

Tunable confined space in discrete metal-organic supercontainers for catalytic biomass conversion

Background. 5-Hydroxymethylfurfural (HMF) is a particularly attractive target for the investigation of catalytic biomass conversion. It is versatile platform molecule that can be transformed into a diverse range of high-value downstream products such as fuel additives, pharmaceuticals, etc.¹⁻³ Hydrolysis of glucose/fructose represents a classical route to HMF. Nevertheless, production of HMF from biomass-derived glucose remains a significant challenge. Various types of catalysts, including Brønsted acids,³⁻⁴ Lewis acids,² and nanoporous materials such as zeolites⁵⁻⁶ and metal-organic frameworks (MOFs),⁷⁻⁸ have been studied for the conversion of glucose to HMF. However, many of these traditional catalysts have severe limitations due to their low reactivity, poor selectivity, high cost, or other practical issues such as toxicity and safety hazards.

We hypothesize that a new class of discrete supramolecular hosts, known as metal-organic supercontainers (MOSCs), provide unique opportunities to address these issues. MOSCs feature a diverse range of nanoporous structures (pore dimension ranging from ca. 0.5 ~3 nm) and can be obtained from the assembly of divalent metal ions (e.g., Co^{2+}), carboxylate linkers, and cup-shaped sulfonylcalix[4]arene precursors.⁹⁻¹¹ The most salient feature of MOSCs is the presence of both *endo* and *exo* cavities within a single host (Figure 1), affording tunable confined nano-space suited for encapsulating and transforming small molecules (e.g., glucose). A second notable structural element of the MOSCs is a metal-bound $\mu_4\text{-H}_2\text{O}$ species serving as a Brønsted acid or hydrogen-bond donor.⁹ These characteristics distinguish MOSCs from related zeolites and MOFs. While zeolites and MOFs are polymeric, insoluble materials, MOSCs are discrete, molecular species readily dissolved in common organic or aqueous solutions. The molecular nature of MOSCs means that, unlike zeolites and MOFs, the MOSC catalysis can be manipulated on a truly single-site basis and the diffusion/pore blockage issues can be readily addressed. The solubility of MOSCs can be precisely tuned through chemical derivatization of the organic components, which not only allows easy manipulation of targeted homogeneous catalysis, but also permits the use of solution characterization techniques (e.g., NMR) not readily accessible to zeolites and MOFs. Thus, the discrete “supercontainer” architecture, functional nano-cavity environment, tunable active sites, and solution processibility of MOSCs make for a unique class of catalysts promising for biomass conversion to value-added products.

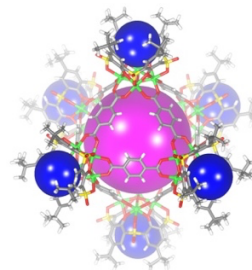


Figure 1. A representative metal-organic supercontainer (MOSC). Purple and blue spheres indicate the *endo* and *exo* binding cavities, respectively.

Research Approach. 1) *Synthesis and Characterization of MOSCs.* Syntheses of MOSC catalysts with desired structure and catalytic properties will be achieved using a modified “solvothermal synthesis” method following our previously reported protocols. Organic precursors containing desired functionalities will be obtained following known or modified organic synthesis procedures. Phrase identity and purity of MOSCs will be characterized by both solid-state and solution techniques, including X-ray crystallography, thermal gravimetric analysis (TGA), mass spectrometry (MS), nuclear magnetic resonance (NMR), Fourier-transform infrared spectroscopy (FT-IR), ultraviolet-visible spectroscopy (UV-vis), etc. 2) *MOSC-Mediated Catalytic Conversion of Glucose to 5-Hydroxymethylfurfural.* Two pertinent mechanisms of MOSC-catalyzed conversion of glucose to HMF will be examined: a $\mu_4\text{-H}_2\text{O}$ based, Brønsted acid assisted cyclic mechanism,³ and a carboxylate linker based, Lewis-acid promoted, open-chain pathway.^{2, 6} In a

typical catalytic experiment, MOSC catalyst (<10 mol%) will be dissolved in an organic or aqueous solution containing the reactant(s) in a 4-mL vial. The reaction will be conducted at room temperature or heated for several hours or up to 2~3 days. The reaction will be evaluated by ¹H NMR, GC-MS, or LC-MS. The product may be further isolated and purified by flash chromatography and characterized by ¹H NMR and mass spectrometry.

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