

Metal-Organic Framework and Bimetallic Nanoparticle Composite for One-Pot CO₂ Hydrogenation and PET Methanolysis

Background

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. 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.

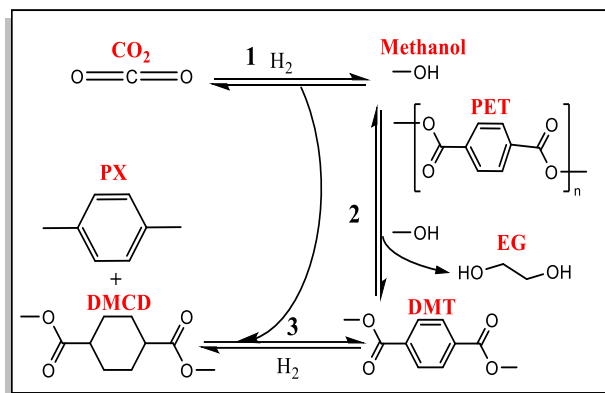


Figure 1. Proposed mechanism for dual-promotion reactions. CO₂ hydrogenation **1** is promoted by PET methanolysis **2**. Excess hydrogen then promotes DMT hydrogenation **3** to produce value-added products.

Recently, nanoparticles (NP) have been at the forefront of heterogeneous catalysis. Bimetallic nanoparticles (NP) are also advancing in literature and may be more advantageous to monometallic NPs. These NPs may exhibit combination of properties of the two metals, introduce synergistic effects, and impose new properties. Drawbacks involving bimetallic NPs involve tendency to be thermodynamically

unfavorable because of higher surface energies.^[1] As a result, these particles irreversibly aggregate with each other during catalytic processes, reducing catalytic activity. To counteract this, the investigation of bimetallic NPs combined with other composites for enhanced catalytic performance is an important area of research.

Metal-organic frameworks (MOFs) are a suitable examples to minimize the drawbacks of bimetallic NPs while also synergistically enhancing catalytic performance. Metal-organic frameworks are a type of coordination polymer consisting of metal centers bridged by organic bridging linkers. These linkers can be tailored judiciously to afford functionality and porosity. The large internal surface area of MOFs allows ample free space for nanomaterial loading, minimizing agglomeration of bimetallic NPs within their pore apertures.^[1] The benefits of using MOF composites with bimetallic NPs for promoting reactions **1** and **2** include confining the bimetallic NP, offering additional active sites, and increased selectivity compared to monometallic NPs.^[1] These properties for MOF/NP particles can be tuned for various reactions leading to synergistically enhanced heterogeneous catalytic performance.

MOF/NP Composites for Tandem and Coupled Reactions

Tandem reactions have been investigated using MOF/NPs, demonstrating the improved activity. Liu et al reported the deposition of Au-Pd NPs on the external surface of MIL-101.^[2] The authors show that the bimetallic NPs could contribute to synergistically enhanced catalytic performance, where they could selectively catalyze the oxidation of C—H bonds, obtaining initially alcohols and aldehydes then proceed cascading reactions.^[2] The authors suggest that the interaction between Lewis acidic Cr sites of the MIL-101 and the aromatic ring of toluene influences the electron distribution of the methyl group of toluene. They then postulate that the carbons of the methyl group are more easily reacted with activated oxygen species formed from the Au-Pd NP, catalyzing benzaldehyde formation into benzyl benzoate. The expected oxidation of benzaldehyde to benzoic acid is inhibited naturally from acid-base interactions between that of benzaldehyde and Lewis acid.

Catalytic tandem reactions may be enhanced with bimetallic NPs through synergistic effects. Metal-organic frameworks are important in facilitating bimetallic NPs catalysis by not only hosting the NPs, but through tunable active sites in pore structures which may enhance performance and selectivity. Thus, it is plausible that metallic NPs supported on multifunctional

MOFs can be demonstrated for tandem CO₂ hydrogenation and PET methanolysis. Further research on the right combination of NPs and MOF framework, however, need to be further investigated. To begin this study, understanding the synthesis and interaction of NPs with MOF framework is critically important for these reactions.

Synthesis of NP/MOF Composite

The exact mechanism and interaction of bimetallic NPs on MOFs have seen a larger increase in relation to their catalytic performance. Synthesis techniques to incorporate MOF/NP composites range from incipient wetness impregnation or “ship in a bottle”, “bottle around the ship” and one pot synthesis method (**Figure 2**).^[1] Each of these methods offer varying control in size, distribution and more interestingly, the location of the NP on the MOF structure.

Briefly put, the “ship in a bottle” method prepares pre-synthesized MOFs as supports and the nanoparticle precursors may be impregnated in the frameworks through decomposition or reduction processes. The “bottle around the ship” method creates MOF/NP composite by using NPs capped by protecting agent such and assembling the MOF with the NP. Oftentimes, the polyol method is performed to synthesis capped NPs. The one-pot synthesis combines NP and MOF precursors to the same reaction system to create the composite structure. Depending on synthesis, NPs can be deposited on the surface or confined in pore-apertures of the MOF.

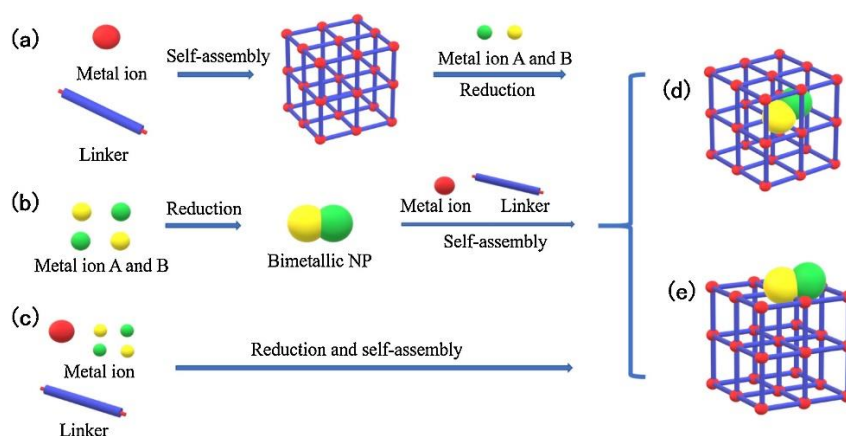


Figure 2. Main approaches for the fabrication of bimetallic NP/MOF composites: (a) ship in the bottle; (b) bottle around the ship; and (c) one-pot method. (d) active bimetallic NPs defined inside the framework of MOF. (e) active bimetallic NPs immobilized on the surface of MOF. Referenced from <https://doi.org/10.1016/j.apmt.2020.100564>

Bunyarat et al. report copper nanocrystals (NC) encapsulated in a zirconium MOF framework, UiO-66, for **1**.^[3] They produce Cu NC through polyol process and precisely place them on the surface of UiO-66 (Cu on UiO-66) by mixing colloidal solution of MOF and NC together (**Figure 3**). To investigate impact of NC location, they also encapsulate the NC in the framework (Cu \subset UiO-66) via “bottle around the ship method” using aqueous zirconium chloride to prevent dissolution of the NC in the MOF framework.

The authors employ XPS to investigate the interaction and activity between Cu and Zr. They report a peak shift of the Zr 3d_{5/2}, between UiO-66 without Cu and UiO-66 with Cu. The sample with Cu NCs on UiO-66 exhibited a decreased shift in binding energy, signaling the reduction of Zr (IV) when in contact with Cu NCs. This also

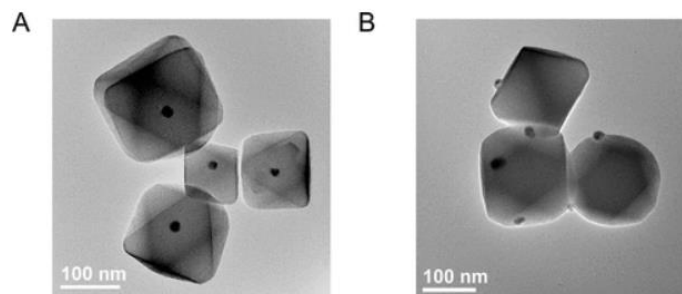


Figure 3. TEM images of (A) Cu \subset UiO-66 (single Cu NC inside UiO-66), (B) Cu on UiO-66. Referenced from <https://doi.org/10.1021/acs.nanolett.6b03637>

implied that Cu must be oxidized inherently from this observation. The changes in oxidation state are indicative of the strong metal-support interaction effect where metallic Cu and Cu cation species are present after reduction. Such species support hydrogenation as they play a cooperative role in dissociation of hydrogen and stabilization of chemical intermediates. The authors propose that interaction between Cu NCs and Zr secondary building unit suggest that the active site for Cu Nc on UiO-66 catalyst lie on that interface between Cu Nc and ZrO. When comparing the difference in NC location relative to the MOF, the TOF for Cu \subset UiO-66 was increased dramatically compared to Cu on UiO-66. A two-fold increase of Cu \subset UiO-66 and enhanced stability suggest that the location of the Cu NC on the MOF affected the catalyst behavior reactivity. The authors suggest that that this is because of the higher number contact points between the Zr oxide secondary building unit and Cu surface and due to the confinement of the Cu NC in the MOF environment. The Cu NCs are encapsulated by the secondary building unit, thus promote creating active Cu sites and by virtue, Cu cation species to promote CO₂ hydrogenation. In summary, interaction of the metal precursor of the NP and MOF species along with location of the NP plays a critical factor for activity the MOF catalyst. Placement of NP (on

the surface or encapsulated) will need to be investigated for a MOF/NP capable of tandem reactions proposed by this paper.

Designing MOF/bimetallic NP for Tandem Reaction of **1 and **2****

Research on the one-pot reaction of **1** and **2** is limited. Yinwen et al. first reported the use of a CuFeCr catalyst derived from layered double hydroxide precursors to catalyze the reaction with conversion of less than 5% for **1**.^[4] While the catalyst used is non-porous was not used as support for nanoparticles, their structural tuning of the catalyst can provide insight on what metal active sites are important for these coupled reaction. The authors interchange the M metal of the CuFe(M) catalyst with transition metals (where M = Cr, Ag, Mn, In, Nb, Re and Mo) to select the metal with highest promotion of **1**. The results from this study do not show a straightforward correlation with the choice of M except that Cr had the highest conversion. Traditional supports such as CuZnAl, Pd/C and Ru/C were also studied with much lower methanol yield than CuFeCr. The interactions of these metals are not studied for their role in the self-promoting reaction but based on their studies and those from Yinwen et al. and by Bunyarat et. al, using Cu as one of the NPs for the MOF is a reasonable first course of action to first catalyze **1**

In recent literature, Cu/ZnO NPs on Al₂O₃ have been effectively used as catalysts for CO₂ hydrogenation and ZnO NPs for PET methanolysis^[1]. Jin-Tao-du and authors report using ultrasmall ZnO NPs at elevated temperatures (>160 C) for efficient PET methanolysis, resulting in 95% yield of DMT product.^[5] These temperatures are consistent with the temperatures to for CO₂ hydrogenation and low enough for most MOFs to resist thermal degradation. The choice framework is still an important consideration for catalyzing tandem reaction. The self-promoting reaction depends on the successful production of methanol for **1**. Therefore, designing a multifunctional composite catalyst should take in consideration selectivity of CO₂ over the RGWS reaction. Zhu, Yifeng, et al report that copper-zirconia interfaces in UiO-66 enable 100% selectivity.^[6] They utilize XAS to attribute that Cu NP occupy missing-linker defects maximize the fraction of Cu interfaced to zirconia. Higher adsorption capacity for CO₂ at these interfaces are determined by DFT compared to adsorption on Cu NP and ZrO₂ nodes separately. Their experimental results support that the NP interface with the metal site of MOF favored selectivity for lower temperature methanol synthesis. From all these considerations, a Cu/ZnO nanoparticle on Zr-framework, such as UiO-66, is suggested for dual-catalyst reaction of **1** and **2**

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