Desulfurization by MOFs as Sorbents for Thiophene Sulfides

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Abstract. Metal-organic frameworks UMCM-150 [Cu₃(BHTC)₂] and its heterobimetallic analogue Co₁Cu₂(BHTC)₂ based on an asymmetrical ligand, biphenyl-3,4',5-tricarboxylate (H₃BHTC), were studied for desulfurization of model oils. The adsorption experiments were conducted under room temperature and atmospheric pressure. The total sulfur concentration of model oils was 250 ppmw determined by WK-2D coulomb integrated micro-analyzer through adding benzothiophene (BT) and dibenzothiophene (DBT) into liquid alkanes. Adsorptive desulfurization experiments were conducted in a consecutive fixed bed adsorption system. The results indicate that Cu₃(BHTC)₂ has a higher sulfur-capacity than Co₁Cu₂(BHTC)₂. Taking DBT as an example, Cu₃(BHTC)₂ and Co₁Cu₂(BHTC)₂ have breakthrough adsorption capacities of 10.6 and 5.8 g S/kg of sorbent for model oils.

1. Introduction
Sulfur exists in fossil fuel should be removed because the combustion of sulfur is the primary cause of acid rain. Besides, sulfur also can severely poison the catalyst used in automotive emission control, petrochemicals production and fuel cells [1-3]. Consequently, the sulfur emission should be strictly regulated. The traditional hydrodesulfurization (HDS) can effectively remove thiols, sulfides and disulfides, but in the removal of thiophene derivative, such as benzothiophene (BT), dibenzothiophene (DBT) and 4, 6-dimethyl dibenzothiphene (DMDBT), encountered a serious challenge [4]. Commonly, HDS processes always need higher pressure (60-100 atm) and elevated temperatures (>573 K) to achieve deep desulfurization [5]. Hence, the adsorption desulfurization got great attention owing to some advantages, such as low-cost and feasible under normal temperature and pressure and can be selective in the removal of thiophene derivatives in the fuel [6]. Recently, many adsorbents, such as molecule sieves, activated carbon or alumina [7-10], have been studied for adsorption desulfurization. However, the capacities, adsorption kinetics, and selectivity of these materials for the organosulfur compounds have not reached industrial requirements. Development of new adsorbents with high sulfur-capacity, selectivity, and regenerability is the key to an efficient adsorption desulfurization process.

Metal-Organic Frameworks (MOFs) are highly ordered, porous materials that have aroused increasing attention in the world [11-13]. They are composed of metal ions and organic ligands, which make up diverse topology frameworks by forming bridging linkers. As is well-known, MOFs have large pore size, guest exchange kinetics and remarkable volume in the gas adsorption performance compared with traditional molecular sieve and activated carbon [14-16]. However, there are only several reports about MOFs to possess a significant sulfur adsorption capacity. Cychosz [17] and co-workers made
some pioneering work in this area. They studied five different MOFs materials and their adsorption characteristics for organosulfur compounds, such as BT, DBT and DMDBT in the model oil. Adsorption capacity is determined by pore size and the inner contact area between the organosulfur compound and the channel of frameworks [18]. However, there is little study on the influence of open metal active sites to the desulfurization. Accordingly, we choose a heterobimetallic UMCM-150 isostructural analogue Co1Cu2(BHTC)2 as the adsorbents of organosulfur compounds presented in transportation fuels. Finally, regenerability was tested under suitable conditions.

2. Experimental section

2.1 Materials
All the reagents and solvents were commercially available and used as received. Cu3(BHTC)2 and Co1Cu2(BHTC)2 were prepared by solvothermal synthesis and activated according to the published reports [19, 20]. Benzothiophene (98%), dibenzothiophene (98%), n-octane (CP) was purchased from Sinopham Chemical Reagent Co. Ltd.

2.2 Desulfurization experiments
The materials were packed into a stainless steel column (15 cm L × 2.0 mm ID) and a certain amount of zeolites 4A were filled in the entrance of the adsorption column to eliminate the influence of water dissolved in the model oil to desulfurization. As-synthesized materials and zeolites were separated by adsorbent cotton. The adsorption desulfurization experiments were performed at a room temperature and atmospheric pressure. Before the experiments, the adsorbent should be activated under N2 atmosphere at 393 K for 2 h. After heating, the sorbents were allowed to cool down to room temperature also in dry nitrogen. In order to expel the gas adsorbed in the MOFs, the n-octane was injected in the fixed bed at a flow rate of 0.5 ml/min using SZB-1 computer control double-plunger micro-pump. Model oils were spiked to 250 ppmw with n-octane and BT or DBT. All the model oil samples collected during the breakthrough experiments were measured by GC SP 3400 with a capillary column (L= 30 m, ID= 0.32 μm) outfitted with a flame ionization detector (FID) and calibrated using solutions of known sulfur concentration. The liquid hourly space velocities (LHSV) for MOFs using in the experiment are 289 h⁻¹, compared with the typical conditions for zeolite Y of between 1 h⁻¹ and 10 h⁻¹ [17]. The phenomena can be attributed to the much more open pore structures in MOFs making rapid guest diffusion [21].

3. Results and Discussion

3.1 XRD analysis
The XRD patterns in Figure 1 show that the characteristic peaks of Co1Cu2(BHTC)2 were identical to Cu3(BHTC)2 in line with the simulated pattern of Co1Cu2(BHTC)2 [19], which implies that the structure of the two adsorbents are resemble. The peaks of sample are at 2θ: 4.44, 7.02, 10.44, 10.93, 14.39, 19.84 and 28.80°, respectively. What’s more, no peak from impurities can be found from as-synthesized XRD spectra.
Figure 1. XRD patterns for as-synthesized Co1Cu2 (BHTC) 2 (a), UMCM-150 (b) and stimulated pattern of Co1Cu2(BHTC)2 (c).

3.2 Pore structure analysis
The porous structure details were measured by N2 adsorption-desorption isotherms. The results were shown in Table 1. The partial exchange of active metal site can not change the pore size and pore volume, which also suggests Co1Cu2(BHTC)2 has the same structure with UMCM-150. However, the specific area of Co1Cu2(BHTC)2 is higher than that of UMCM-150.

Table 1. Textural structures of MOFs.

| MOFs         | Mean pore size (Å) | Pore volume V (ml/g) | Specific area (m²/g) |
|--------------|--------------------|-----------------------|----------------------|
| UMCM-150     | 9.14               | 1.11                  | 2300                 |
| Co1Cu2(BHTC)2| 9.13               | 1.10                  | 2715                 |

3.3 Thermal stability analysis
As shown in Figure 2, there are three steps for UMCM-150 in the weight loss process. The first step (<50 ºC) is attributed to the amounts of adsorbed gas in the adsorbents. The second step (50–150 ºC) is the weight loss of water and guest molecules embed in the frameworks of UMCM-150. The third step (>300 ºC) reveals the collapse of structure. In order to remove the water and guest molecules embed in the adsorbents, the adsorbents were activated under 150 ºC for 2 h in helium gases before adsorption experiments.

Figure 2. TG and DTG curves for UMCM-150.
3.4 Adsorption of thiophene sulfides on MOFs

Figure 3 shows the results of Co$_1$Cu$_2$(BHTC)$_2$ adsorption capacities for the BT and DBT. The two organosulfur compounds breakthrough at 106, 346 ml/g, respectively. This sorbent can greatly desulfurize significant amount of solution before the breakthrough point (defined as 1 ppmw S). These correspond to the breakthrough capacities of 0.39%, 0.58% for BT, DBT (capacities calculated by integrating the Boltzmann function mentioned above). It is known to us that adsorption desulfurization capacity of previous reported MOFs is determined by pore size and shape, namely, contact area between the MOFs and organo-sulfur compound. Based on the breakthrough curves, Co$_1$Cu$_2$(BHTC)$_2$ has a higher capacity for DBT than BT. Total capacities for BT and DBT were 1.18%, 4.03%, and the results greatly verified the former conclusion.

![Breakthrough curves for 250 ppmw BT and DBT in model oils for Co$_1$Cu$_2$(BHTC)$_2$ (dash line) and UMCM-150 (solid line).](Image)

To assess the effectiveness of the open metal sites on organo-sulfur compound adsorption in fixed bed experiment, Cu$_3$(BHTC)$_2$ was compared with Co$_1$Cu$_2$(BHTC)$_2$. It was seen from Figure 2, the breakthrough point for the two organo-sulfur compound at 105.9, 346.1 ml/g, respectively, in parallel with the adsorption capacity 0.44%, 1.06%. The BT and DBT breakthrough adsorption capacities are in the order of Co$_1$Cu$_2$(BHTC)$_2$<Cu$_3$(BHTC)$_2$ and overall adsorption is in the same way.

The adsorptive removal of S-compound has been explained with high porosity and interaction like acid-base and $\pi$ complexation [19]. Due to the same topology and similar porosity of UMCM-150 and its heterobimetallic analogue, the open metal site is the only difference. The coordination of Cu$^{2+}$ to organic ligands is dominated by paddle-wheel motif. A trinuclear copper cluster coordinated with six ligands was replaced by a cobalt atom. The change can be explained by acid-base theory. Based on the Hard-Soft Acid Base (HSAB) principle [22], hard acids prefer hard bases; soft acids prefer soft bases. While Cu$^{2+}$ and Co$^{2+}$ belong to d$^9$ transition metal cations, in addition, metal cations with low valent state and more d electron number, it will be increasingly closed to 18e$^-$ soft acid. S-compound can supply isolated couple of electrons. Compared with Co$^{2+}$, Cu$^{2+}$ has more d electrons, so it is easier to interact with S-compound. That is why Cu$_3$(BHTC)$_2$ present superiority than Co$_1$Cu$_2$(BHTC)$_2$.

4. Conclusions and outlook

In conclusion, Co$_1$Cu$_2$(BHTC)$_2$ and Cu$_3$(BHTC)$_2$ are found to offer significant potential for the reduction of sulfur levels in transportation fuels, which can meet the regulations of administration and act as the complementary to the HDS. H$_3$BHTC was an appropriate ligand, which can be synthesized MOFs with suitable pore size and shape. In addition, regeneration of MOFs fixed bed has been shown to be feasible using a combination of solvent and heat. The adsorption capacity of Co$_1$Cu$_2$(BHTC)$_2$ is weaker than
Cu$_3$(BHTC)$_2$, which implies that the interaction of S-atom of organosulfur with Co$^{2+}$ is weaker than that of Cu$^{2+}$.

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