Introduction

Metal-organic frameworks (MOFs) are a promising class of porous materials currently under investigation for enhanced air purification (filtration) systems. MOFs are made by reacting metal oxide secondary building units with organic ligands to form reticulated, porous, 3-dimensional structures. The ability to tailor both the type of metal, type of organic linker, and functional groups on the organic linker make MOFs prime nanostructured materials for targeted reactions against toxic chemicals.

Of particular note are CuBTC (aka HKUST-1) and the UiO-66 series of MOFs. CuBTC has been shown to provide ammonia removal capabilities in excess of any known porous sorbent. Yet, this material is also unstable to moisture, a major shortcoming. Methods to stabilize this material will prove beneficial for integration into filtration devices.

Mesopore Creation in UiO-66-X

Water on UiO-66-NH$_2$ pellet
Pore apertures of UiO-66, and especially UiO-66-NH$_2$, are ~ 6Å excellent for physical adsorption of small molecules but not so for larger molecules nor for diffusion, especially in packed beds.

Nitrogen isotherm data show formation of mesopores (hysteresis) at higher wattages. A higher power results in more mesopores

Although there is localized bond-breaking, as seen through the formation of mesopores, the long range and even short range order remains intact for both C$_2$F$_4$ and C$_2$F$_6$-treated samples, as shown by PXRD.

Treatment of UiO-66-NH$_2$ with a C$_4$F$_8$ plasma results in formation of mesopores large enough to allow diffusion of VX into the pores. Resulting catalytic hydrolysis provides a 60% improvement in half-life. Further optimization is underway to re-hydrxelrize the SBU, thus increasing reaction rates even more.

Status & Future Work: mesopore formation appears to be tunable – we plan to optimize for V, G, & H agents, as well as scale technology for increased mass transfer rates in packed beds (filters). Focus on Cl$_2$ and NH$_3$ optimization.

Experimental Design

The experiment was performed using a Diener Femto-8R-PRCCE-c plasma system with a 100 W 13.56 MHz RF Generator.

Stabilization of CuBTC

CuBTC is hydrophobic, and degrades after exposure to moisture. Water clusters near at the undercoordinated copper sites of the SBU paddlewheel, breaking bonds that reticulate the structure.

Untreated CuBTC immediately begins to degrade upon exposure to moisture, especially liquid water. PXRD patterns show long range order peaks immediately degrade, with structural collapse occurring as well.

C$_2$F$_4$ treated CuBTC shows no degradation after 24 hours of exposure to liquid water. SEM images show no structural degradation, whereas untreated CuBTC show loss of structure and agglomeration

Ammonia loadings (fresh vs. aged) as a function of treatment time. Aging conducted at 45°C, 80% RH for 7 days

Varying Sample

Sample

NH$_3$ Loading (mg/g)

Aged NH$_3$ Loading (mg/g)

CuBTC

CuBTC-CF$_4$-10

CuBTC-CF$_4$-30

CuBTC-CF$_4$-50

Ammonia microbreakthrough of C$_2$F$_4$-treated CuBTC vs. untreated CuBTC after aging

Status & Future Work: Materials have been transitioned to prototype filters as polishing layers for ammonia removal. Currently working on scaling technique for technology transition at TRL 6.

Treatment of Metal-Organic Frameworks via Plasma-Enhanced Chemical Vapor Deposition

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