Metal-Organic Frameworks for Highly Efficient Adsorption of Dibenzothiophene from Liquid Fuels

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By taking desulfurization of liquid fuels as a demonstrative example, a bottom-up selection was performed to find the metal-organic frameworks (MOF)-type adsorbents with highly efficient adsorption performance of large molecules. Through carefully analyzing the adsorption mechanism for typical S-heterocyclic compounds like dibenzothiophene (DBT), PCN-10 was selected in consideration of the simultaneous inclusion of several kinds of interactions in the framework. Experimental results demonstrate that this MOF exhibits extraordinary high DBT adsorption capacity (75.24 mg S g\(^{-1}\)), showing record uptake among all the reported porous materials for the removal of thiophenic sulfur from fuels (below 1000 ppmwS), to the best of our knowledge. Moreover, the removal rate for the low sulfur concentration (50 ppmwS) can reach beyond 99%. This strategy can be conveniently extended to the screening and design of MOFs for the efficient removal of other important large guest molecules. © 2016 American Institute of Chemical Engineers AIChE J, 00: 000–000, 2016

Keywords: adsorption, deep removal, desulfurization, metal-organic frameworks, separation

Introduction

Desulfurization of liquid fuels is vital important for the stringent demand to reduce the sulfur content of liquid fuels aiming to lowering the harmful exhaust emissions from the engines and improving the quality of environment.\(^1,2\) To overcome the limitations of hydrodesulfurization (HDS) used in industry like harsh operating conditions, various alternative processes have been studied where adsorptive desulfurization (ADS) is considered to be one of the most promising methods owing to the low-energy consumption.\(^3,4\) Up to now, many kinds of materials have been reported for ADS, including activated carbons,\(^5–11\) zeolites,\(^12–14\) mesoporous materials,\(^15–17\) and mixed metal oxides.\(^18,19\) The efficient removal of thiophenic sulfur content, however, still remains to be a great challenge and the adsorption capacity is not good enough to meet the practical requirements.

As a new class of inorganic-organic porous materials, metal-organic frameworks (MOFs) have received considerable interests during the past decades, thanks to their adjustable pore structures and chemical functionalities at a broad range. MOFs have exhibited excellent performances in adsorption and separation for small molecules, especially for gas molecules.\(^20\) Recently, it is observed that several MOFs can also efficiently adsorb large adsorbates,\(^3,21–28\) including S-compounds in liquid fuels.\(^3,26–28\) Though there are exciting results for the removal of these large adsorbates, the majority of the current works are mainly focused on enhancing the uptakes using try-and-error method. Considering the extremely large number of existed MOFs, it is time-consuming and inefficient to find the promising candidates for a given adsorption target. Moreover, unlike small gas molecules, the simulations of large molecules adsorbed in MOFs are generally difficult and unreliable due to the limitation of accurate force field.\(^29\) Thus, MOFs have not been fully utilized by taking advantage of their unique properties as novel adsorbents in such applications so far.

In this work, we used a bottom-up method to find the most promising MOF for highly efficient ADS of liquid fuels. First, the characteristics of guest molecule are fully analyzed as well as the reported possible adsorption mechanisms. Then, various substructures of MOFs are extracted which have the potentials to endow such mechanisms, and most of MOFs can be ruled out accordingly. Finally, the most promising candidate is selected containing these substructures as much as possible, followed by the experimental confirmation. Herein, dibenzothiophene (DBT) was selected as the demonstrative S-compound which is always found in diesel fuels and fluid catalytic cracking (FCC) gasoline. From the reported works, it is suggested that coordinatively unsaturated site (CUS), π-complexation and appropriate pore size/shape may be the main mechanisms for adsorption of S-compounds in liquid fuels. For example, Peralta et al. believed that MOFs with CUS (such as Cu-BTC and CPO-27-Ni), contrary to zeolites, exhibit stronger selective affinity for thiophene than that for toluene.\(^25\) Khan et al. observed that Cu\(^{2+}\)-loaded MIL-100-Fe is an efficient adsorbent for benzothiophene (BT) adsorption and further investigated the beneficial effect of π-complex formation.\(^30\) Cychosz et al. studied several MOFs with different pore sizes and shapes for the adsorption of dibenzothiophene.
Figure 1. The structural characteristics of PCN-10.

(DBT) and 4,6-dimethyl dibenzo thiophene (4,6-DMDBT) in model oils and found that MOFs are superior to other porous adsorbents like zeolites or activated carbon, due to the high selectivities and capacities of these organic sulfur compounds. On the basis of these studies, it is supposed that the adsorption capacity may be further enhanced if the various kinds of interactions can be included into the framework simultaneously. Bearing these in mind, by combining the unrivalled designable characteristics of MOFs, we selected PCN-10 as a candidate in this work. PCN-10 is constructed by paddlewheel binuclear copper(II) cluster and 3,3',5,5'-azobenzene tetracarboxylic acid (H$_4$abtc) ligand, as shown in Figure 1. Two copper atoms connect 4 bridging carboxylates to form a paddlewheel secondary building unit (SBU) and every 12 ligands are linked by 6 paddlewheel SBUs to form an octahedral cage with 8 triangular openings of 8.13 × 9.26 Å. By analyzing the structure of DBT, we know that the S atom of DBT is able to be strongly interacted with CUS like Cu$_2$$. In addition, DBT has a conjugate plane structure. Both open metal sites in SBU and two benzene rings connected by N=N bond in ligand as well as the pore size of PCN-10 may endow excellent adsorption performance for DBT. Fortunately, the adsorption experiments confirmed our conjecture and the DBT uptake on PCN-10 could reach 75.24 mg S g$^{-1}$ for 1000 ppmwS model oil, which is much higher than the values of all the other reported materials up to now, to the best of our knowledge. In addition, the removal rate can reach 99.03% for the low sulfur concentrations.

**Experiment**

**Materials**

All chemicals were purchased from different companies: toluene (AR grade), isooctane (>97%, AR grade) from Tianjin Guangfu Technology Development; 5-nitroisophthalic acid (99%, AR grade), glucose (99%, AR grade), and 1,3,5-benzenetricarboxylic acid (H$_3$BTC, 98%) from Beijing HWRK Chem; 4,6-dimethyl dibenzo thiophene (4,6-DMDBT, 98%), sodium hydroxide (NaOH, AR grade), and dimethylacetamide (DMA, AR grade) from Sinopharm Chemical Reagent; benzo thiophene (BT, 99%), dibenzothiophene (DBT, 99%), and cupric nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O, AR grade) from Xilong Chemical. All reagents were used as received without further purification.

**Synthesis of 3,3',5,5'-azobenzene tetracarboxylic acid (H$_4$abtc)**

The synthesis procedure was obtained from literature. Fifty grams of NaOH and 250 mL of distilled water were placed into a 1 L 3-neck round bottom flask, and then cooled down. Nineteen grams of 5-nitroisophthalic acid was added to the solution and stirred at 333 K continually. This first formed a pink slurry that became yellow after 1 h. Meanwhile 100 g of glucose were dissolved into 150 mL of distilled water at 333 K. The glucose solution was added slowly to the slurry, which became immediately dark brown. This was left to cool down for 15 min, and air was bubbled into it for 24 h under stirring at room temperature. The reaction mixture was cooled in an ice-bath and the sodium salt of H$_4$abtc was recovered by centrifugation. The solid was then dissolved in 200 mL of distilled water, and then this solution was acidified to pH = 1 using 37% HCl solution. This yielded a bright orange precipitate. The product was recovered by filtration, washed with distilled water and dried at 393 K.

**Synthesis of PCN-10**

PCN-10 was prepared according to the procedure developed by Zhou group. The synthesized H$_4$abtc (2.0 g, 5.59 × 10$^{-3}$ mol) was dissolved in 600 mL DMA with 1-L round bottom flask and the resulting suspension was sonicated for 30 min. Cu(NO$_3$)$_2$·3H$_2$O (5.0 g, 2.07 × 10$^{-2}$ mol) was added to the solution, and then sealed at 353 K for 2 d. After being cooled down to room temperature, the resulting green powders were recovered by centrifugation and washed with DMA. The powders were extracted with methanol overnight using a Soxhlet extractor to remove solvated DMA, and then was centrifuged and soaked in dichloromethane for 3 d. Finally, the sample was kept under a dynamic vacuum at 393 K for 6 h to obtain dehydrated PCN-10. The dehydrated PCN-10 was exposed to air for a few minutes, which can obtain hydrated PCN-10.

**Characterization**

The powder X-ray diffraction pattern (PXRD) of the samples were recorded on a Rigaku D/MAX 2500 VBZ + PC diffractometer with Cu Kα radiation under 40 kV and 200 mA in the scan range of 2θ from 3° to 50° with a step size of 0.02°. The morphologies of PCN-10 was observed by Scanning electron microscopy (SEM BCPAS4800) under 5.0 kV. The hydrated PCN-10 (60 mg) was previously degassed under vacuum at 298 K for about 24 h and the dehydrated PCN-10 was degassed under vacuum at 393 K for about 24 h. Then, the Brunauer–Emmett–Teller (BET) surface areas and the pore size distributions of the materials are determined from the nitrogen adsorption–desorption isotherms recorded at 77 K using an Autosorb-iQ-MP (Quantachrome Instruments) surface area analyzer. The Fourier transform infrared spectra (FT-IR) of PCN-10 were measured in the range 4000–500 cm$^{-1}$ by a Thermo Fisher Nicolet 6700 instrument. Thermal stability was performed with differential Thermal Analyzer 60A and the sample was heated at the rate of 10 K min$^{-1}$ to 773 K under N$_2$ flow.

**Adsorption experiment**

The BT, DBT, and 4,6-DMDBT were dissolved in isooctane as model oil, with different initial S-concentrations (50 ppmwS, 200 ppmwS, 500 ppmwS, 800 ppmwS, 1000 ppmwS, and 1600 ppmwS). All these solutions were used directly in the following adsorption experiments. Prior to adsorption experiments, dehydrated PCN-10 was dried under vacuum at 393 K for 10 h to further remove the guest molecules from CUS.

The model oil (5.0 g or 10 g) was mixed with the adsorbent (0.02 g) in the glass reactor under stirring. The liquid phase was then separated from the adsorbs by filtration, and the S-concentration of the treated model oil was determined by a Gas Chromatograph Mass Spectrometer (GC-MS), which was equipped with a capillary column (TR-WAXMS 30 m ×
0.25 mm × 0.25 μm). The adsorption capacity and desulfurization rate were calculated by the following formula:

\[ q_i = \frac{m}{M} \times (C_0 - C_i) \times 10^{-3} \]  

(1)

\[ w = \frac{C_0 - C_i}{C_0} \times 100\% \]  

(2)

where \( q_i \) is the adsorption capacity of sulfur adsorbed on the adsorbent (mg S g\(^{-1}\)), \( m \) is the mass of model oil (g), \( M \) is the mass of the MOF (g), \( C_0 \) and \( C_i \) are the initial and final S-concentrations in the model oil (μg g\(^{-1}\)), respectively, \( C_e \) is the equilibrium S-concentrations in the model oil (μg g\(^{-1}\)), and \( w \) is the removal rate.

**Regeneration experiment**

After the adsorption in model oils, the sample was washed with methanol and dichloromethane, and then dried in vacuum at 393 K for 6 h. The regenerated sample was used as the fresh adsorbent for the adsorption of DBT.

**Results and Discussion**

**Characterization of PCN-10**

The powder XRD pattern of PCN-10 is exhibited in Figure 2a, which is basically consistent with the simulation and also in accordance with the reported value. The adsorption capacity and desulfurization rate were calculated by the following formula:

The FT-IR spectrum of PCN-10 is plotted in the 450–4000 wavenumber region as shown in Supporting Information Figure S2. The characteristic peaks of PCN-10 are 1613 cm\(^{-1}\) for N\(\equiv\)N group and 1561 cm\(^{-1}\) for benzene group. BET surface area and pore size distributions of PCN-10 is determined from the nitrogen adsorption–desorption isotherms recorded at 77 K (Supporting Information Figure S3). The pore sizes for dehydrated PCN-10 and hydrated PCN-10 are 12.7 Å and 10.8 Å. As reported in Table 1, the dehydrated PCN-10 is characterized by BET surface area of 1987 m\(^2\) g\(^{-1}\), which is in the range of the reported values in literature (1404–2189 m\(^2\) g\(^{-1}\)).

**Adsorption of DBT**

For the commercial liquid fuels like FCC gasoline, the sulfur concentration of thiophenic feed is generally below about 1000 ppm S. Therefore, we first measured the DBT adsorption behavior on PCN-10 for 1000 ppm S model oil at 303 K as a function of time. Figure 3 shows that the DBT adsorption capacity increases rapidly in the initial 5 min to reach 54.12 mg S g\(^{-1}\). With the increase of contact time, the adsorption rate becomes more and more slow. When the adsorption time is prolonged to 480 min, the adsorption almost reaches saturation and the adsorption amount is up to 75.24 mg S g\(^{-1}\). Supporting Information Figures S4 and S5 show that the adsorption fits better to the pseudosecond-order model than pseudofirst-order kinetic model. As shown in
Supporting Information Table S1, the correlation coefficient for the pseudosecond-order model is 0.999, and the adsorption capacity obtained by the pseudosecond-order model is very close to the experimental value. Element analysis was performed for PCN-10 after adsorption. As shown in Supporting Information Table S2, the content of S is 4.37%, which can further confirm the existence of S-compound in the adsorbent. Considering that arenes usually exist in liquid fuels, the control experiment was performed to illustrate the influence of arenes on the adsorption of DBT on PCN-10 by taking 1000 ppmwS model oil at 303 K as an example. The mixture of isooctane/toluene (90%/10%) was used as model oil. The result shows that in presence of 10% toluene, the adsorption capacity of PCN-10 decreased to 62.33 mg S g⁻¹ by 17.16%. The decrease is mainly due to the competitive adsorption of DBT and toluene. The adsorption isotherm of DBT on PCN-10 is exhibited in Figure 4. It can be seen that with the increase of initial S-concentration, the adsorption capacity is increased and almost reaches the maximum adsorption amount (77.51 mg S g⁻¹) at 1600 ppmwS. As shown in Figure 5, the adsorption capacity of PCN-10 is obviously larger than those in several typical porous materials like Y-zeolite, activated carbon, BN, Cu-BTC, and UCMC-150 at different initial S-concentrations, especially for below 200 ppmwS. That is, PCN-10 actually exhibits excellent performance in adsorption of DBT as we expected. The comprehensive comparison can be found in Table 2. It can be seen that the adsorption capacity in PCN-10 is distinctly larger than all the reported experimental values in other materials, to the best of our knowledge. Motivated by these results, we also measured the BT and 4.6-DMDBT adsorption behavior on PCN-10 at different initial S-concentrations. As can be seen from Supporting Information Figure S6, PCN-10 has adsorption capacities of 61.63 mg S g⁻¹ for BT and 34.78 mg S g⁻¹ for 4.6-DMDBT for 1000 ppmwS model oil, which are also larger than the majority of reported adsorbents. Therefore, PCN-10 may be an excellent adsorbent candidate for the removal of thiophenicsulfur.

To explain such best adsorption performance, we further performed the control adsorption experiments in the corresponding other MOFs. As shown in Figure 4, the adsorption capacity is dropped significantly compared with that on dehydrated PCN-10, for example, by 74% in 200 ppmwS mode oil. These results confirm that CUS plays the dominant role for the adsorption of DBT in PCN-10. Figure 6 shows that the stretching vibration band of N=N group (1613 cm⁻¹) and benzene ring (1561 cm⁻¹) are slightly shifted to 1630 cm⁻¹ and 1583 cm⁻¹, respectively, after the DBT adsorption. It indicates that the N=N group and the benzene ring have the conjugated π-complexation interaction with the benzene ring of DBT. In addition, it is found that the stretching vibration band of Cu-S

![Figure 4. Adsorption isotherms of DBT on dehydrated PCN-10 and hydrated PCN-10 at 303 K. (m_adsorbent = 0.02 g, m_oil = 5.0 g).](image)

![Figure 5. The adsorption capacities of several typical porous materials at different S-concentrations.](image)

<table>
<thead>
<tr>
<th>Materials</th>
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<th>Adsorption Capacity (mg S g⁻¹)</th>
<th>Ref.</th>
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<tr>
<td>MIL-101(Cr)-SO₃Ag</td>
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</table>
(1065 cm\(^{-1}\)) appears after the adsorption\(^{57}\) demonstrating that the Lewis acid sites have interaction with the DBT molecules through the lone pair of electrons on sulfur atom (\(\sigma\)-metal).\(^{58}\)

**Deep removal**

Deepening removal is necessary and urgent not only to reduce the environment pollution, but also to minimize the harmfulness to people generated by the S-compounds in liquid fuels. Motivated by the high adsorption capacity, we further investigated the DBT adsorption on PCN-10 in model oils with low S-concentrations. Supporting Information Table S3 shows that 99.03 wt % of the sulfur content can be removed from 50 ppmwS model oil, which can reach EU5 standard.\(^{59}\) This may be due to the cooperative effect of various interactions between framework and DBT combined with the appropriate pore size. Calculated from the equilibrium adsorption value at 50 ppmwS, this is also the highest value among all the reported porous materials to the best of our knowledge, as shown in Supporting Information Table S3. Therefore, PCN-10 has a remarkable deep removal performance for DBT.

**Regeneration**

Besides the high adsorption capacity, an excellent adsorbent should have good regenerability and resusability. Thus, the regeneration of PCN-10 was further studied and the results are listed in Supporting Information Figure S7. It can be seen that compared with that of the fresh adsorbent, the adsorption capacity of the regenerated one does not change for the first cycle considering the experimental error. In the fifth recycle process, the adsorption capacity is decreased less than 2.0%. As shown in Supporting Information Figure S8, the PXRD of the fresh PCN-10 is consistent with that of the fifth regenerated sample, indicating that the framework is not destroyed. Moreover, from the FT-IR spectra in Supporting Information Figure S9, there is no obvious difference between the fresh sample and fifth regenerated one. BET of the regenerated PCN-10 is also measured as shown in Supporting Information Figure S10, which is 1843 m\(^2\) g\(^{-1}\). Though there is a slight decrease compared with the fresh PCN-10 (1987 m\(^2\) g\(^{-1}\)), it confirms the successful regeneration of adsorbent. As a result, it is concluded that this material may be a potential candidate for ADS for industrial applications.

**Conclusions**

In this work, a bottom-up method was performed to find MOFs for the efficient removal of large guest molecules by taking desulfurization of liquid fuels as an example. PCN-10 was selected due to the fact that the framework can include several kinds of interactions with S-compound like DBT molecules. Thanks to the cooperative effect of these interactions combined with the large surface area, this MOF exhibits extraordinary high adsorption capacity of DBT (75.24 mg S g\(^{-1}\)) at 1000 ppmwS, which is much higher than those in all the other reported porous materials. More importantly, the removal rate for the low S-concentration on PCN-10 can reach beyond 99% at 50 ppmwS. This strategy can be conveniently extended to the screening and design of MOFs for the efficient removal of other important large guest molecules.

**Acknowledgments**

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**Literature Cited**


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