

Mechanistic Study of CO₂ Hydrogenation to High-value Products Using Fe₃O-Based MIL-Type Metal-Organic Frameworks Catalysts Project

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1. Project Purpose

Carbon capture and utilization (CCU) provides a promising pathway for converting CO₂ into value-added chemicals, fuels, and polymers, thereby helping to mitigate greenhouse gas emissions. In this project, density functional theory (DFT) is employed to investigate CO₂ hydrogenation over Fe₃O-based metal-organic framework (MOF) catalysts and CO₂ copolymerization with propylene oxide using Al(III)-porphyrin catalysts. The study elucidates key mechanistic pathways and demonstrates how catalyst composition and reaction energetics govern product selectivity, including the formation of fuels (CO, CH₄, and CH₃OH) and polyurethane-poly(propylene carbonate) (PU-PPC) copolymers. The results highlight the critical roles of kinetic and thermodynamic factors, particularly the rate-limiting carbonate formation step and the favored insertion of TsNCO, in determining catalytic efficiency while suppressing undesired side reactions. Overall, this work provides fundamental insights that guide the rational design of advanced catalysts for selective and efficient CO₂ conversion, contributing to the development of sustainable materials and a net-zero carbon future.

2. Results

This project has yielded significant insights into the catalytic conversion of CO₂ into high-value polymers and fuels. The key findings are summarized below:

2.1 Bifunctional Al-Porphyrin Catalysis

A comprehensive density functional theory (DFT)-based mechanistic study was conducted on CO₂/PO and TsNCO polymerizations. The results reveal that both kinetic and thermodynamic factors govern catalytic performance. In particular, the rate-limiting step of carbonate formation plays a decisive role in polycarbonate synthesis, while the thermodynamically favored insertion of TsNCO drives efficient polyurethane production. These findings provide a

detailed mechanistic framework for optimizing catalyst design.

Status: *Phys. Chem. Chem. Phys.* (2026), accepted February 24, 2026.

2.2 Fe₃O-Based MOF Catalysis

This study demonstrates that secondary metal promotion significantly enhances the hydrogenation of CO₂ to formic acid. The work establishes a fundamental relationship between catalyst composition and product selectivity, highlighting how tailored metal incorporation can suppress side reactions while improving catalytic efficiency.

Status: Manuscript in preparation.

3. Roles of the MCRP and its significance

The Multidisciplinary Cooperative Research Program (MCRP) provided the essential high-performance computing (HPC) infrastructure required to execute complex density functional theory (DFT) simulations.

- **Computational Necessity:** The investigation of Fe₃O-based MOF catalysts and Al(III)-porphyrin catalysts involves modeling intricate molecular interactions and transition states. These calculations are computationally intensive and require the parallel processing capabilities provided by the MCRP resources, specifically the **Pegasus** supercomputer.
- **Mechanistic Clarity:** Access to these resources allowed for the detailed mapping of kinetic and thermodynamic preferences, such as identifying TsNCO insertion and carbonate formation as critical factors in reaction efficiency.
- **Impact:** By supporting this research, the MCRP facilitates the development of Carbon Capture and Utilization (CCU) technologies, contributing to global efforts in mitigating greenhouse gas emissions and moving toward a net-zero future.

4. Future plan

Building upon the current mechanistic insights, the project will focus on the following area:

Finalizing Manuscripts: Complete the preparation and submission of the manuscript titled "Boosting CO₂ Hydrogenation to Formic Acid through Secondary Metal Promotion in Fe₃O-Based MOF Catalyst".

5. Publications and conference presentations

(1) Journal papers

- 1) **Ratanasak, M.**; Y. Injongkol*, Shigeta, Y.* DFT-Based Mechanistic Study of Bifunctional Al-Porphyrin Catalysts for CO₂/PO and TsNCO Polymerizations toward Polycarbonates and Polyurethanes. *Phys. Chem. Chem. Phys.*, (Accepted 24th February 2026).

- 2) Apilardmongkol, P.; **Ratanasak, M***; Kongkaew, S.; Santiwarodom, W.; Kuamit, T.; Chokbunpiam, T.; Mulya, F.; Rungrotmongkol, T.; Hasegawa, J.; Shigeta, Y.; Parasuk, V*. Boosting CO₂ Hydrogenation to Formic Acid through Secondary Metal Promotion in Fe₃O-Based MOF Catalyst. (*Manuscript in preparation*)

(2) Presentations

(3) Others

Supercomputer	Use	Allocated resources*		
		Initial resources	Transferred resources**	Purchased resources
Pegasus	Yes/No	3240		
Miyabi-G	Yes/No	-		
Miyabi-C	Yes/No	-		
*in units of node-hour product				
** If the budget transfer was performed, fill in here, such as "+2000" and "-1000".				