobilization on the surface, due to the preferential gas catalysis occurring within abundant pore/metal interfaces.

Optimization of NPs: My second and most challenging goal will be to optimize Cu, ZnO and Zr atomic abundances, detailing how their concentrations impact selectivity and catalytic activity. This year, the Cargnello Group at Stanford published a paper using Ru/TiO₂ NPs encapsulated in porous organic polymers to optimize CO₂ hydrogenation TOF 10-fold^[4]. The Cargnello Group's lab facility and experience with pore/metal interfacial research specifically caters to studying nanotechnology and will help me be successful with this goal. My first plan is to tailor polyol NP synthesis, allowing me to control Cu/ZnO-NP size and individual metal distributions. I can characterize corresponding nanoarchitecture with TEM and EDS, creating a structure-property relationship study by optimizing metal concentrations. This will allow me to examine individual NP effects on selectivity and catalytic activity for **1** and **2**.

Intellectual Merits: With 35% of the world's GDP influenced by catalysts, promoting reactions such as that in this proposal offer a strategy to assuage thermodynamic limitations commonly presented. A challenge with introducing promoting reactions is born from the need to simultaneously catalyze multiple reactions *in situ*. MOFs have not been widely reported as catalysts for CO₂ hydrogenation due to scaling requirements needed to meet industry standards. However, their high surface areas make them beneficial for CO₂ capture, thus tailored MOF/NP composites for this application may expand the field of sustainable chemistry as multifunctional catalysts. From researching in three material science groups, structure-property characterization and materials development of MOF/NP composites will be familiar. My experience in synthesis, NMR, electron microscopy and EDS will enable me to relate NP impacts on **1** and **2**, respectively, and optimize catalyst performance.

Broader Impacts: My experience leading CO₂ upcycling research during my undergraduate program is my motivation for developing catalysts to recycle harmful waste products into reusable ones. Carbon dioxide from flue gas over the last century has drastically increased greenhouse gas emissions, leading to global warming. Polyethylene terephthalate, often found in single-use disposable water bottles, is the most used polyester plastic in the world; only around 30% of the 87 million metric tons produced annually gets recycled^[5]. This proposal simultaneously recycles waste CO₂ and PET *in situ* to produce several value-added products: methanol, ethylene glycol, and p-xylene. I recognize that making a sizeable impact on the greenhouse gas crisis and global plastic pollution is a monumental task, not feasibly solved by oneself. While communicating my research at chemical engineering conferences is progress, I also plan to educate the populace on how they can also creatively aid these causes. I believe this starts by acclimating young researchers to the scientific method and making STEM accessible to all. This is something I will do and will continue through my educational website and portfolio. I will also continue my outreach through OSTEM, encouraging LGBTQ+ and other underrepresented students to consider research through summer programs a local research showcases.

References: [1] X. Jiang, *Chemical Reviews* **2020**. [2] J. Du, *Chemical Engineering Science* **2020**. [3] Y. Zhu, *Nature Communications* **2020**. [4] C. Zhou, *Proceedings of the National Academy of Sciences* **2022**. [5] D. Lakshika and L. Jayakody, *Frontiers in Bioengineering and Biotechnology*, **2021**.