

Adsorptive removal of dimethyl disulfide in model gasoline using Cu-BTC loaded with phosphotungstic acid

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ABSTRACT

To deeply remove dimethyl disulfide (DMDS) from oil, phosphotungstic acid (HPW) was supported on $\text{Cu}_3(\text{BTC})_2$ (Cu-BTC) by impregnation to improve the adsorption desulfurization performance. A series of Cu-BTC with different amounts of HPW were prepared and studied in batch adsorption desulfurization experiments. X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive spectrometer (EDS), nitrogen adsorption-desorption were used to study the structural properties of adsorbents. Besides, reusability and adsorption performance under ultra-low sulfur conditions were also studied. The experimental results of adsorption desulfurization indicated that the HPW impregnation solution's greatest concentration was 20% and showed the best performance of desulfurization-the maximum sulfur adsorption capacity of adsorbent was 45.1 mg S/g. The ultra-low sulfur adsorption experiment showed the same result. In the model oil with a sulfur content of 50ppm, the desulfurization rate of 20%HPW/Cu-BTC reached 86.4%, and the sulfur content of the model oil after adsorption was about 7 ppm, which could satisfy the requirements of clean oil. The results could provide an excellent adsorbent for removing DMDS from oil.

Keywords: Adsorption desulfurization, Dimethyl disulfide, Phosphotungstic acid.

1. INTRODUCTION

With the continuous development of society, the consumption of oil products is increasing, which brings huge environmental problems. SO_x produced by burning sulfur-containing compounds in oil products could corrode automobile engines and poison catalysts in automobile exhaust treatment devices, which is also the main reason for acid rain. In order to obtain clean oil,

deep desulfurization has become a research focus. DMDS is a sulfur compound with high content in light oil. It is difficult to remove from oil because of the characteristics of low reactivity and low dissolution activity. Thus, the work to remove DMDS is a crucial point for clean oil.

Adsorption desulfurization is an excellent method because of its high selectivity, mild operating conditions, and low cost. A series of porous materials have been studied for adsorption desulfurization, such as activated carbon, ion exchange molecular sieve, mesoporous silica, graphene, activated alumina, bentonite, metal-organic framework materials (MOFs) and so on. MOFs have been widely studied and applied because of its high specific surface area, large porosity, various pore structures, large sulfur adsorption capacity, and easy preparation and modification. A series of MOFs materials have been used for adsorption desulfurization, and significant progress has been made. Matzger et al.[1] used MOFs materials to study adsorption desulfurization. They studied the adsorption desulfurization performance of MOF-5, HKUST-1, MOF-177, MOF-505 UMCM-150. They found that the adsorption desulfurization performance of three Cu^{2+} -based MOFs was better than the other two Zn^{2+} -based MOFs, and the specific surface area was not the key factor affecting the adsorption capacity. The coordinately unsaturated metal active sites (CUS) of MOFs were the key factors which affected adsorption desulfurization performance. According to Pearson's soft and hard acid-base theory, DMDS belongs to a soft Lewis base, which has a stronger interaction with soft Lewis acids, such as Cu^{2+} , Cu^+ and Ag^+ . Cu-BTC (HKUST-1) is a typical Cu^{2+} -based MOF, which has attracted wide attention because of its open metal sites and good stability. HPW is an oxygen-containing polyacid widely used as a catalyst. Because of the acid-base interaction

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between phosphotungstic acid and sulfur-containing compounds, HPW can improve the adsorption capacity of adsorbents[2]. Chuan Su et al.[3] used wasted FCC catalyst to support HPW and prepared adsorbent for adsorption desulfurization of Liquefied Petroleum Gas(LPG). It was found that after loading HPW, both lewis acid sites and Bronsted acid sites of adsorbent increased, and the ratio of lewis acid sites to Bronsted acid sites also increased. The increasing number of lewis acid sites increased active adsorption sites and improved adsorption performance. In the current research, a lot of adsorbents were prepared for desulfurization. But, the performance was not satisfactory. Besides, much research didn't study the performance for ultra-low sulfur-containing oil. It is necessary to investigate whether adsorbents are still effective.

The aim of this work was to prepare a new adsorbent for further improving the performance of adsorption desulfurization. HPW could increase the acid adsorption sites of adsorbent. The CUS combined with the acid sited could increase the adsorption sulfur capacity. In our work, Cu-BTC supported phosphotungstic acid adsorbents with different amounts of HPW were prepared by the impregnation method. The effect of HPW loading on the removal of DMDS was investigated by batch adsorption. In addition, the performance of adsorption desulfurization ability in ultra-low sulfur model oil and reusability was investigated.

2. EXPERIMENTAL SECTION

2.1 Material

Phosphotungstic acid ($\geq 99.9\%$ purity), ethanol (anhydrous, $\geq 99.5\%$), n-octane ($\geq 98\%$), dodecane ($\geq 99\%$), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, AR), N, N- dimethylformamide(DMF, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,3,5-benzenetricarboxylic acid (H_3BTC , $\geq 98\%$) and dimethyl disulfide ($>98\%$) was purchased from Aladdin Co., Ltd.

2.2 Synthesis of adsorbent

Cu-BTC was prepared according to the methods reported in the literature[4]. Firstly, 6 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 40mL deionized water to prepare solution I, and 3g H_3BTC was dissolved in the mixed solution of 40mL ethanol and 40mL DMF to prepare solution II. Then the two solutions were stirred. After that, the mixture was transferred to a 150mL Telfon and kept at 85°C for 24 hours. After cooling, the blue product was separated by filtration and washed with ethanol and

DMF, respectively. The Cu-BTC product was dried in a vacuum at 150°C for 15 hours.

X%HPW/Cu-BTC was prepared by impregnation. Firstly, 0.2g HPW was dissolved in 100mL deionized water to obtain a phosphotungstic acid aqueous solution. 1g Cu-BTC sample was added to the phosphotungstic acid solution and stirred at room temperature for 5 hours. Thereafter, the solid was separated by filtration, washed with deionized water three times, and dried to obtain the HPW/Cu-BTC adsorbent, which was named 20%HPW/Cu-BTC adsorbent. Adsorbents with different amounts of phosphotungstic acid were prepared using the same method and named as x% HPW/Cu-BTC.

2.3 Adsorption desulfurization experiment

Before the adsorption experiment, the activated adsorbent was obtained by drying in a vacuum at 150°C for 15 hours. The batch adsorption desulfurization experiment was carried out in a sealed glass sample bottle. The model oil was consisted of DMDS (1000ppm), n-octane (solvent), and dodecane (internal standard). For the experiment, 60mg adsorbent and 3g model oil were added into a glass container filled with magnetons. Adsorption desulfurization experiment was carried out at 30°C for 2 hours to achieve adsorption equilibrium. The mixture was then centrifuged, and the supernatant was collected. All samples were analyzed quantitatively by gas chromatography.

Adsorption desulfurization capacity was calculated according to the initial and equilibrium sulfur concentration in the solution,

$$Q = \frac{w(c_0 - c)}{m} \times 10^{-3}$$

where w and m were the mass (g) of model oil and adsorbent respectively. C_0 and C were the initial concentration and equilibrium concentration of sulfur in model oil. Q was the saturated sulfur adsorption capacity of the adsorbent (mg S/g).

3. RESULTS AND DISCUSSION

3.1 Structure of adsorbent

Fig. 1 shows XRD spectra of Cu-BTC and HPW/Cu-BTC adsorbents with different loadings. The diffraction peaks ($2\theta = 6.9, 9.5, 11.6, 13.4, 17.5, 19.0$) of Cu-BTC could be seen from the figure, consistent with those reported in the literature, which proved the successful preparation of Cu-BTC. The diffraction peaks of HPW/Cu-BTC with different loadings were consistent with Cu-BTC, and there was no HPW diffraction peak, which indicated

that HPW loading could not destroy the crystal structure of Cu-BTC, and HPW was highly dispersed on the surface of Cu-BTC without agglomeration.

The morphology of adsorbent was studied by SEM. Fig. 2 (a) is an SEM picture of Cu-BTC crystal. It could show the octahedral crystal form of Cu-BTC. Fig. 2(b) is an SEM picture of 20%HPW/Cu-BTC. It could be seen that its crystal form was the same as that of Cu-BTC, the crystal surface was coarser, and some fibrous particles were attached, which was caused by the load of HPW, and a part of HPW was loaded on the crystal surface. Elemental distribution of 20%HPW/Cu-BTC was studied by EDS. Fig. 2 (c) and fig. 2(d) are EDS spectra of Cu element and W element, respectively. The EDS energy spectrum signal of W element could be seen from the figures indicating that HPW was highly dispersed on the surface of Cu-BTC.

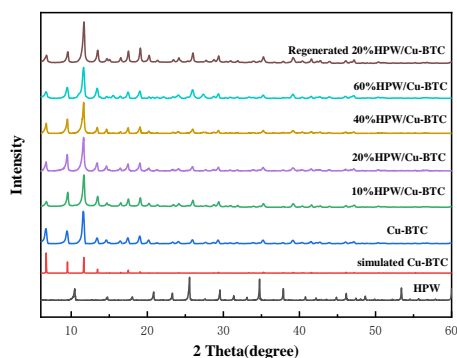


Fig 1 XRD patterns of samples

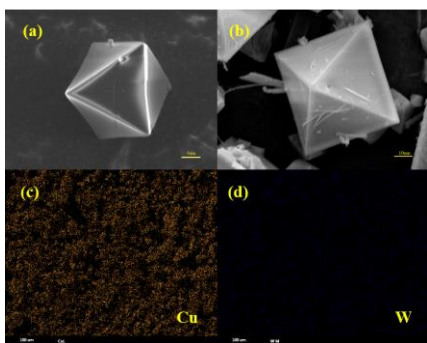


Fig 2 SEM and EDS images of Cu-BTC and 20%HPW/Cu-BTC

Fig. 3 is a nitrogen adsorption-desorption curve. It can be seen from the figure that the adsorption isotherm of Cu-BTC was a typical type I adsorption isotherm, which belongs to microporous material. While the adsorption isotherm of HPW/Cu-BTC was a combination of type I and type IV, which had hysteresis loop under high relative pressure, indicating that the

material had both micropores and mesopores. The morphology properties are shown in Table 1. Cu-BTC had a large specific surface area of 836.80 m²/g. Impregnating HPW could reduce the specific surface area and total pore volume of samples, and with the increase of HPW loading, the specific surface area and total pore volume of x%HPW/Cu-BTC would decrease. This could be attributed to the collapse of some of Cu-BTC channels and the blockage of some channels by HPW.

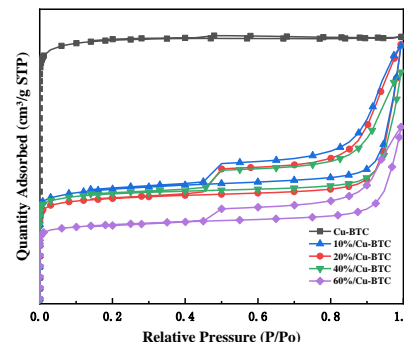


Fig 3 N₂ adsorption/desorption isotherms of Cu-BTC and 20%HPW/Cu-BTC

Table 1 Physicochemical properties

Adsorbent	S _{BET} (m ² /g)	V _{total} (cm ³ /g)
Cu-BTC	836.80	0.42
10%HPW/Cu-BTC	397.53	0.41
20%HPW/Cu-BTC	373.76	0.40
40%HPW/Cu-BTC	356.40	0.36
60%HPW/Cu-BTC	255.29	0.28

3.2 Adsorption desulfurization

Fig.4 is a time-dependent curve of the sulfur adsorption capacity on adsorbents. It could be seen that the sulfur adsorption capacity of DMDS by Cu-BTC was lower than x%HPW/Cu-BTC. The sulfur adsorption capacity of 20%HPW/Cu-BTC was the highest, reached 45.3 mg S/g. It indicated that the loading of HPW could effectively improve the ability to remove DMDS. It was attributed to the increase of acidic sites of HPW. However, with the rise in HPW loading, the sulfur adsorption capacity would decrease. Combined with the characterization results of nitrogen adsorption and desorption experiments, HPW loading would significantly reduce the specific surface area and total pore volume of Cu-BTC. It indicated that HPW blocked some micropores of Cu-BTC, making some Cu²⁺

coordination unsaturated sites unable to be contacted by DMDS.

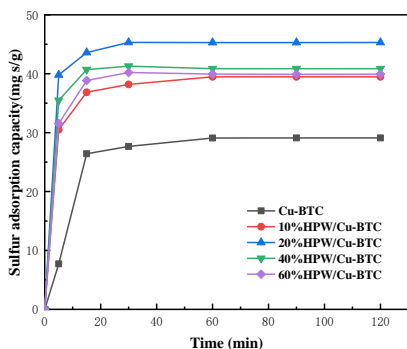


Fig 4 Desulfurization rate with time on Cu-BTC and x%HPW/Cu-BTC

To study the desulfurization performance of adsorbent on ultra-low sulfur oil products, the experiments of adsorption desulfurization in model oil (DMDS, 50ppm) were carried out. Fig.5 shows the saturated adsorption desulfurization rate for ultra-low sulfur model oil. The desulfurization rate of 20%HPW/Cu-BTC was the highest, reaching 86.4%. After removing DMDS by adsorption, the sulfur content in model oil was not higher than 7ppm. It reached the sulfur content requirement for clean oil.

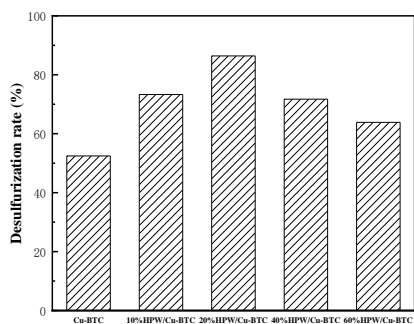


Fig 5 Desulfurization rate of Cu-BTC and x%HPW/Cu-BTC on ultra-low sulfur oil

In addition, the reusability of 20%HPW/Cu-BTC adsorbent was investigated. The adsorbent was refluxed in ethanol for three times, filtered, dried and activated in vacuum. Fig.6 shows that the sulfur adsorption capacity of adsorbent decreased to 85.4% after three times. It revealed that the structure of adsorbent would not collapse after repeated use. This could be confirmed from the XRD spectrum of adsorbent after regeneration

in Fig.6 The reusability experiment showed that the reusability of 20%HPW/Cu-BTC was good.

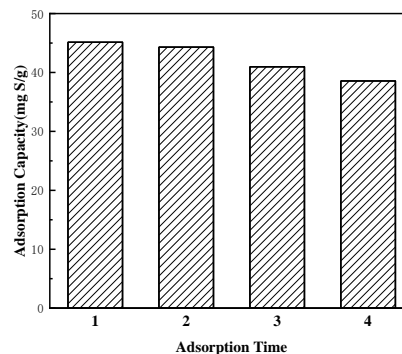


Fig6 Regeneration performance of 20%HPW/Cu-BTC

4. CONCLUSION

x%HPW/Cu-BTC adsorbent was synthesized and used to remove dimethyl disulfide from model oil. The sample loaded by HPW has higher sulfur adsorption capacity than Cu-BTC, which proves that HPW increases the adsorption sites of the adsorbent. Simultaneously, for ultra-low sulfur model oil, the adsorbent still has a good adsorption performance. The sample can be regenerated by refluxing in ethanol solution. After three times of regeneration, the desulfurization ability was reduced to 85.4%. High sulfur adsorption capacity, excellent ultra-low sulfur desulfurization ability and good reusability indicated that HPW/Cu-BTC was an excellent adsorbent for deep desulfurization.

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