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Role Of Zirconium Metal-organic Framework Defects On Chemical Warfare Agent Performance Studied Through Novel Synthesis And Mass Transfer Methods

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It has been shown that metal-organic framework (MOF) defect levels can contribute to chemical warfare agent (CWA) reactivity and filtration. It was of interest to prepare samples with controlled density of defects within zirconia cluster based UiO-66 and prepare a pristine sample (no detectable defects). Defects in zirconium-based MOFs, both missing cluster and missing linker, have been linked to the modulated synthetic procedure used to produce the particles.

We developed two series of defected UiO-66; (1) changing particle size with consistent defect level and (2) changing defect level with consistent particle size by changing the organic modulator, which provides an easily tunable synthetic handle that has significant literature precedent. This required that we benchmark known techniques for defect analysis and consider unexplored characterization methods for quantitative determination of defects.

By generating these series of defect and size-dependent materials, the relationship between particle size, defect level, and reactivity was observed via hydrolysis of nerve agent simulant dimethyl p-nitrophenyl phosphate (DMNP). MOFs with higher defect level and smaller particle size were the most favorable catalysts for the hydrolysis of DMNP. Turn-over-number (TON) results for the size-dependent series suggests that larger particle sizes may allow for DMNP to access nodes below the surface by promoting correlation of defect sites, but the reactivity is still largely surface confined likely due to the large size of DMNP. In addition to these physical characteristics affecting MOF accessibility, and role of modulator in modifying active site reactivity, critical to the development of Zr-based MOFs for catalytic applications, was studied here.

A simulation study was conducted to support this effort by characterizing adsorption and diffusion of analyte molecules within the pores of select MOF materials through the use of molecular modeling. We have focused on modeling adsorption and diffusion of acetone, isopropyl alcohol (IPA), sarin, soman, DMMP, and DMP in UiO-66. We have modeled diffusion of select analytes through pristine UiO-66 using molecular dynamics simulations. However, not all molecules can be observed to diffuse over the length of a simulation, which is typically less than 100 ns. We have estimated diffusion barriers for molecules having diffusivities slower than can be directly measured from molecular dynamics using umbrella sampling combined with weighted histogram analysis.

I submitted this abstract yesterday but never received a reply response from the website that my management is asking for.
So I am resubmitting the abstract again today.