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Enabling Cleaner Fuels: Desulfurization by Adsorption to Microporous Coordination Polymers

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Abstract: Microporous coordination polymers (MCPs) are demonstrated to be efficient adsorbents for the removal of the organosulfur compounds dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) from model diesel fuel and diesel fuel. For example, packed bed breakthrough experiments utilizing UMCM-150 find capacities of 25.1 g S/kg MCP for DBT and 24.3 g S/kg MCP for DMDBT from authentic diesel indicating that large amounts of fuel are desulfurized before the breakthrough point. Unlike activated carbons, where selectivity has been a problem, MCPs selectively adsorb the organosulfur compounds over other, similar components of diesel. Complete regeneration using toluene at modest temperatures is achieved. The attainment of high selectivities and capacities, particularly for the adsorption of the refractory compounds that are difficult to remove using current desulfurization techniques, in a reversible sorbent indicates that fuel desulfurization may be an important application for MCPs.

Introduction

As the world waits for viable clean energy solutions for the transportation sector, consumption of petroleum continues to rise dramatically. Pollution from combustion of gasoline and diesel can be broadly categorized into the inevitable (CO_2) and the byproducts arising from impurities in the hydrocarbons and/or undesired combustion byproducts (SO_x, NO_x, particulate matter). Although CO_2 capture from point sources may be feasible, there does not seem to be an actionable plan for capture from mobile sources resulting instead in a focus on reducing the other class of pollutants. The need for “cleaner” transportation fuels is recognized by increasingly stringent U.S. Department of Transportation regulations. In particular, sulfur in fuels poisons the catalysts that are necessary to remove pollutants such as nitrogen oxides (NO_x) and particulate matter from combusted fuels. This is particularly relevant for diesel, as it is responsible for much of the emissions from the transportation sector. Currently, ultralow sulfur diesel (ULSD), with sulfur concentrations of 15 ppmw, is mandated for use in diesel vehicles—a significant reduction from 500 ppmw S low sulfur diesel that was available until 2006 Department of Transportation regulations.[1] With ULSD, diesel engines can now be designed with advanced emissions control devices to more effectively remove the pollutants before they enter the atmosphere. According to the EPA, the new fuel standards for diesel will reduce NO_x emissions by 2.6 million tons a year and particulate matter by 110 000 tons a year.[2]

The move to ULSD has proven challenging for refineries because large organosulfur compounds such as dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) are difficult to remove during the fuel refining process by traditional hydrodesulfurization techniques because of poor catalyst efficiency.[3] As a consequence, these refractory organosulfur compounds make up a higher proportion of refined diesel because less hindered thiophenes and benzothiophenes are removed effectively by hydrodesulfurization leading to considerable challenge in further reducing sulfur concentrations to the level needed to, for example, enable on-board reforming to power hydrogen fuel cell vehicles. One alternative strategy for removal of these compounds is to adsorb them to solid phases such as zeolites[4] or activated carbons;[5] however, the capacities, adsorption kinetics, and selectivities of these materials for the organosulfur compounds have yet to make them feasible for significant use in industry.

We have previously reported that a new class of sorbents, microporous coordination polymers (MCPs), are well suited for

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the adsorption of large organosulfur compounds from model fuel solutions.[6] MCPs demonstrated extremely high capacities, exceeding those of their zeolite counterparts, in equilibrium adsorption experiments. The surface areas and pore sizes of MCPs make large molecule adsorption feasible, but selectivity has not been addressed and its study is required to determine if a sorbent is promising for fuel desulfurization. In addition, packed bed flow-through experiments are crucial to characterize adsorption behavior toward organosulfur compounds in an industrially relevant configuration. Unlike gas phase adsorption, liquid phase adsorption in MCPs is only beginning to be explored, with few examples of liquid breakthrough in MCPs being reported.[7−9] Certainly no liquids with the complex combination of components encountered in diesel have been investigated. In addition to organosulfur compounds, fuels contain other aromatic compounds such as benzene, alkyl benzenes (e.g., toluene, xylenes), and polycyclic aromatic compounds such as naphthalenes. In total, the aromatic compounds make up ~17% of the diesel fuel, with variation depending on the crude source of the diesel.[10] These aromatic compounds compete for adsorption sites typically leading to a decrease in the sulfur adsorption capacity of the material. This has been the case for both zeolites and activated carbons; for example, Na(Y) zeolite has been shown to favorably adsorb toluene over thiophene.[11] Furthermore, when increasing amounts of benzene are present in solution, a dramatic decrease in the DBT adsorption capacity of activated carbon has been observed.[5c] MCPs may have an advantage in this regard over other adsorbents because of the ability to tailor the shape and electronics of the structure by changing the metal cluster and the organic linker to tune selectivities for the organosulfur compounds.

In this paper, packed bed breakthrough curves for the MCPs MOF-177,[12] MOF-5,[13] HKUST-1,[14] MOF-505,[15] and UMCM-150[16] are reported for isooctane solutions of DBT and DMDBT, the two organosulfur compounds most difficult to remove using current catalytic techniques. To determine the effect of aromatic compounds on adsorption capacity in MCPs, we tested solutions of DBT and DMDBT in isooctane/toluene mixtures in both equilibrium and breakthrough experiments. To fully understand the consequence of competing aromatic molecules in the complex milieu of fuels, we also tested DBT and DMDBT in authentic diesel in breakthrough experiments. Finally, regenerability was tested under several conditions.

Experimental Section

Materials. MOF-177,[17] MOF-5,[17] HKUST-1,[18] MOF-505,[15,19] and UMCM-150[16] were synthesized and activated according to published procedures. Surface areas and pore volumes of the studied MCPs have been previously tabulated.[6] Na(Y) zeolite (powder) was obtained from Strem Chemicals and activated carbon (50−200 mesh) was obtained from Fisher. Both were used as received. Dibenzothiophene (99%, Acros), 4,6-dimethyldibenzothiophene (97%, Aldrich), isooctane (HPLC grade, Fisher), and toluene (ACS reagent grade, Fisher) were used as received. Ultralow sulfur diesel was obtained from Citgo in Ann Arbor, MI and was found to contain 32 wt % aromatic compounds using ^{1}H NMR methods[20] and 21.5 ppmw S (13.2 ppmw S dibenzothiophene and 8.3 ppmw S 4,6-dimethyldibenzothiophene) using GC-FPD. Ultralow sulfur diesel was spiked to 300 ppmw S with DBT and DMDBT to obtain the solutions used in the experiments.

Methods. Equilibrium adsorption experiments were performed as previously described.[6]

Breakthrough curves were measured by packing a stainless steel column (30 mm L × 2.1 mm ID) with the material to be studied. All packed bed experiments were performed at room temperature. The packed bed was equilibrated with isooctane at a flow rate of 0.5 mL/min using a Hitachi L-7100 HPLC pump. A 300 ppmw S solution of the organosulfur compound was delivered at a flow rate of 0.5 mL/min. The concentration of organosulfur compound in the effluent was measured using either a single wavelength UV−vis detector (Waters 486) at 330 nm for dibenzothiophene or 333 nm for 4,6-dimethyldibenzothiophene for the isooctane and isooctane/toluene solutions or a Shimadzu GC-2010 equipped with a capillary column (L = 15 m, ID = 0.25 mm) outfitted with both a flame ionization detector (FID) and a flame photometric detector (FPD) for the diesel solutions. Sulfur concentrations were determined using the FPD detector and were calibrated using solutions of known sulfur concentration. Breakthrough curves were corrected for dead volume. With the UV−vis detector, the organosulfur compound concentration exhibited non-Beer's Law behavior and correction factors were applied for each solution.

Regeneration of MOF-5 packed bed was performed by flowing room-temperature isooctane through the packed bed at a flow rate of 0.5 mL/min until no more organosulfur compound was eluting from the bed (as evidenced by UV−vis spectroscopy).

Regeneration of UMCM-150 packed bed was performed by flowing dry toluene through a 90 °C packed bed at a flow rate of 0.5 mL/min. The packed bed was heated using an Analytical TCM 2000 column heater.

Results and Discussion

To benchmark the capacity of different MCPs for organosulfur compounds in the absence of competing aromatic species, packed bed breakthrough experiments were conducted with solutions of 300 ppmw S DBT in isooctane and 300 ppmw S DMDBT in isooctane. Figure 1 shows the resulting breakthrough curves for the five MCPs tested. These MCPs have the ability to desulfurize significant amounts of solution before the breakthrough point (defined as 1 ppmw S) with, for example, DBT breakthrough at 28, 30, and 131 mL/g MCP for MOF-

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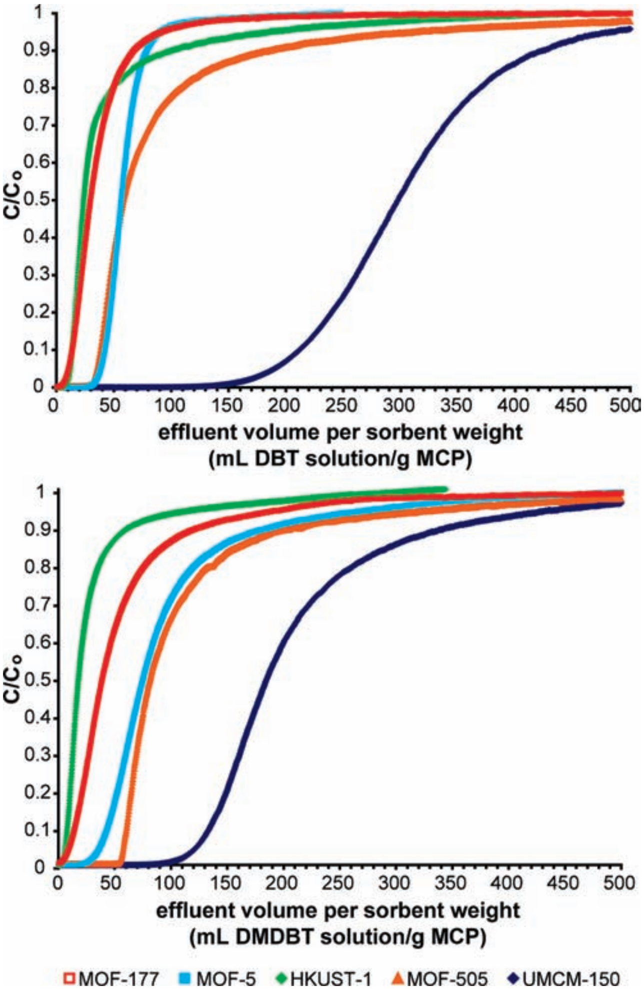

Figure 1. Breakthrough curves for 300 ppmw S dibenzothiophene in isooctane (top) and 300 ppmw S 4,6-dimethyldibenzothiophene in isooctane (bottom) for MOF-177, MOF-5, HKUST-1, MOF-505, and UMCM-150.

505, MOF-5, and UMCM-150 and DMDBT breakthrough at 53, 23, and 92 mL/g MCP for MOF-505, MOF-5, and UMCM-150. These correspond to capacities, at breakthrough, of 5.8, 6.2, and 27.2 g S/kg MCP for DBT and 11.0, 4.8, and 19.1 g S/kg MCP for DMDBT (capacities determined by integrating above the breakthrough curve). Total capacities for these three MCPs were 20.5, 12.7, and 66.3 g S/kg MCP, respectively, for DBT and 23.8, 20.4, and 44.4 g S/kg MCP, respectively, for DMDBT; these numbers are more diagnostic for inherent materials properties than the breakthrough point because they are not subject to bed packing effects. For both organosulfur compounds, based on the breakthrough curves, UMCM-150 has the best desulfurization performance and MOF-177, the highest surface area MCP studied, is among the worst. It has been previously determined that the physicochemical parameters such as surface area and pore volume do not correlate with organosulfur compound adsorption capacity, but rather, adsorption capacity is increased with a pore size and shape that maximizes the interaction between the MCP and the organosulfur compound.[6] As a comparison, Na(Y) zeolite was also tested using the same organosulfur compound solutions. Both organosulfur compounds break through immediately for this zeolite, indicating that MCPs are favorable over this prototypical zeolite for the adsorption of DBT and DMDBT.

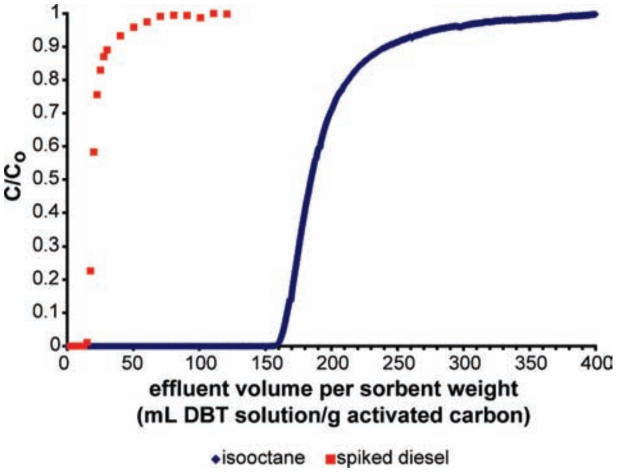

Figure 2. Breakthrough curves for 300 ppmw S dibenzothiophene in isooctane and 300 ppmw S dibenzothiophene in ULSD for activated carbon.

Current industrial desulfurization techniques such as hydrodesulfurization suffer in that the larger organosulfur compounds are more difficult to remove. On the basis of the breakthrough curves, MOF-505 is capable of desulfurizing more DMDBT solution before breakthrough than DBT solution, indicating that the bigger the organosulfur compound, the more successful it is at adsorbing it from solution. There are limited examples of MCP liquid phase breakthrough curves reported in the literature,[7−9] and none for the removal of compounds as large as these organosulfur compounds, but the data presented here for the large organosulfur compounds from the liquid phase signify that MCPs are quite capable of high performance under flow-through packed bed conditions. Significantly, the liquid hourly space velocities (defined as the relationship between flow rate and bed volume) achievable with MCPs are very high because of favorable adsorption kinetics and offer conditions ideal for large scale production processes. Space velocities for MCPs used in this work are 289 h^{-1} in comparison to typical values for zeolites of between 1 and 10 h^{-1},[4d,21] which are necessary because of diffusion limitations of the organosulfur compounds in the zeolites.[21] This result can be understood on the basis of the much more open pore structure in MCPs offering rapid guest diffusion.[22]

Removing organosulfur compounds from model hydrocarbon solutions is trivial in comparison to removing the organosulfur compounds from much more complicated fuels because of selectivity issues. One material that illustrates this selectivity problem is activated carbon (Figure 2). Activated carbon breakthrough curves were measured for both the model solution (300 ppmw S DBT in isooctane) and for spiked ULSD (300 ppmw S DBT in ULSD). From the breakthrough curves, it is evident that although a large capacity is seen in the aliphatic model solution, rivaling the capacities observed for MCPs, activated carbon displays virtually no selectivity for the organosulfur compound in the presence of the other components of the spiked diesel with a decrease in breakthrough point from 159 mL/g activated carbon for the isooctane solution to 13 mL/g activated carbon for the spiked diesel. This is a decrease in breakthrough capacity from 33.0 to 2.7 g S/kg activated carbon and a decrease in total capacity from 41.3 to 5.1 g S/kg activated

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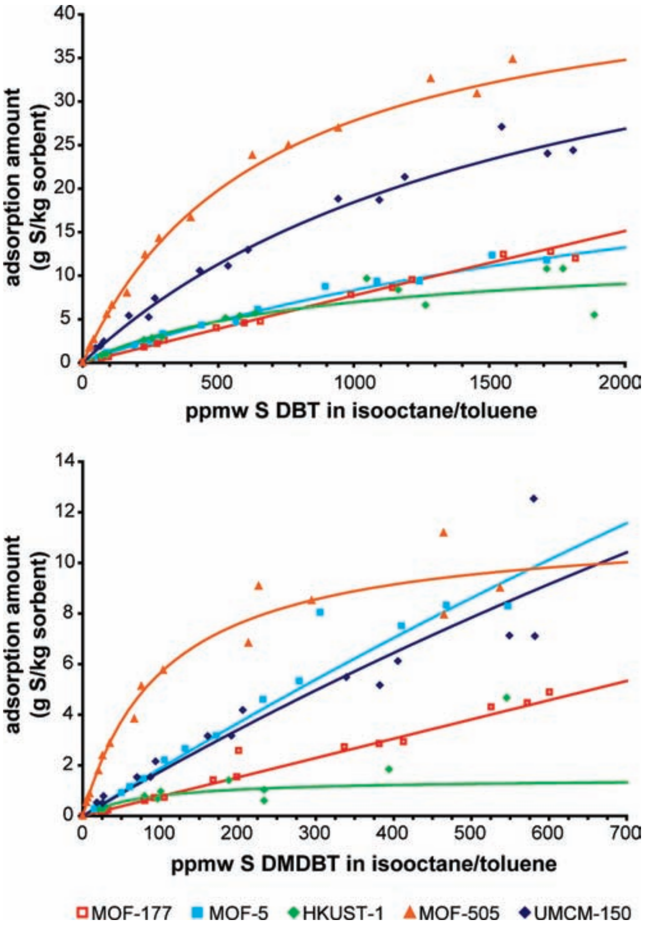

Figure 3. Adsorption isotherms for dibenzothiophene in 85:15 (v:v) isooctane:toluene (top) and 4,6-dimethyldibenzothiophene in 85:15 (v:v) isooctane:toluene (bottom) for MOF-177, MOF-5, HKUST-1, MOF-505, and UMCM-150. The curves represent a fit to the Langmuir equation and are intended as guides to the eye.

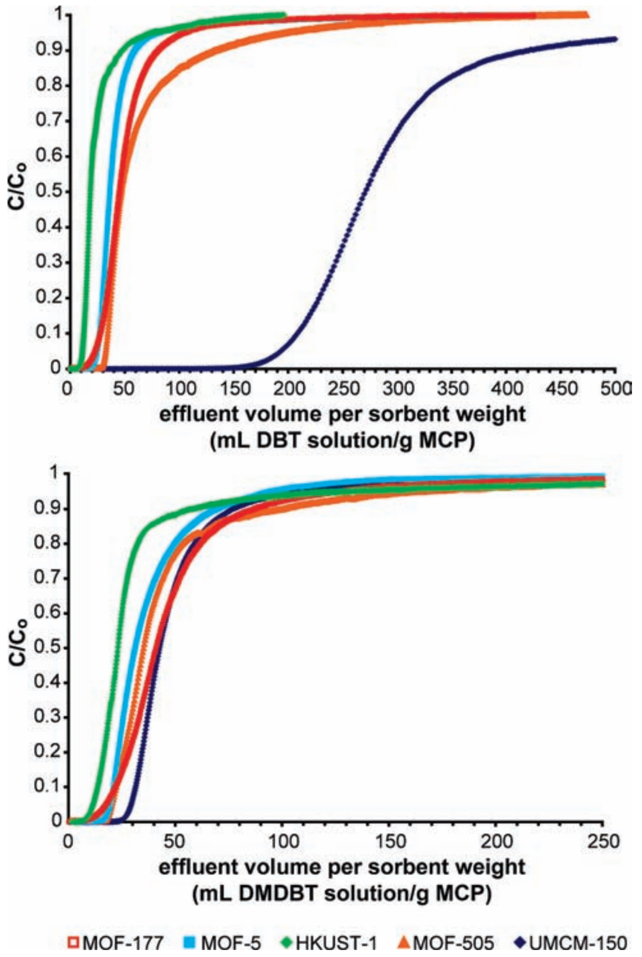

Figure 4. Breakthrough curves for 300 ppmw S dibenzothiophene in 85:15 (v:v) isooctane:toluene (top) and 300 ppmw S 4,6-dimethyldibenzothiophene in 85:15 (v:v) isooctane:toluene (bottom) for MOF-177, MOF-5, HKUST-1, MOF-505, and UMCM-150.

carbon. The selectivity of activated carbon for the organosulfur compounds is very low in the presence of the other aromatic compounds in diesel.

To conduct an initial assessment of the effect of competition with aromatic molecules on the adsorption of the organosulfur compounds using MCPs, toluene was chosen as a representative competitive binder. Equilibrium adsorption isotherms were plotted for 85:15 (v:v) isooctane:toluene DBT and DMDBT solutions to 2000 ppmw S for DBT and to 700 ppmw S for DMDBT (due to low solubility) and are shown in Figure 3. In the equilibrium adsorption experiments, with the introduction of toluene a decrease in capacity is observed for all cases in comparison to previously published isooctane adsorption isotherms.[6] However, this decrease, especially at the low concentrations that are most applicable to industry, is minimal and large capacities are still observed, particularly for MOF-505 which has DBT and DMDBT capacities of 14 and 9 g S/kg MCP at 300 ppmw S, representing uptakes of 18 and 6.5 wt % for DBT and DMDBT, respectively. Additionally, the capacities at 300 ppmw S of MOF-177 and MOF-5 exhibit only a small decrease from the capacities in pure isooctane, demonstrating that the capacities of the two materials studied with the largest pore volumes and surface areas are less affected by the addition of toluene to the solution. For both DBT and DMDBT, Na(Y) zeolite removed <1 g S/kg zeolite up to 1500 and 700 ppmw S DBT and DMDBT, respectively. Unlike the MCPs, Na(Y) offers little selectivity for the organosulfur compounds over the toluene in the solution.

To assess the effect of aromatic content on organosulfur compound adsorption in packed bed experiments, breakthrough curves were plotted for 300 ppmw S DBT and DMDBT 85:15 (v:v) isooctane:toluene solutions for five MCPs (Figure 4). DBT breakthrough occurs at 18, 29, and 151 mL/g MCP for MOF-5, MOF-505, and UMCM-150, which correspond to capacities at breakthrough of 3.7, 6.0, and 31.3 g S/kg MCP and overall capacities of 9.1, 14.9, and 66.6 g S/kg MCP. In comparison to the isooctane breakthrough curves shown earlier for DBT, a decrease in the breakthrough point is seen only for MOF-5, which now has a breakthrough point of 18 mL/g MCP compared to 30 mL/g MCP in the case without toluene. For the other MCPs studied, there is no decrease seen in the amount of solution that is desulfurized before the breakthrough point and overall capacities remain similar from isooctane to isooctane/toluene. The toluene has more of an effect on the DMDBT breakthrough curves, such that DMDBT break through occurs at 15, 17, and 24 mL/g MCP for MOF-5, MOF-505, and UMCM-150, respectively, corresponding to breakthrough capacities of 3.1, 3.5, and 5.0 g S/kg MCP, which is an earlier breakthrough point for these three materials than for the isooctane solution. For the other two materials, a small increase is observed in the amount of solution that can be desulfurized before break through. Even with 15% toluene in the solution,

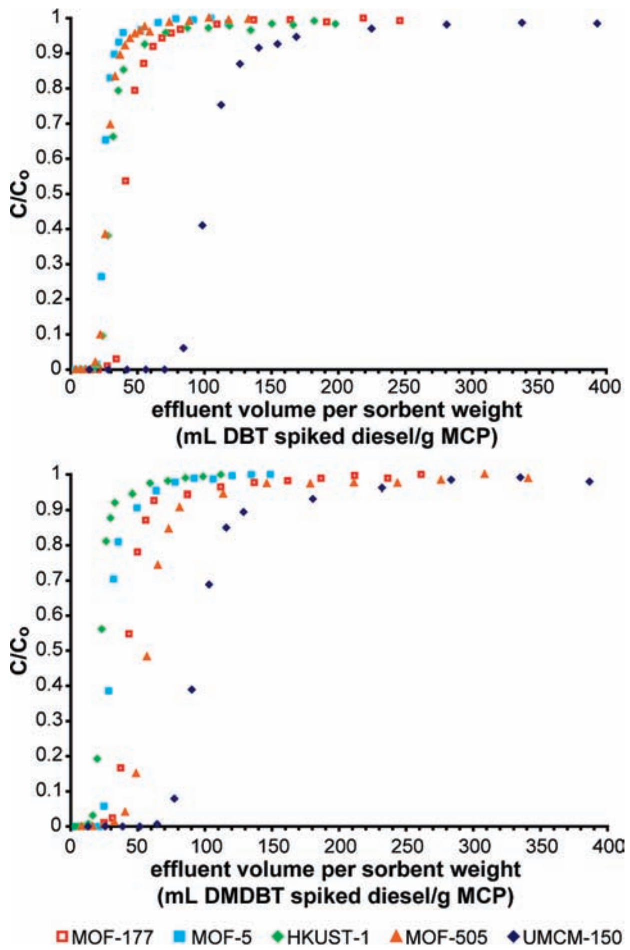

Figure 5. Breakthrough curves for 300 ppmw S dibenzothiophene in ULSD (top) and 300 ppmw S 4,6-dimethyldibenzothiophene in ULSD (bottom) for MOF-177, MOF-5, HKUST-1, MOF-505, and UMCM-150.

UMCM-150 continues to outperform the other MCPs studied at breakthrough and still desulfurizes 24 mL/g MCP before sulfur breakthrough occurs. Total capacities for these three materials reach 8.0, 10.7, and 10.4 g S/kg MCP. For comparison, Na(Y) zeolite was tested using the same organosulfur compound solutions. For both DBT and DMDBT, a breakthrough point of 6 mL/g MCP was observed. This is lower than the breakthrough point observed for any of the MCPs.

Encouraged by the high capacity and selectivity for the organosulfur compounds over toluene, breakthrough experiments were conducted for authentic diesel solutions. ULSD was spiked to 300 ppmw S with DBT and, separately, to 300 ppmw S with DMDBT. Figure 5 shows the breakthrough curves for the spiked diesel solutions. The curves clearly illustrate that even in the presence of the complex mixture of aromatic compounds found in diesel, MCPs are selective for the organosulfur compounds and are able to desulfurize significant amounts of fuel before the breakthrough point. For example, UMCM-150 has a breakthrough point of 70 mL/g MCP (breakthrough capacity of 14.5 g S/kg MCP and total capacity of 25.1 g S/kg MCP) for DBT spiked diesel, making it the best MCP for the flow-through packed bed removal of DBT from diesel. UMCM-150 also desulfurizes the most DMDBT spiked diesel before the breakthrough point which occurs at 52 mL/g MCP (breakthrough capacity of 10.8 g S/kg MCP and total capacity of 24.3 g S/kg MCP). Additionally, both MOF-5 and MOF-505 have breakthrough points that occur later for DMDBT than for DBT.

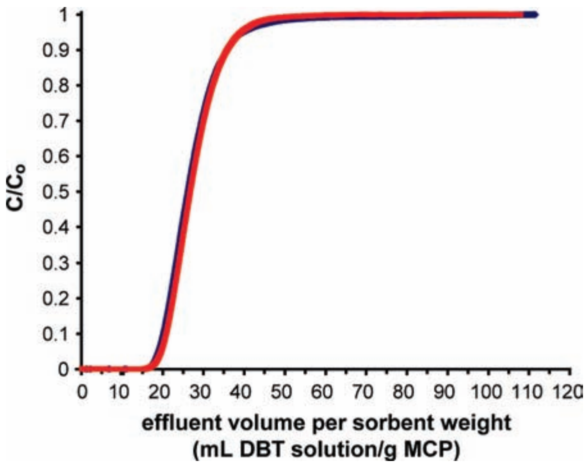

Figure 6. Breakthrough curves before and after regeneration of MOF-5 with dibenzothiophene in isooctane. Run 1 (blue) is the initial breakthrough curve. Run 2 (red) is after regeneration with room-temperature isooctane.

Again, the ability to desulfurize more fuel with the larger, more sterically hindered organosulfur compound is the opposite trend observed for state-of-the-art desulfurization techniques, highlighting the advantages of adsorption to MCPs over hydrodesulfurization and adsorption to zeolites and activated carbon for the desulfurization of fuels. Comparing the MCP/spiked diesel breakthrough curves with the breakthrough curves for activated carbon (Figure 2), indicates that MCPs substantially outperform activated carbon. For activated carbon, a breakthrough point of 13 mL/g MCP is observed for the spiked diesel, which is earlier than for any of the MCPs tested. Additionally, the overall capacity for activated carbon (5.1 g S/kg activated carbon) is lower than the overall capacity for any of the MCPs studied.

It is extremely important that in order for an adsorption process to be cost-effective, the packed bed can be regenerated for multiple uses. Packed beds of zeolites and activated carbons have been regenerated with varying amounts of success using combinations of heat and either gas or solvent.[5b,23] To assess the ultimate utility of MCP packed beds for the desulfurization of fuels, we carried out regeneration. A packed bed of MOF-5 was fully regenerated (Figure 6) by flowing room-temperature isooctane through the packed bed. A breakthrough curve was plotted for 300 ppmw S DBT in isooctane, regeneration was performed and the breakthrough experiment was repeated. As can be seen in the figure, there is no difference between the initial and second breakthrough curves indicating that MOF-5 is fully regenerable under these conditions. The regeneration of a packed bed of a higher affinity material, UMCM-150, was also performed using dry toluene at 90 °C (Figure 7). Under these conditions, the UMCM-150 packed bed is completely regenerated with a total capacity of 72.8 g S/kg MCP for run 1 and a total capacity of 72.4 g S/kg MCP for run 2. Further proof that the organosulfur compound was completely desorbed was provided by elemental analysis, which showed that, within error,

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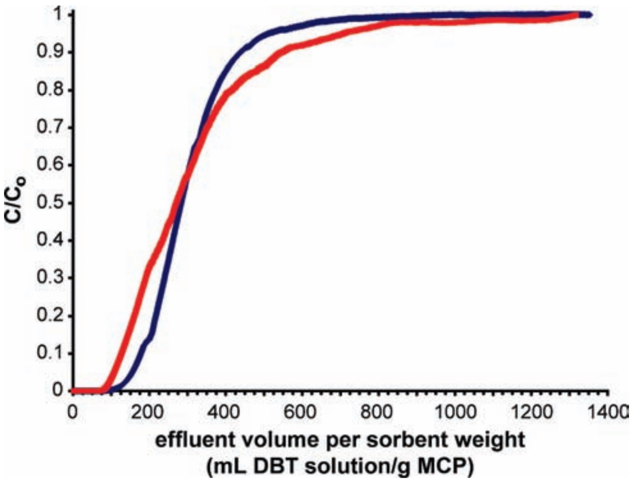

Figure 7. Breakthrough curves before and after regeneration of UMCM-150 with dibenzothiophene in isooctane. Run 1 (blue) is the initial breakthrough curve. Run 2 (red) is after regeneration with dry toluene at 90 °C.

no sulfur was present in the regenerated sample. This indicates that even the higher affinity material can be fully regenerated using only modest temperatures.

Conclusions

In conclusion, a uniquely complex case of liquid phase purification using MCPs has been successfully executed. The data presented demonstrate that MCPs are efficient adsorbents for fuel desulfurization. Exceptional amounts of solution are desulfurized before the breakthrough point, particularly for UMCM-150, demonstrating the utility and practicality of MCPs for this important environmental application. MCPs exhibit a selectivity for the organosulfur compounds that is not seen in other materials, such as zeolites and activated carbon, that are also used for desulfurization. In addition, regeneration of MCP packed beds has been shown to be feasible using a combination of solvent and heat. Adsorption to MCPs is a practical way to effectively eliminate the sulfur in transportation fuels to meet the stringent current environmental standards, particularly for diesel, as well as a complementary technique to hydrodesulfurization to reduce sulfur levels in fuels to the <0.1 ppmw S necessary for fuel cell applications. Future work will focus on determination of the nature of the interaction between the organosulfur compound and the MCP framework. This information will then be used to design new MCPs with higher capacities and selectivities for organosulfur compound adsorption.

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