

A Combined Experimental/Computational Study on the Adsorption of Organosulfur Compounds over Metal Organic Frameworks from Fuels

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Supporting Information

Characterization of MOFs

The textural properties of the MOF materials were measured by nitrogen adsorption/desorption isotherms at -196 °C using an ASAP2020 accelerated surface area and porosimetry analyzer (Micromeritics). The total surface area and pore volume were calculated using BET method and the amount of nitrogen adsorbed at $P/P_0 = 0.95$, whereas S_{micro} was derived from t-plot method. The pore size distribution was determined according to density functional theory method. Prior to each measurement, the samples were outgassed at 150 °C. The textural properties of MIL-101(Cr), MIL-100(Fe), and Cu-BTC are listed in *Table S1*.

Table S1. Textural properties of MIL-101(Cr), MIL-100(Fe), and Cu-BTC

	S _{BET} (m ² /g)	S _{meso} (m ² /g)	S _{micro} (m ² /g)	V _{total} (cm ³ /g)	V _{meso} (cm ³ /g)	V _{micro} (cm ³ /g)	D _{ave} (Å)
MIL-101(Cr)	2789	1710	1145	1.32	0.99	0.42	18.9
MIL-100(Fe)	1907	944	962	0.86	0.41	0.36	18.0
Cu-BTC	1024	131	893	0.53	0.41	0.10	-

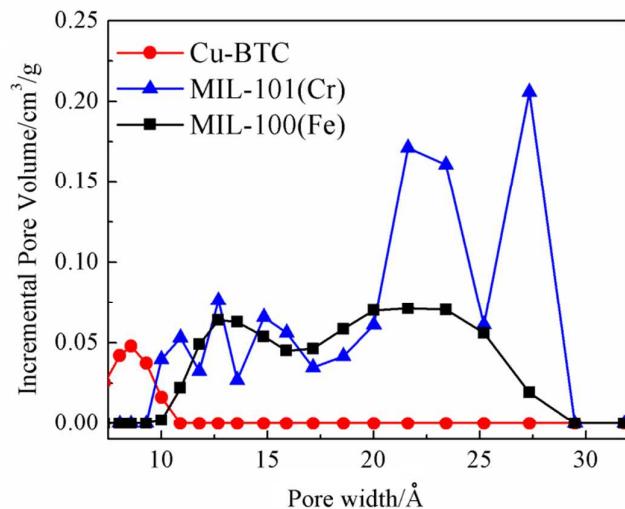
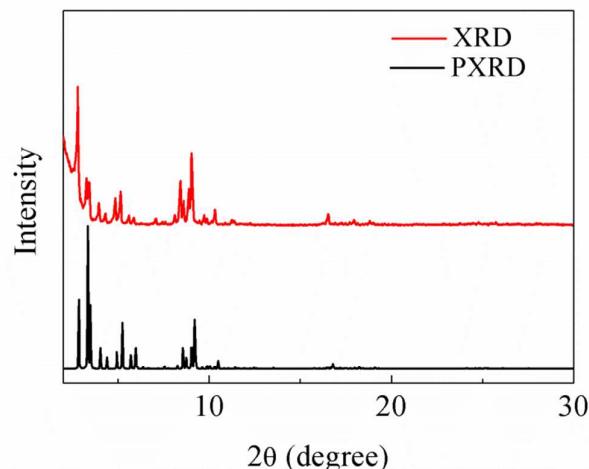


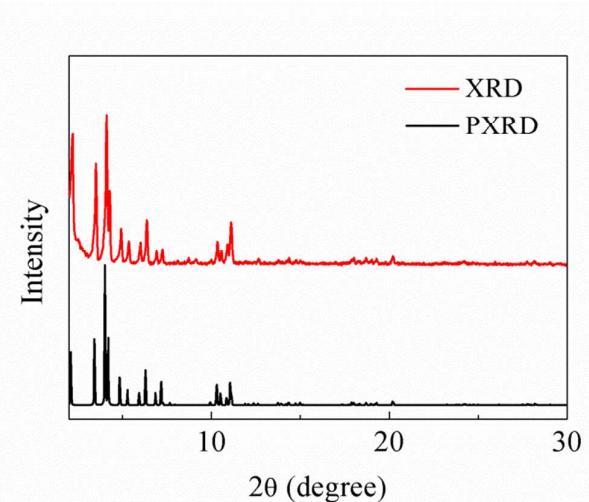
Figure S1. Pore size distributions (DFT) of MIL-101(Cr), MIL-100(Fe), and Cu-BTC

The crystalline structures of the MOFs were characterized by powder X-ray diffraction (XRD) with a D8 advance diffraction meter (Bruker, Germany) operating in transmission mode using Cu-K α radiation ($\lambda = 0.1540$ nm) in the scanning range of 20 from 2° to 50° with a scan step of 0.02°. Figure S2 shows XRD (experimental) and PXRD (simulated) patterns of (a) MIL-101(Cr), (b) MIL-100(Fe), and (c) Cu-BTC synthesized in the lab. The well-resolved peaks imply that the synthesized samples

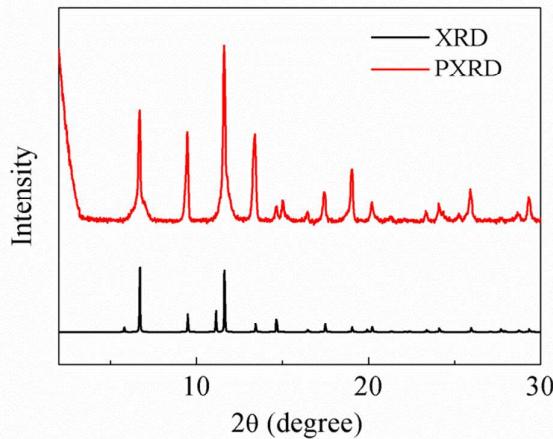
have high crystallinity. Moreover, the main peaks of the XRD patterns match well with the simulated PXRD patterns, as well as those of the corresponding MOF materials reported.¹⁻³ The results confirm the materials synthesized in the lab are MIL-101(Cr), MIL-100(Fe) and Cu-BTC.



(a)



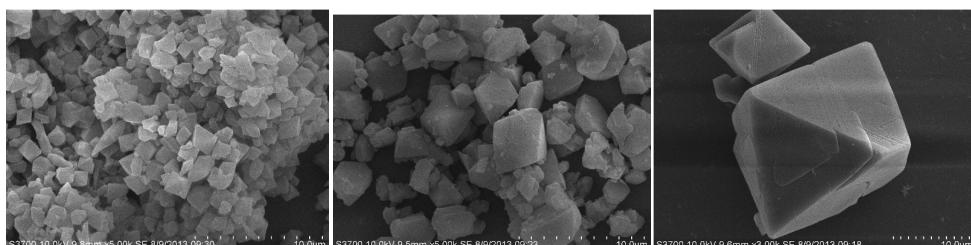
(b)



(c)

Figure S2. XRD (experimental) and PXRD (simulated) patterns of (a) MIL-101(Cr), (b) MIL-100(Fe), and (c) Cu-BTC

The morphologies and particle sizes of the synthesized MOFs were characterized by a FEI XL-30 scanning electron microscope (SEM) at an accelerating voltage of 20 kV after gold deposition. Figure S3 shows the SEM images of (a) MIL-101(Cr), (b) MIL-100(Fe), and (c) Cu-BTC synthesized in the lab. The samples were typically octahedral. The crystal sizes of the samples was almost the same as those reported in the literatures.¹⁻³ The results further suggest that the materials synthesized in the lab are MIL-101(Cr), MIL-100(Fe) and Cu-BTC.



(a)

(b)

(c)

Figure S3. SEM images of (a) MIL-101(Cr), (b) MIL-100(Fe), and (c) Cu-BTC.

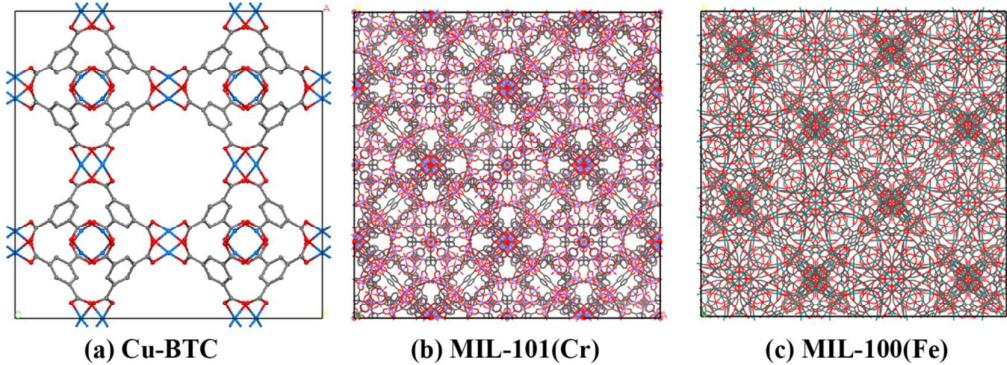


Figure S4. The unit cells of Cu-BTC, MIL-101(Cr), and MIL-100(Fe). Color code: C, gray; O, red; Cu, blue; Cr, purple; Fe, green.

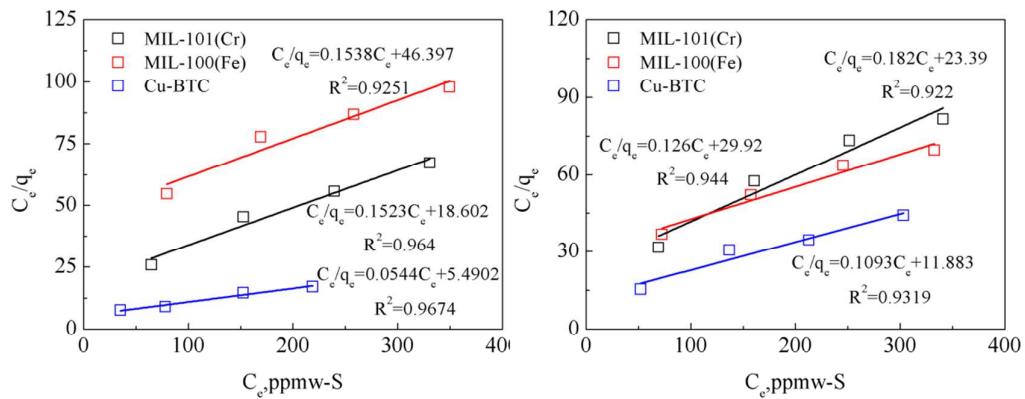


Figure S5. Plots of C_e/q_e versus C_e for (a) DBT; (b) DMDBT adsorption over MIL-101(Cr), MIL-100(Fe), and Cu-BTC.

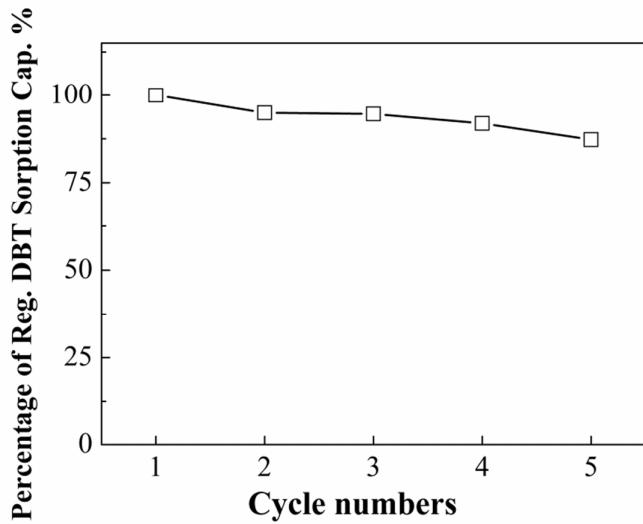


Figure S6. Recovery percentage of the DBT sorption capacity of Cu-BTC as a function of the cycle number during the multiple regeneration cycles

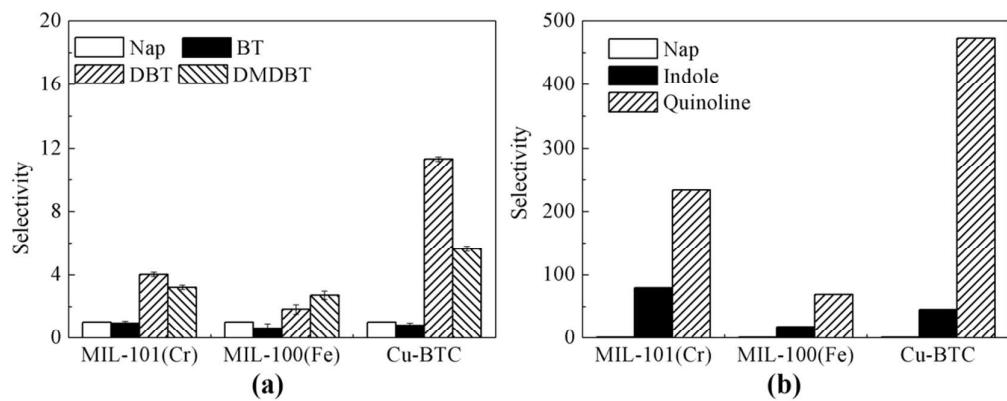


Figure S7. Adsorption selectivities of various S/N- compounds over MIL-101, MIL-100, and Cu-BTC using Nap as the reference: (a) thiophenic compounds; (b) organonitrogen compounds

Table S2. Adsorptive Capacity and Selectivity for Each Compound in MDF3

adsorbent		Nap	BT	DBT	DMDBT	In	Qu
Cu-BTC	Q $\mu\text{mol-S/g-sorb}$	28.71	21.57	46.20	34.72	134.3	214.95
	Ce $\mu\text{mol/g}$	2.72	2.820	2.472	2.635	1.228	0.089
	α	1.000	0.724	1.770	1.245	10.360	228.721

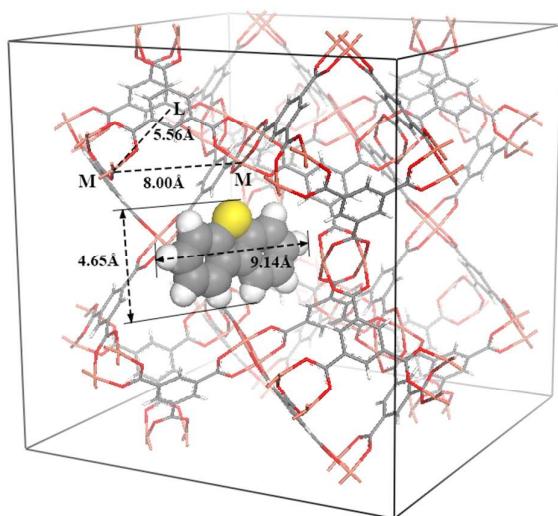


Figure S8. Size of DBT molecule compared to the distances of M- and L-sites in Cu-BTC.

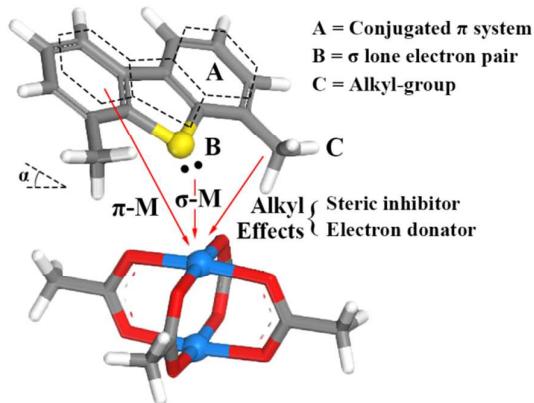


Figure S9. Interaction mechanism between thiophenic compounds and Cu-BTC

Reference

1. Ferey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surble, S.; Margiolaki, I. A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area. *Science* **2005**, *309*, 2040.
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3. Li, Y.; Yang, R. T. Hydrogen storage in metal-organic and covalent-organic frameworks by spillover. *AIChE J.* **2008**, *54*, 269-279.