Supporting Information

Removal of Chlorine Gas by an Amine Functionalized Metal-Organic Framework via Electrophilic Aromatic Substitution

Jared B. DeCoste,^{1*} Matthew A. Browe², George W. Wagner², Joseph A. Rossin³, and Gregory W. Peterson^{2*}

¹ Leidos, Inc., PO Box 68, Gunpowder, MD 21010

²Edgewood Chemical Biological Center, 5183 Blackhawk Rd., Aberdeen Proving Ground, MD 21010, United States

³Guild Associates, Inc., 5750 Shier Rings Rd., Dublin, OH 43016, United States

Experimental Procedures

Synthesis MOFs

All chemicals were obtained from Sigma Aldrich and used without further purification. The synthesis each of the UiO analogs was performed by the following method, adapted from Cavka et al.¹ An equal molar ratio (0.641 mmol) of ZrCl₄ and the organic linker (terephthalic acid, 2-amino terephthalic acid, 2-hyroxy terephthalic acid) was dissolved in DMF (10 mL) at room temperature, and sonicated if necessary to dissolve the organic linker. The mixture was sealed in a 20 mL scintillation vial and heated to 120 °C for 24. The resulting solid was retrieved and solvent exchanged with methanol via Soxhlet extraction overnight. MIL-53, Cu-BTC, and ZIF-8 were purchased from Sigma Aldrich under the tradenames Basolite A100, Basolite C300, and Basolite Z1200 respectively. Mil-53-NH₂(Al) was synthesized by known methods published elsewhere.² The XRD and surface areas of each MOF are reported below in the supplemental information, and were in good agreement with the previously published data.

Microbreakthrough experiments

A miniaturized breakthrough apparatus was used to evaluate milligram-scale quantities of MOF samples for the adsorption of chlorine as described in depth elsewhere.^{3,4} Approximately 10-15 mg of material was loaded into a nominal 4 mm i.d. fritted glass tube that was subsequently loaded into a water bath for isothermal testing at 20 °C. Prior to testing, each MOF was regenerated for one hour at 150 °C under flowing dry air to remove any physisorbed water. A ballast with a predetermined quantity of challenge gas was then mixed with a stream of dry (-40°C dew point) air at a rate necessary to achieve a challenge concentration of 2,000 mg m⁻³. The contaminated air stream was then sent through the fritted glass tube at a flow rate of 20 mL min⁻¹, equivalent to a residence time of approximately 0.10 seconds. The effluent stream was sent through a photoionization detector with an 11.7 eV argon lamp

to monitor the chlorine concentration. The data is reported and plotted as Normalized time (the time divided by the mass of the sample used) verse the signal at a given time divided by the signal at saturation (C/C_0). The corresponding breakthrough curve was integrated to determine the loading at saturation. In a separate experiment the effluent was flown through a gas cell, which is analyzed using a Nicolet 380 FTIR. Each spectrum is an average of 16 scans from 4000 to 650 cm⁻¹.

Powder X-ray diffraction (PXRD)

Each MOF was analyzed using powder X-ray diffraction (PXRD). PXRD measurements were taken using a Rigaku Miniflex 600 X-ray powder diffractometer with a D/Tex detector. Samples were scanned at 40 kV and 15 mA, using Cu Ka radiation ($\lambda = 1.54$ Å), and a scan rate of 5° min⁻¹ over a 20 range of 5 to 50°. Zero-background discs were used to minimize background scattering. PXRD diffraction patterns were processed using the Reflex module in Material Studio 6.1 by Accelrys.

X-ray Photoelectron Spectroscopy (XPS)

XPS spectra were recorded using a Perkin Elmer Phi 570 ESCA/SAM system employing MgKα xrays. All binding energies were referenced to the C1s photoelectron peak at 284.6 eV. Samples were placed on double-stick tape, placed in the chamber, and off-gassed for one hour, and then placed in the chamber for analysis.

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR)

Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of each MOF were taken using a Bruker Tensor 27 FTIR with a Bruker Platinum ATR accessory equipped with a single reflection diamond crystal. Sixteen scans were averaged over a range of 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹.

¹H Nuclear Magnetic Resonance (NMR) Spectroscopy

Approximately 5 mg of each MOF sample was digested in a 10%H₂SO₄/d₆-DMSO solution and studied using ¹H nuclear magnetic resonance. A Varian INOVA 300 NMR spectrometer was utilized for the experiments. A 10 ms pulse followed by a 4 s acquisition time and a 1 s delay were performed for 64 iterations. Spectra were referenced to the internal DMSO peak at δ = 2.5 ppm.

Results



Figure S1. Chlorine microbreakthrough plots of various materials vs. normalized time. Plots on right are zoomed out to capture the higher performing materials.



Figure S2. PXRD patterns from $2\theta = 3$ to 90° of UiO-66-NH₂ pre and post-exposed to Cl₂.



Figure S3. PXRD patterns from $2\theta = 3$ to 90° of UiO-66 pre and post-exposed to Cl₂.



Figure S4. PXRD patterns from $2\theta = 3$ to 60° of each material studied.



Figure S5. Chlorine 2p XPS spectrum for UiO-66-NH $_2$ after exposure showing the presence of Zr-Cl and C-Cl bonds.



Figure S6. Carbon 1s XPS spectra of UiO-66-NH₂ before and after chlorine exposure.

Ratio	UiO-66-NH ₂	UiO-66-NH ₂ (Cl ₂ -exposed)
O/Zr	4.76	4.64
O/C	0.54	0.49
Zr/C	0.11	0.11
N/C	0.06	0.03
Cl/Zr	-	1.12

Table S1. Atomic ratios for UiO-66-NH₂ before and after exposure to chlorine.



Figure S7. FTIR spectra from 1800 to 400 cm⁻¹ of UiO-66 pre and post-exposed to Cl₂.



Figure S8. FTIR spectra from 1800 to 400 cm⁻¹ of UiO-66-NH₂ pre and post-exposed to Cl_2 . ZrOCl₂ spectra is given as a reference.



Figure S9. ¹H NMR spectra of UiO-66-NH₂ pre and post exposed to Cl_2 digested in a 10% H₂SO₄/DMSO solution.



Figure S10. ¹H NMR spectra of 2-amino terephthalic acid (2-ATA) exposed to Cl₂ in acetonitrile, 2-ATA is represented at $\delta \approx 7.82$ (d), 7.35 (d), and 7.10 (dd) ppm, while 2-amino-3-chloroterephthalic acid is represented at $\delta \approx 7.82$ (d), and 6.87 (d) ppm and 2-amino-5-chloroterephthalic acid $\delta \approx 7.78$ (s), and 7.12 (s) ppm.

Table S2. GC-MS results for 2-ATA exposed to Cl_2 in acetonitrile. ¹H NMR showed two separate isomers, but they could not be separated by GC and appear as one product in the MS. The parent peak was not observed, due to the ease of fragmentation of the aryl carboxylate bond.

m/z	Relative to parent	Species
215.0	М	$C_6H_2(Cl)(NH_2)(COOH)_2$
171.1	M-44	$C_6H_3(Cl)(NH_2)(COOH)^+$
154.0	M-61	$C_6H_2(Cl)(COOH)^+$
137.1	M-78	$C_6H_4(NH_2)(COOH)^+$
126.1	M-89	$C_6H_3(Cl)(NH_2)^+$
120.1	M-95	$C_6H_3(COOH)^+$



Figure S11. PXRD patterns from $2\theta = 3$ to 90° of MIL-53-NH₂ (AI) pre and post-exposed to Cl₂.



Figure S12. FTIR spectra from 1800 to 400 cm⁻¹ of MIL-53-NH₂ (AI) pre and post-exposed to Cl₂.



Figure S13. ¹H NMR spectra of MIL-53-NH₂ (Al) pre and post exposed to Cl_2 digested in an HF/DMSO solution.

(1) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. J. Am. Chem. Soc. **2008**, 130, 13850.

(2) Couck, S.; Denayer, J. F. M.; Baron, G. V.; Rémy, T.; Gascon, J.; Kapteijn, F. *J. Am. Chem. Soc.* **2009**, *131*, 6326.

(3) Glover, T. G.; Peterson, G. W.; Schindler, B. J.; Britt, D.; Yaghi, O. *Chem. Eng. Sci.* **2011**, *66*, 163.

(4) Decoste, J. B.; Peterson, G. W. *Journal of Visualized Experiments* **2013**, e51175.