Liquid Phase Adsorption by Microporous Coordination Polymers: Removal of Organosulfur Compounds

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New U.S. Department of Transportation rules mandating that diesel and gasoline have sulfur levels less than 15 and 30 ppm by weight (ppmw), respectively,[1] and the need for virtually sulfur-free hydrogen streams for fuel cells has reignited interest in novel desulfurization technology. Hydrodesulfurization, the industry standard process, effectively eliminates nonaromatic sulfur compounds and thiophenes, but is challenged by more sterically hindered benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (DMDBT) fuel contaminants.[2] Adsorption presents an attractive alternative for removal of these compounds; well-studied classes of porous materials such as activated carbons and zeolites have been shown to adsorb organosulfur compounds from hydrocarbon streams.[3]
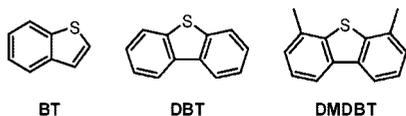
Microporous coordination polymers (MCPs) excel at gas adsorption and capacities greatly exceeding those of activated carbons and zeolites have been reported.[4] Quantitative determination of adsorption of large molecules by MCPs has seen little scrutiny despite the fact that they display adequate pore size and guest exchange kinetics.[5,6] To address this paucity of data in the context of an important remediation challenge, the adsorption capacities of five chemically diverse MCPs were determined for BT, DBT, and DMDBT over a wide concentration range from solutions of the organosulfur compound in isooctane. MOF-5 and HKUST-1, two of the earliest examples of highly porous MCPs, were chosen as prototypical zinc and copper materials.[7,8] MOF-177 has superior surface area and large pore size.[6] UMCM-150 represents a new class of MCPs with reduced symmetry linkers,[9] and MOF-505 is a copper material constructed from a tetracarboxylic acid.[10] These MCPs possess different pore sizes, shapes, and metal clusters thus offering a test of the key factors dictating adsorption behavior.

Adsorption isotherms (Figure 1) were measured out to 2000 ppmw S in isooctane for BT and DBT and to 700 ppmw S in isooctane for DMDBT (due to low solubility). These MCPs exhibit excellent capacities for the organosulfur compounds investigated at high concentrations with, for example, BT capacities (g S/kg MCP, 1500 ppmw S) of 25, 40, and 51 for HKUST-1, UMCM-150, and MOF-505; DBT capacities (g S/kg MCP, 1500 ppmw S) of 45, 83, and 39 for HKUST-1, UMCM-150, and MOF-505; and DMDBT capacities (g S/kg MCP, 600 ppmw S) of 16, 41, and 27 for HKUST-1, UMCM-150, and MOF-505. This represents uptakes of 48 wt % and 27 wt % for DBT and DMDBT in UMCM-150 (for regenerability see Supporting Information). Significantly, saturation has not been reached for all isotherms, indicating that these materials have the potential for even higher adsorption
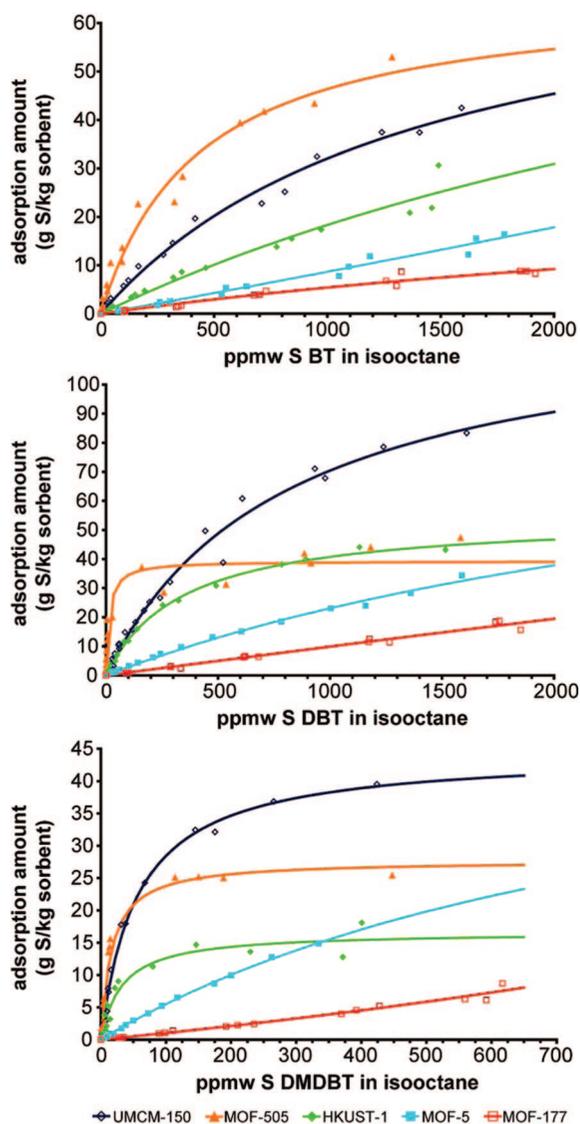
Figure 1. Adsorption isotherms for benzothiophene (top), dibenzothiophene (middle), and 4,6-dimethyldibenzothiophene (bottom) for UMCM-150, MOF-505, HKUST-1, MOF-5, and MOF-177 from isooctane solutions. The curves represent a fit to the Langmuir equation and are intended as guides to the eye.

amounts. For comparison, capacities (g S/kg zeolite) were measured for a benchmark zeolite material, Na(Y), at 1500 ppmw S for BT and DBT and at 600 ppmw S for DMDBT and are 8, 5, and 3, respectively. Capacity at low concentrations is an equally important performance metric, and several MCPs studied operate extremely efficiently at low concentration indicating high affinity between the
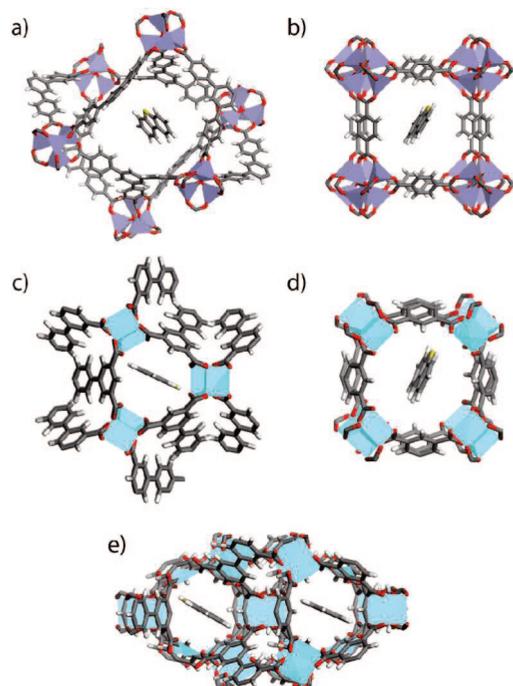
Figure 2. Crystal structures of (a) MOF-177 (b) MOF-5 (c) UMCM-150 (d) HKUST-1 (e) MOF-505 with one molecule of dibenzothiophene added in the pore of each MCP to represent scale.

organosulfur compounds studied and the framework. MOF-505 has capacities (g S/kg MCP, 25 ppmw S) of 25 and 17 for DBT and DMDBT. In comparison, Na(Y) zeolite has a DBT capacity of 1.5 g S/kg zeolite and a DMDBT capacity of 2 g S/kg zeolite both at 25 ppmw S.

Typically, correlations are observed between the surface area or pore volume of an MCP and the amount of gas adsorbed. In the concentration regime studied for large organosulfur compound adsorption, neither of these correlations holds. For example, MOF-177 has the highest surface area and pore volume of these five materials (for these data see Supporting Information), but it adsorbs the least for all three organosulfur compounds. Figure 2 illustrates models of one molecule of dibenzothiophene in the pore of each MCP studied. DBT is in closest contact with the framework of UMCM-150 and MOF-505: two MCPs with the highest DBT affinity as evidenced by uptake at low concentrations. However, it is also important to note that upon activation UMCM-150, MOF-505, and HKUST-1 are MCPs with coordinatively unsaturated metal centers. Although π-complexation between the organosulfur compound and the metal center is unlikely on steric grounds, other interactions with these sites may be functional.

The greatest challenge for desulfurization, and an issue common to both hydrodesulfurization and adsorption processes, has been the removal of DMDBT due to its size and the sterically hindered sulfur. MCPs excel here; for three of the five materials studied, the DMDBT capacity is larger than for BT and DBT at 300 ppmw S. For example, UMCM-150 has capacities (g S/kg MCP, 300 ppmw S) of 14, 34, and 37 for BT, DBT, and DMDBT. Larger guests lead to increased contact with the framework. This enhances interaction leading to higher adsorption for DMDBT. However, pore size is also a factor governing the adsorption capacity for a given

organosulfur compound. For example, MOF-505, the MCP with the smallest pores studied, has its largest capacity at 300 ppmw S for DBT (38 g S/kg), but the amount adsorbed drops to 27 g S/kg for DMDBT, showing that DMDBT does not fit as well into the pores. These examples illustrate that MCPs are capable of readily removing the compound most challenging to eliminate by hydrodesulfurization thus making this an excellent complementary technique for the achievement of extremely low sulfur fuels.

In conclusion, MCPs can adsorb large quantities of organosulfur compounds from the liquid phase and the exceptional levels of uptake suggest that liquid phase adsorption will be an important application for this class of materials.[11] Adsorption capacity in a given MCP is determined by pore size and shape, where the interaction between the organosulfur compound and the framework plays a key role. This suggests considerable potential for the rational design of new MCPs for desulfurization. Flow-through experiments and determination of the selectivity of MCPs for BT, DBT, and DMDBT in the presence of other aromatic compounds found in fuels are underway to assess the practicality of desulfurization by adsorption to MCPs.

Supporting Information Available: Experimental details, regeneration results, surface areas and pore volumes, and isotherm data in tabular form. This material is available free of charge via the Internet at http://pubs.acs.org.

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SUPPORTING INFORMATION

Contents

I. MCP Activation Procedures

MOF-5, MOF-177: Millward, A.R.; Yaghi, O.M. *J. Am. Chem. Soc.* **2005**, *127*, 17998-17999.

HKUST-1: Rowsell, J.L.C.; Yaghi, O.M. *J. Am. Chem. Soc.* **2006**, *128*, 1304-1315.

MOF-505: Chen, B.; Ockwig, N.W.; Millward, A.R.; Contreras, D.S.; Yaghi, O.M. *Angew. Chem. Int. Ed.* **2005**, *44*, 4745-4749.

UMCM-150: Wong-Foy, A.G.; Lebel, O.; Matzger, A.J. *J. Am. Chem. Soc.* **2007**, *129*, 15740-15741.

II. Materials and Methods

Benzothiophene, (97 %, Acros), dibenzothiophene (99%, Acros), 4-6-dimethyldibenzothiophene (97%, Aldrich), and isooctane (HPLC grade, Fisher) were used as received. Na(Y) zeolite (powder) was obtained from Strem Chemicals and used as received. Sulfur concentrations were determined using a Shimadzu GC-2010 equipped with a capillary column (L = 15 m, ID = 0.25 mm) and outfitted with both a flame ionization detector (FID) and flame photometric detector (FPD). Isotherm capacities were determined using the FID detector and were calibrated using control solutions of known sulfur concentration.

III. Batch Adsorption Procedure

In a typical experiment, ~10, 15, and 20 mg (precisely weighed) of MCP were added to three GC vials. Isooctane (500 μL) was added to each vial. Aliquots (20.0, 50.0, 100, 250, and 500 μL) of 3000 ppmw S benzothiophene or dibenzothiophene in isooctane, or 1000 ppmw S 4,6-dimethyldibenzothiophene in isooctane were added sequentially. Between aliquots, the vials were agitated on a shaker for 2 hours (benzothiophene), 3.5 hours (dibenzothiophene), or 12 hours (4,6-dimethyldibenzothiophene) and then analyzed by GC. Equilibration times were determined for each organosulfur compound by monitoring (GC) the concentration change until no further changes in the adsorption capacity were observed.

IV. Regeneration Experiment

UMCM-150 was added to a GC vial. DBT (1 mL, 3000 ppmw S) in isooctane was added to the solid. The vial was agitated on a shaker overnight. The DBT solution was removed and the UMCM-150 was rinsed with isooctane (6 × 20 mL) over a 24 hour period to remove adsorbed DBT. The isooctane solution was removed and the regenerated UMCM-150 was used to plot an isotherm using the batch adsorption procedure given in Section III. The results are shown below.
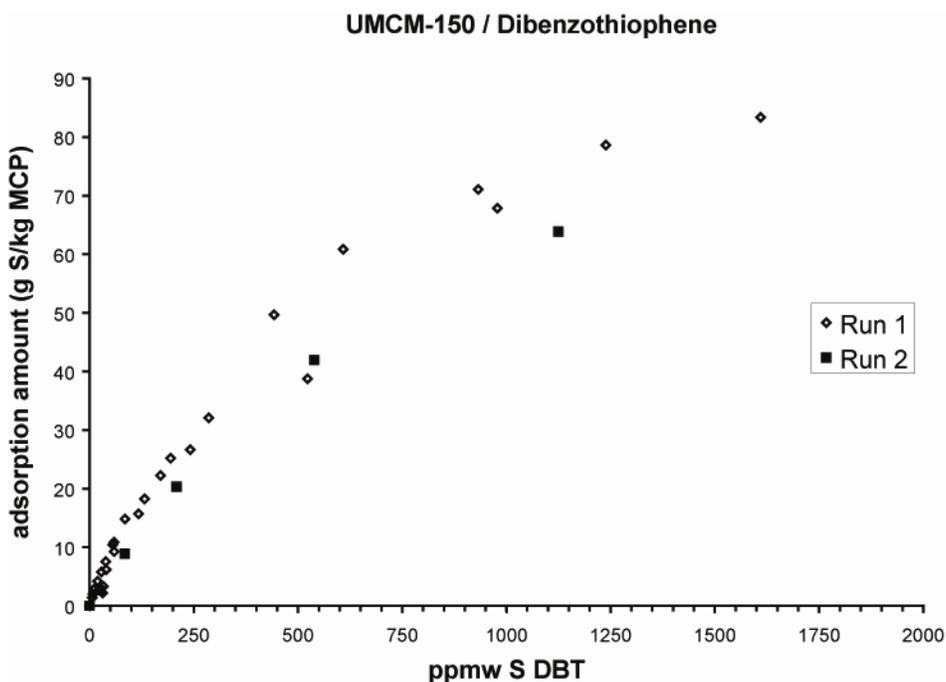
V. MCP Surface Areas and Pore Volumes

Table S1.

MCP	Langmuir Surface Area (m^2/g)	Pore Volume (cm^3/g)[a]
UMCM-150	3100[b]	1.11
MOF-505	1830[c]	0.71
HKUST-1	2260[d]	0.79
MOF-5	4170[d]	1.31
MOF-177	5640[d]	1.86

a) Pore volumes were calculated using the SOLV routine in PLATON (v. 1.10, University of Glasgow, 2006). The default probe radius of 1.2 Å was used with a grid spacing of 0.2 Å. All solvent molecules (bound and free) were removed from the structure generated from the published CIF files prior to use of the SOLV routine. For UMCM-150 and MOF-177, disorder in the structures was not removed as it did not appreciably affect the pore volume.

b) Wong-Foy, A.G.; Lebel, O.; Matzger, A.J. *J. Am. Chem. Soc.* **2007**, *129*, 15740-15741.

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VI. Kinetic Diameters
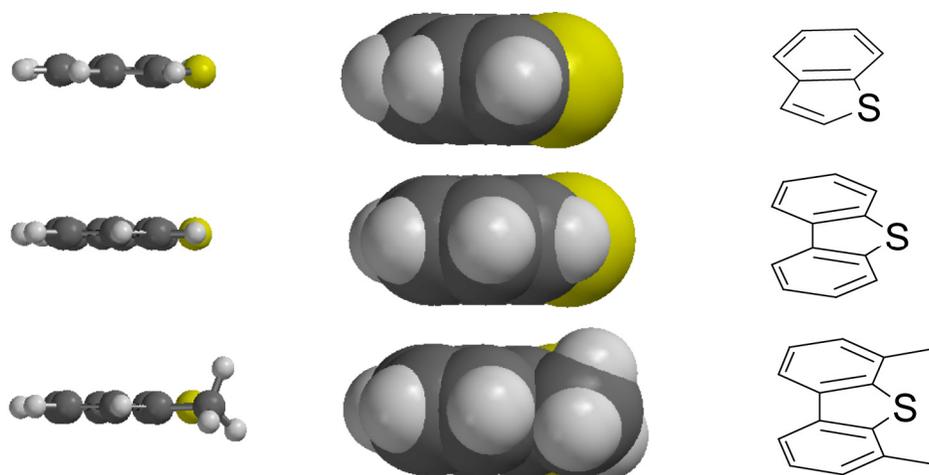
Figure S1. Kinetic diameters were approximated using the minimum cross-sectional area and were found to be 5.45 Å for benzothiophene (top), 5.54 Å for dibenzothiophene (middle), and 5.97 Å for 4,6-dimethyldibenzothiophene (bottom).

VII. Adsorption Isotherm Data Tables

(a) MOF-177

	concentration	adsorption amount
	(ppmw S)	*(g S/kg sorbent)*
BT	0.00	0.00
	103.62	0.41
	107.04	0.42
	108.64	0.77
	332.19	1.38
	341.44	1.50
	354.86	1.69
	675.86	3.82
	700.76	3.94
	729.12	4.70
	1259.09	6.79
	1305.45	5.73
	1326.62	8.65
	1851.00	8.79
	1880.07	8.78
	1917.17	8.23
DBT	0.00	0.00
	89.28	0.86
	90.42	0.91
	101.44	0.86
	288.36	2.89
	289.53	3.15
	333.72	2.36
	614.70	6.22
	620.69	6.60
	680.59	6.43
	1172.94	11.45
	1176.13	12.48
	1266.18	11.33
	1739.66	18.34
	1755.58	18.73
	1851.52	15.58
DMDBT	0.00	0.00
	27.64	0.28
	30.77	0.31
	34.65	0.39
	89.51	0.94
	98.68	1.06
	110.66	1.36
	192.69	2.03
	210.40	2.24
	235.32	2.43
	369.32	3.99
	392.31	4.55
	427.85	5.20
	559.17	6.26
	591.85	6.13
	616.78	8.70

(b) MOF-5

	concentration (ppmw S)	adsorption amount (g S/kg sorbent)
BT	0.00	0.00
	76.10	0.55
	79.13	0.72
	94.72	0.76
	249.77	1.81
	260.16	2.36
	305.15	2.56
	533.49	4.07
	552.49	5.34
	642.40	5.65
	1051.06	7.82
	1093.03	9.72
	1187.12	11.90
	1621.40	12.21
	1656.69	15.56
	1780.94	16.39
DBT	0.00	0.00
	28.54	0.97
	41.05	1.32
	60.66	1.94
	102.02	3.25
	142.22	4.40
	209.12	6.20
	242.88	7.44
	335.27	9.74
	474.98	13.10
	603.97	15.09
	782.19	18.45
	1003.53	23.01
	1158.32	23.89
	1360.76	28.25
	1589.36	34.37
DMDBT	0.00	0.00
	5.15	0.27
	9.15	0.51
	14.29	0.90
	19.40	0.92
	31.65	1.74
	38.15	2.26
	49.92	2.97
	72.55	4.06
	93.38	5.24
	117.44	6.53
	174.31	8.69
	200.30	9.97
	262.36	12.77
	334.77	14.88

(c) HKUST-1

	concentration (ppmw S)	adsorption amount (g S/kg sorbent)
BT	0.00	0.00
	37.81	1.02
	42.38	1.21
	52.06	1.57
	133.97	3.38
	151.32	3.95
	192.90	4.76
	319.63	7.48
	356.92	8.65
	463.22	9.49
	775.53	13.83
	842.00	15.50
	972.59	17.36
	1363.25	20.85
	1461.21	21.87
	1489.98	30.63
DBT	0.00	0.00
	10.01	1.46
	13.47	2.02
	18.01	3.59
	42.07	4.97
	49.19	6.95
	81.13	11.61
	100.77	11.81
	138.74	15.93
	252.97	24.15
	323.72	25.68
	491.52	30.85
	784.86	38.15
	892.09	39.86
	1131.23	44.06
	1515.05	43.17
DMDBT	0.00	0.00
	2.34	0.43
	2.61	0.61
	2.76	0.96
	5.54	3.81
	7.38	1.51
	9.02	2.12
	9.25	5.34
	14.31	3.18
	21.76	8.00
	27.08	9.04
	79.73	11.31
	146.37	14.69
	229.45	13.60
	371.66	12.80
	400.70	18.07

(d) UMCM-150

	concentration	adsorption amount
	(ppmw S)	*(g S/kg sorbent)*
BT	0.00	0.00
	22.72	1.81
	27.07	2.25
	43.41	3.18
	99.94	5.74
	121.35	6.91
	165.84	9.80
	275.47	12.20
	317.29	14.58
	415.68	19.65
	709.82	22.75
	811.81	25.16
	954.01	32.45
	1240.08	37.45
	1406.26	37.42
	1591.26	42.48
DBT	0.00	0.00
	6.26	1.41
	8.47	1.99
	11.44	2.85
	19.49	4.20
	28.54	5.81
	31.69	2.18
	33.43	3.31
	39.13	7.56
	39.74	6.20
	55.54	10.41
	58.65	10.86
	59.10	9.24
	84.85	14.81
	117.58	15.71
	132.02	18.25
	170.18	22.26
	194.76	25.19
	241.16	26.64
	285.69	32.10
	442.99	49.68
	523.23	38.77
	608.47	60.84
	932.53	71.09
	978.33	67.84
	1238.44	78.62
	1609.47	83.35
DMDBT	0.00	0.00
	1.44	0.87
	1.95	1.29
	2.73	2.31
	8.03	2.97
	9.39	4.39
	10.95	7.92
	11.86	7.36
	15.73	10.82
	31.23	17.78
	38.00	17.95
	67.68	24.27
	145.01	32.45
	175.26	32.14
	265.39	36.86
	423.79	39.53

(e) MOF-505

	concentration	adsorption amount
	(ppmw S)	*(g S/kg sorbent)*
BT	0.00	0.00
	6.78	1.35
	6.83	3.20
	7.53	1.71
	25.88	5.95
	28.27	4.65
	43.29	10.49
	93.36	10.73
	94.54	13.62
	164.39	22.63
	324.56	23.06
	360.64	28.30
	614.13	39.34
	719.51	41.69
	942.58	43.34
	1284.94	52.95
DBT	0.00	0.00
	0.00	1.22
	0.00	0.84
	0.00	1.67
	1.10	2.42
	1.12	3.74
	1.25	5.83
	1.61	5.45
	1.63	8.50
	2.23	5.43
	2.71	2.64
	4.84	19.11
	7.40	14.06
	7.42	12.08
	28.21	19.96
	160.29	37.13
	258.15	28.47
	535.75	31.18
	885.40	41.85
	915.02	38.57
	1181.06	44.01
	1582.46	47.30
DMDBT	0.00	0.00
	0.62	0.65
	0.83	1.75
	0.85	0.75
	3.85	5.54
	4.41	2.23
	4.60	6.39
	5.40	2.56
	6.51	5.92
	11.58	13.54
	13.57	14.37
	14.34	15.58
	113.90	25.08
	150.20	25.17
	188.46	24.99
	447.52	25.41