Role of Zirconium Metal-Organic Framework Defects on Toxic Chemical Performance Studied Through Novel Synthesis and Mass Transfer Methods

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Abstract

It has been shown that metal-organic framework (MOF) defect levels can contribute to toxic chemical 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 samples.

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 Simulant α by 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 Simulant α 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 Simulant α. 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), Simulant β, and Simulant χ 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.

Mass transfer rate measurements and adsorption equilibria values provide performance information of sorbent materials for toxic chemical filtration. Two well-known techniques, gravimetric uptake and frequency response, capable of obtaining this data have been applied to the defected MOF series of this work. The micron scale diameter of these crystals leads to rapid mass transfer, i.e. external film control, for most small molecules but toxic chemicals do exhibit measurable micropore diffusion effects. The results from the two techniques are in close agreement and agree well with literature. Results of this work show the role MOF defect number, defect type, and crystal morphology play in developing an optimal MOF for toxic chemical filtration.

Defected Sorbent Synthesis
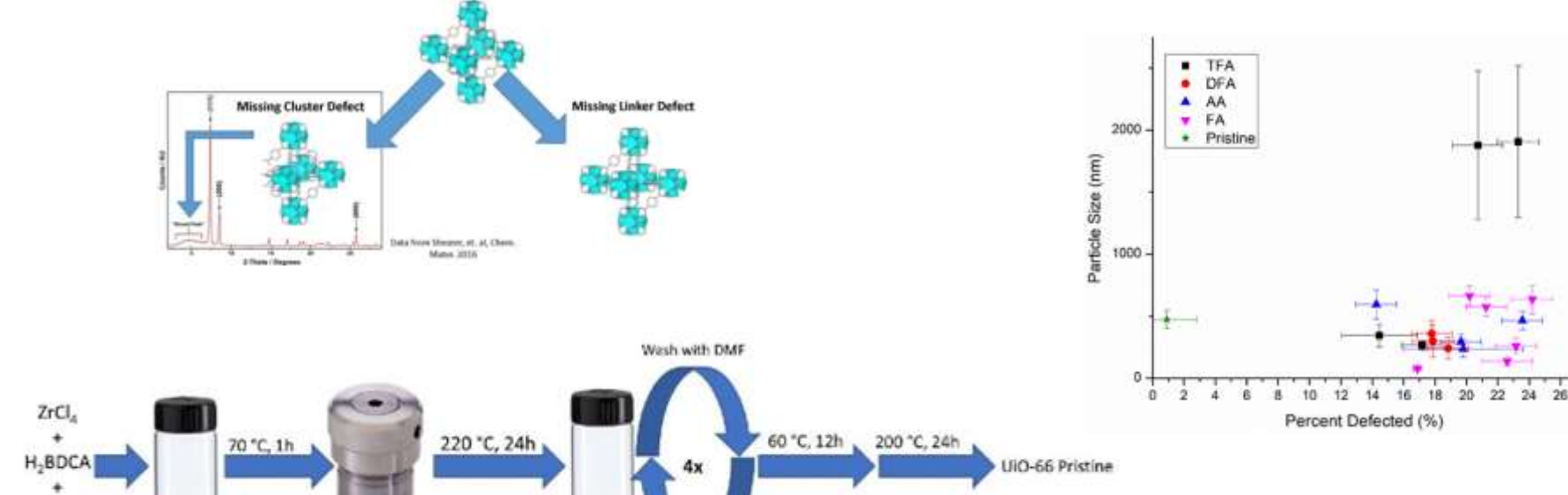
A synthetic screening was conducted, and we identified samples that range from "pristine" to ~30% defected.

| Sample	Capping Agent:BDC	Defect % by NMR (TGA Result)
Pristine	0.12:5.88	2% (0.9%)
AA 300	0.84:5.16	14% (14%)
FA 300	1.5:4.5	25% (24%)
FA 100	1.32:4.68	22% (23%)
FA 200	1.31:4.68	22% (21%)
TFA 33 (as-synth)	3.33:2.66	55% (21%)
TFA 33 (washed)	1.33:4.68	22% (21%)

All missing linker defect sites as synthesized are capped by a modulator and/or formic acid (which results from the degradation of DMF at high temperature). We conducted a series of NMR experiments to confirm the presence of organic capping agents. The ratio of expected capping agent to BDC was calculated from TGA and compared to the NMR data and found consistent, see table.
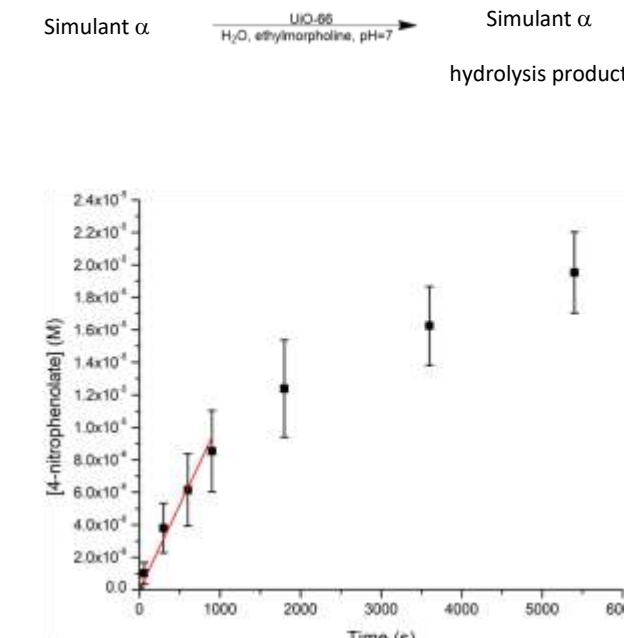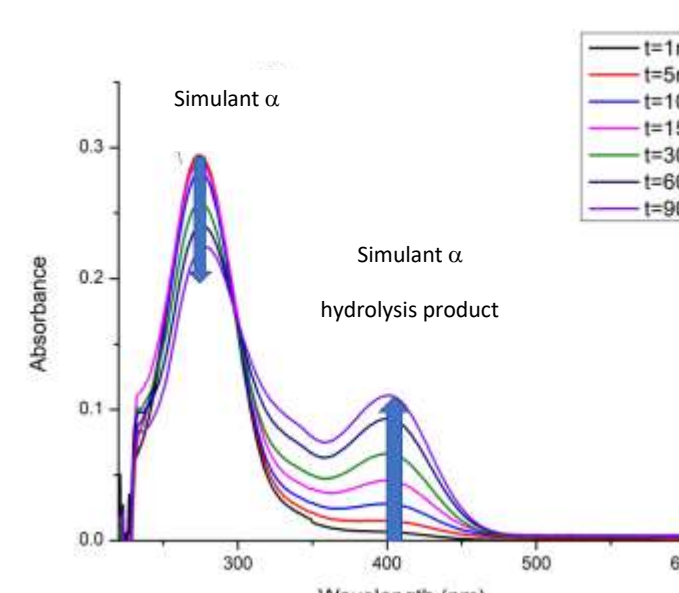
Sorbent Characterization
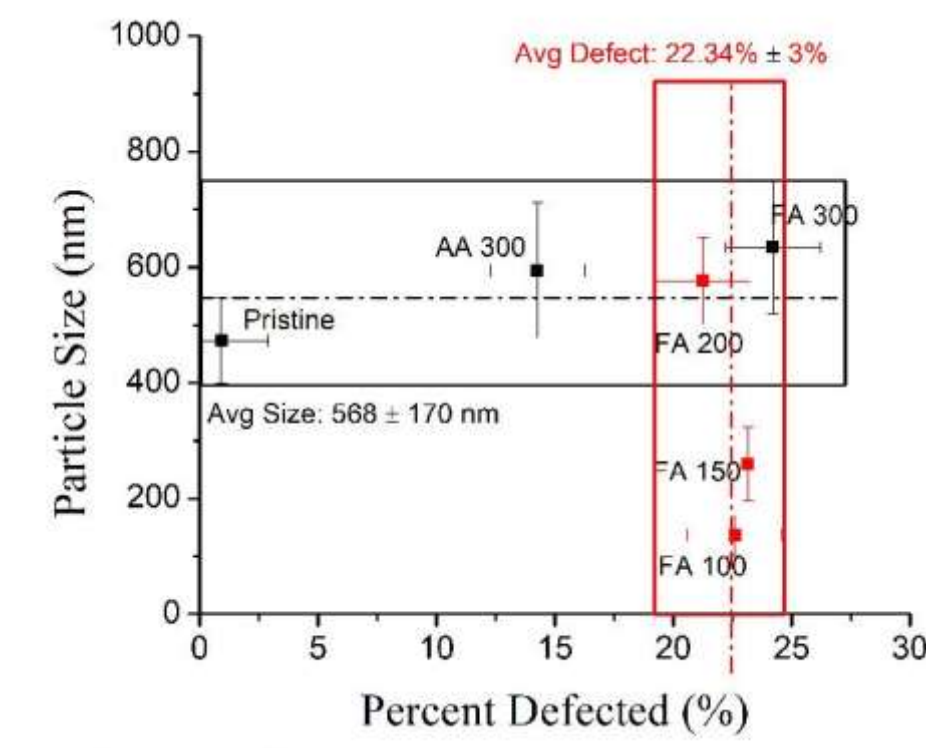
Synthetic protocols were developed to prepare samples of "pristine", 7% defected, and 27% defected quality for comparative studies. Additionally, we prepared a series of samples with different particles sizes at the highest defect level. An important note is that methods to scale these syntheses drastically changed both particle size and defect-level.

Three experimental techniques were used to measure transport properties of the defected UiO-66 series: gravimetric, CSFR, in situ NMR.

Activity of the samples was screened using Simulant α. Observed changes in the UV-Vis spectrum of a reaction mixture of Simulant α, ethyl morpholine, and MOF demonstrating the formation of hydrolyzed product. (Right) Concentration of hydrolysis product as a function of time. The linear fit to initial time points represents the rate of hydrolysis.
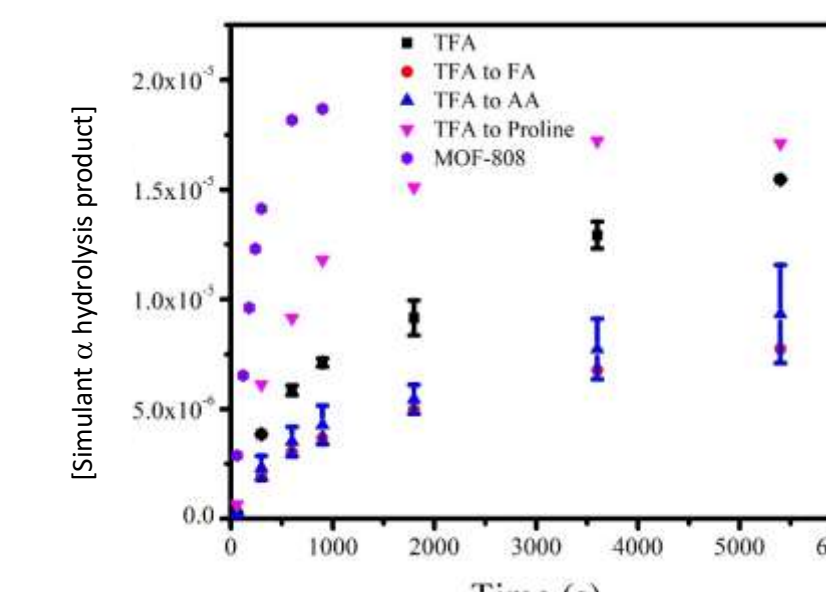

Some samples were significantly more active than expected based on their defect level and particle size. FA 100 synthesized with 100 equivalents of formic acid gives small particles of ~130 nm in diameter. TFA33 synthesized with 33 equivalents of trifluoroacetic acid also gives significantly larger particles (~2000 nm) in diameter, which based on diameter should be lower activity of Simulant α but is higher.
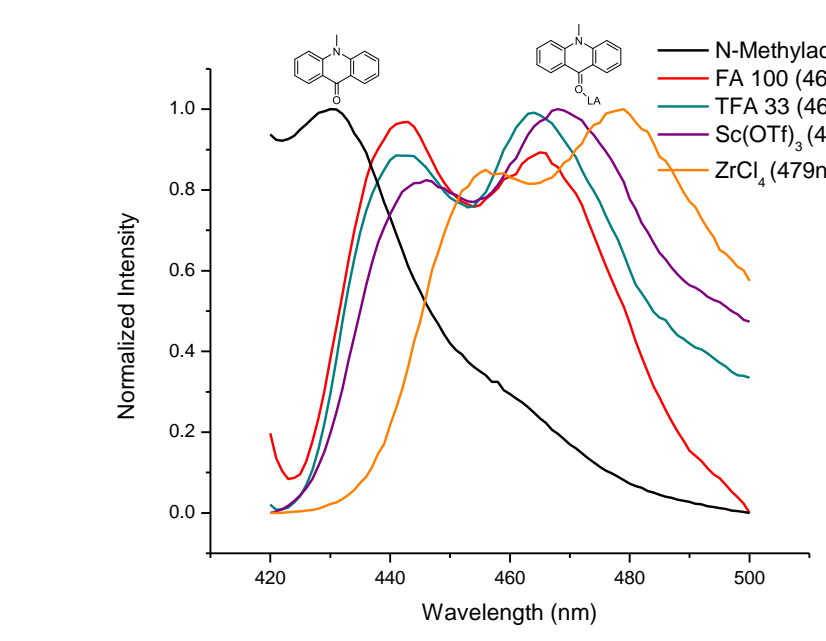

Fluorescence shift with capping agent was measured versus several standards. Since Lewis acidity does not significantly change for the two MOFs with different capping groups, we now believe the difference in reactivity is due to the relative strength of the Zr-COOH bond in each case.
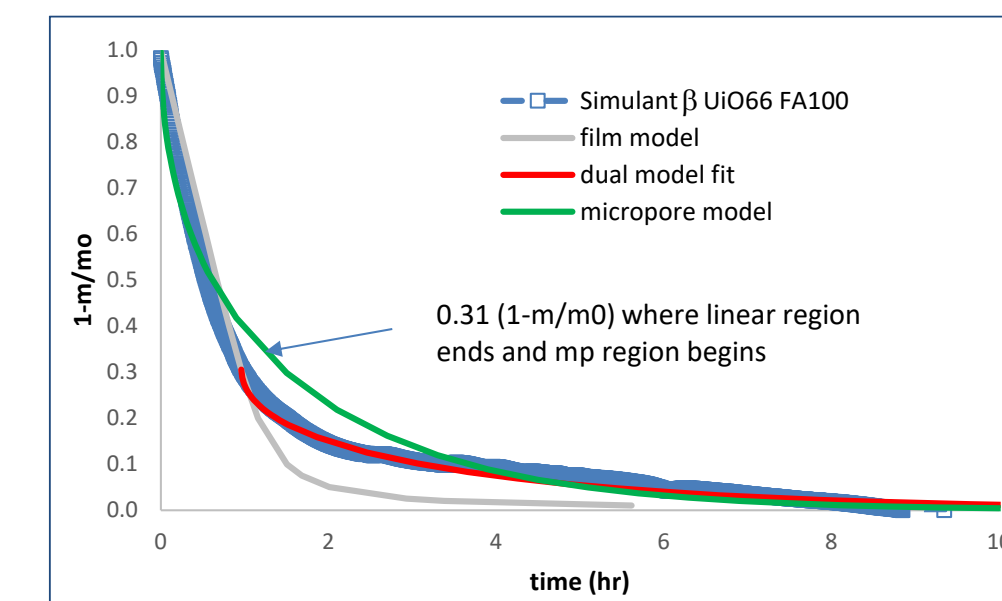
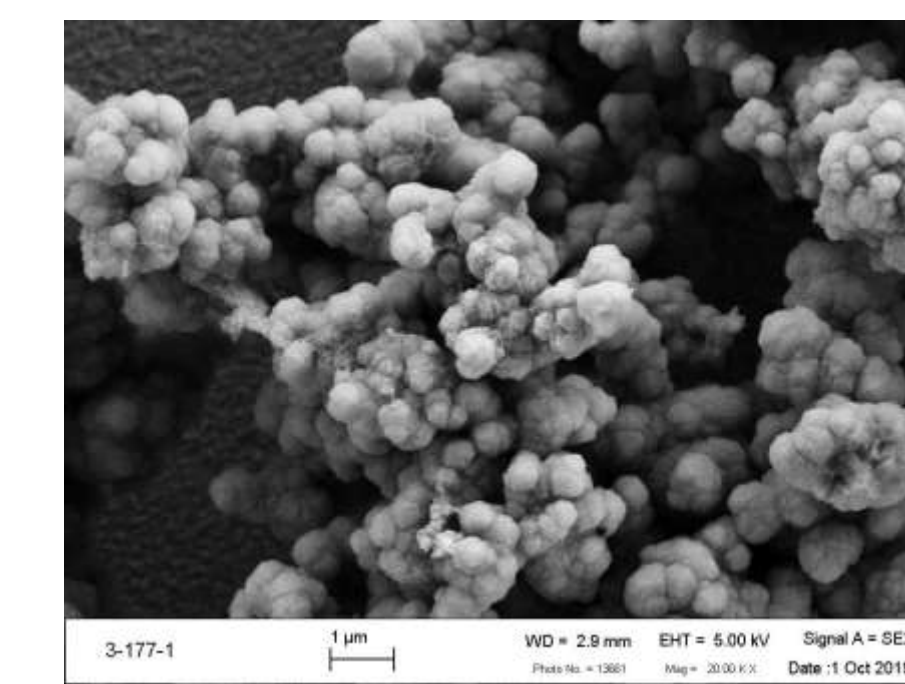## Mass Transfer Measurements
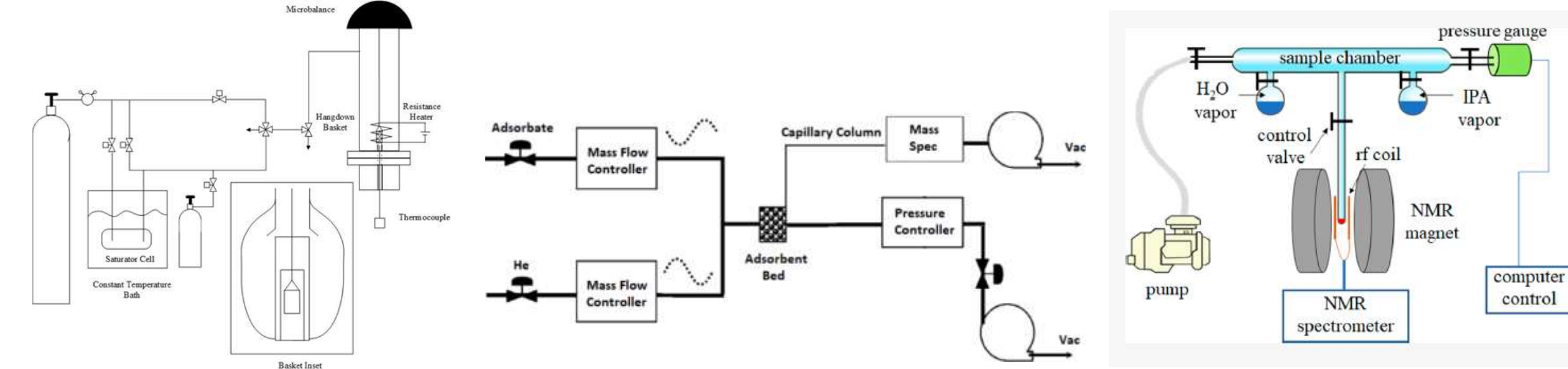
Three experimental techniques were used to measure transport properties of the defected UiO-66 series: gravimetric, CSFR, in situ NMR.
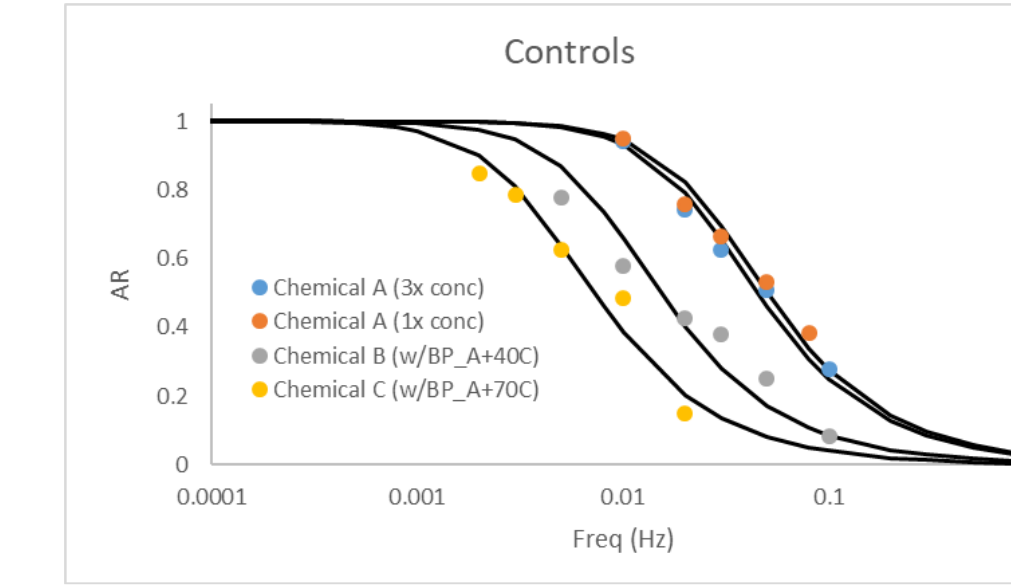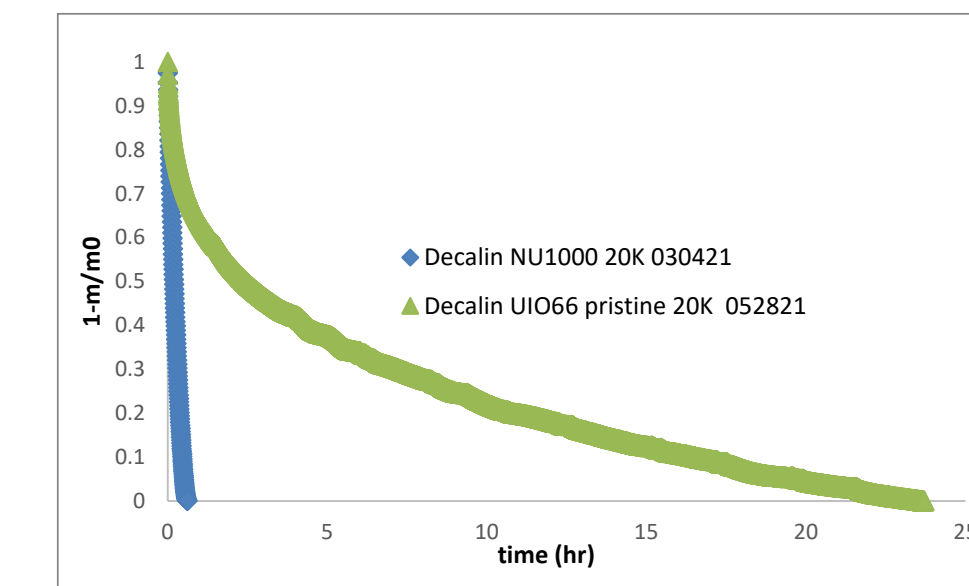
Micropore diffusion is the dominant resistance with pristine UiO-66 and the larger 40um crystal. Film resistance dominant on defected and larger pore MOFs.

Here is the first time that CSFR method has been used with toxic chemicals, shown are well behaved control curves for more volatile toxic Chemicals A and B but not the less volatile Chemical C at faster frequencies.


Simulant β uptake shown on defected UiO66 MOF FA100. Film model fits initial region. Micropore model does not fit whole curve only longest time region. The defected small diameter samples all exhibit a dual film/micropore resistance.

Dp (μm)	Pristine	AA300	FA100	FA200	40 um	TFA33
Simulant β Conc 4X	0.5	0.5	0.2	0.5	40	2
	Uptake	Uptake	8.3e-6	9.7e-6	1.7e-5	1.5e-5
	CSFR	CSFR	CSFR	CSFR	CSFR	
	4e-5			7e-5		
Chemical A Conc 6X	1.7e-5	2.8e-5	Film	8.3e-6	1.7e-5	Film
	Uptake	Uptake			Uptake	
	5.3e-4		1.0e-4	4.8e-4		

The diffusion time constants, D/R², obtained from the gravimetric and CSFR systems are shown. In general, the value obtained by CSFR is faster than gravimetric as it is derived from weakly bound species while gravimetric values are obtained from slowest diffusing species.


D/R² is not easily related to diffusivity for the smallest crystal diameters < 100 um, as agglomeration and secondary mass transfer effects are present.
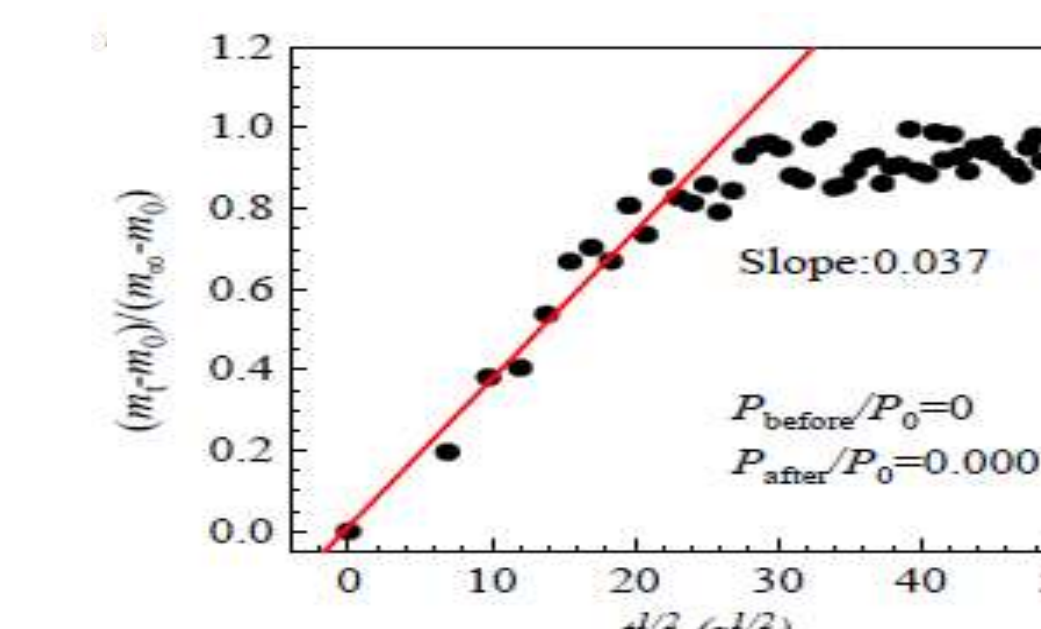
IPA uptake vs $t^{1/2}$ by in situ NMR on pristine UiO66 demonstrates at low loadings the uptake rate is micropore control. This rate is too fast to be measured by gravimetric or CSFR. This indicates that film and micropore rates are both involved over all ranges of transport diffusion regime.

Defected MOF Adsorption and Diffusion Modeling
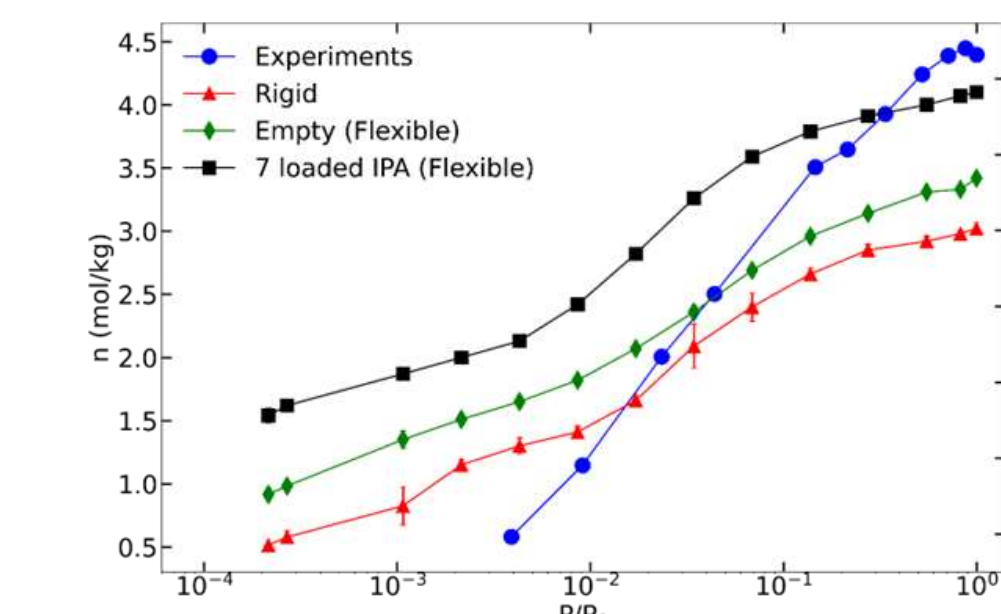
Most GCMC simulations use a rigid model for the framework. We have included the impact of framework flexibility with the "flexible snapshot" method. The snapshots generated by including IPA interactions significantly improve the agreement with experiments near saturation. This indicates that the UiO-66 framework responds to the presence of IPA in such a way as to accommodate more IPA adsorption. While the rigid isotherm is qualitatively correct, quantitative agreement with the adsorption isotherms requires inclusion of framework flexibility.
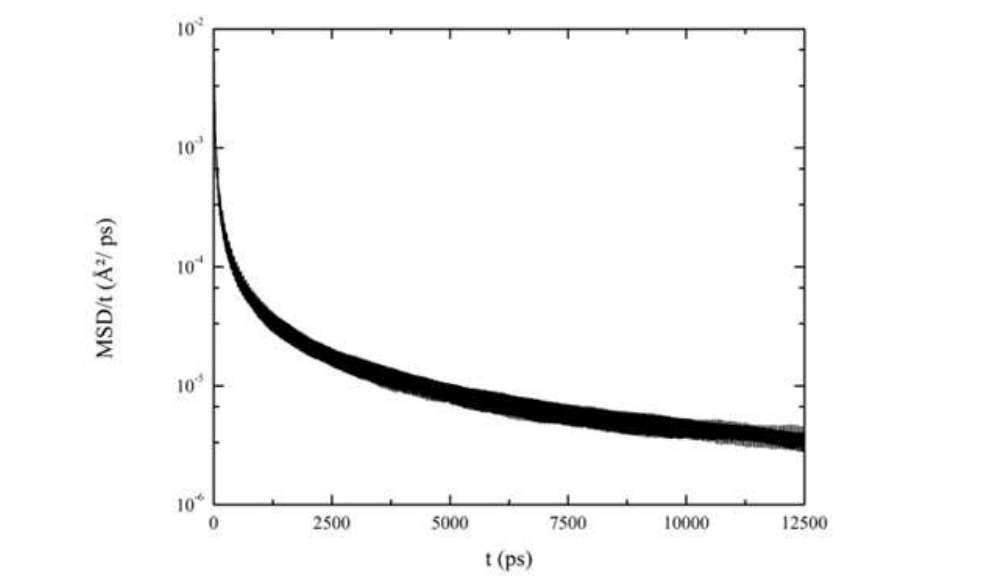
In order to predict diffusivities, we computed the Mean Square Displacement of acetone in UiO-66 holding the atoms of the framework fixed in their equilibrium positions. A plot of MSD/t versus t is shown in the figure. We see that the plot continues to decrease, even on a log scale, meaning that acetone does not diffuse out of the pores when the framework atoms are held fixed. This plot demonstrates that flexible models of UiO-66 must be used in order to get physically realistic diffusion constants.

Compound	tetrahedral μ₃OH – octahedral	octa-tetrahedral μ₃OH	tetrahedral μ₃O – octa	octa -tetrahedral μ₃O	Overall D_s (m²/s)
Simulant β	1.7x10⁻¹⁶	1.9x10⁻¹¹	9.8x10⁻¹⁷	1.3x10⁻¹²	6.6x10⁻¹⁸
Chemical A	5.2x10⁻¹⁶	2.6x10⁻¹⁰	2.1x10⁻¹⁵	2.53x10⁻¹⁰	1.7x10⁻¹⁶
IPA	2.7x10⁻¹³	2.3x10⁻⁶			5.5x10⁻¹⁴

Loading per primitive cell	Pristine	6x1, 2x3 25% Defect	3x4 25% Defect
1	4.57(95) x 10⁻¹²	1.3x(40) x 10⁻¹²	2.20(71) x 10⁻¹¹
2	3.17(62) x 10⁻¹³	5.6(10) x 10⁻¹²	4.95(52) x 10⁻¹²
3	3.41(84) x 10⁻¹⁴	6.39(77) x 10⁻¹³	2.56(58) x 10⁻¹³
7	2.04(36) x 10⁻¹⁵	2.14(32) x 10⁻¹²	7.72(83) x 10⁻¹³

Diffusion of Chemical A and Simulant β, and IPA in pristine and defective UiO-66 was modeled. We have computed barrier heights from umbrella sampling combined with weighted histogram analysis. These values contain up to an order of magnitude of uncertainty.

Conclusions

MOF Synthesis and Characterization:
- Higher defect levels (both missing linker and missing cluster) result from lower pKa modulators and higher concentrations of that modulator.
- Smaller particles result from lower concentrations of modulator.
- Modulators are incorporated into the overall MOF structure by capping defect sites.

MOF Reactivity and Uptake from Solution:
- Reactivity and uptake increase with level of missing linker defects.
- Materials with missing cluster defects have higher uptake and reactivity than pristine materials and also outperform those with missing linker defects with similar properties.
- Defect capping (appears) to play a role in determining the rate of hydrolysis reactivity, when all other things are held constant (particle size and defect level).

Simulation of Defected MOF Properties:
- Diffusion is enhanced in MOFs with missing linker defects when defect sites are capped with non-polar or non-hydrogen bonding groups.
- At low coverage the –OH groups on missing linker sites can actually bind sorbates such as IPA which slows the calculated diffusion even though the increased porosity tends to increase diffusion overall.
- Capping groups that are more weakly bound to defect sites give higher reaction rates for toxic chemical degradation because of smaller energy barriers for displacement of the capping groups by the agents.

Mass Transfer:
- Uptake and CSFR rates on MOFs follow three shapes. Linear uptake corresponds to film resistance, exponential uptake of micropore diffusion and a hybrid combination of linear and exponential. Slower micropore rates are dominant with larger crystal diameters and branched or ringed sorbates.
- The more defected samples FA100, FA200 have higher adsorption capacity than less defected pristine and AA300 samples. However, the magnitude of the rates are similar for a given chemical across the defect levels only fraction that is film or micropore controlled varies.
- This capacity observation agrees with intuition over the range of defect levels studied here. Higher defect levels begin to affect the structural integrity of the crystal. Based on CSFR, missing clusters seem to enhance diffusion rate while missing linkers do not.

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