

Preparation and Performance of Deep Desulphurization Adsorbent of Heavy Naphtha†

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The deep desulphurization adsorbent used on the middle-pressure hydrogenation of heavy naphtha was studied. The results of static adsorption showed that the best components of deep desulphurization adsorbent were Zn/Fe/AT (AT = attapulgite), with the suitable ratio of 2.1:5.4:2.5 (XF-1). Little amount of ammonium carbonate (NC) would be helpful to produce pores, the static sulfur capacity of XF-1-NC was 1.52×10^{-4} g/g, which was 11.7 % higher than that of XF-1.

Key Words: Heavy naphtha, Deep desulphurization, Adsorbent, Zn/Fe/AT, Sulfur capacity.

INTRODUCTION

Heavy naphtha prepared by middle-pressure hydrogenation is the main raw material of benzene, toluene and xylene. The catalysts of aromatics catalytic reforming systems are sensitive to sulfide, so the sulfur content must be strictly controlled to less than 1 mg/L¹, but the sulfur content of domestic heavy naphtha prepared after middle-pressure hydrogenation is 2-4 mg/L, which could not meet the requirement above. At present, the adsorption desulphurization method which can remove sulfur content below 1 mg/L is carried out to achieve the deep desulphurization process of heavy naphtha prepared by middle-pressure hydrogenation. However, most of the adsorbents have disadvantages, such as low sulfur capacity and poor strength, which will lead to short life time and unstable operation²⁻⁴, so, study of deep desulphurization adsorbent used on the middle-pressure hydrogenation is an increasing demand.

EXPERIMENTAL

The heavy naphtha was from a medium-pressure hydrocracker of refinery and original content of sulfur-containing compounds was about 3 ppm/w. All reagents were analytical grade.

Preparation of adsorbent: The adsorbent was prepared by solid mechanical mixing method. Metal oxide powder and auxiliary additives were weighted in required ratio and mixed fully, then the mixture was stirred with a certain concentration of additive solvent and prepared for 1-3 mm ball. Adsorbent balls were baked at 200 °C for 2 h.

Static adsorption experiment: Adsorbent and heavy naphtha were put into conical flask with a certain solid-liquid ratio and rocked on a bain-marie at 45 °C. Sulfur content of heavy naphtha was analyzed by micro-Coulomb meter once for 2 h until equilibrium.

Data analysis: The desulfurization efficiency of each adsorbent was calculated according to the following equations:

$$\text{Static sulfur capacity } q = (c_0 - c_i) \times \frac{v}{m} \text{ (g S/g adsorbent)}$$

$$\text{Desulfurization rate } y = \frac{(c_0 - c_i)}{c_0}$$

The c_i is the sulfur concentration (ppm/w) after desulfurization, c_0 is the initial sulfur concentration, v is the volume of the heavy naphtha and m is the weight of the adsorbent.

RESULTS AND DISCUSSION

Composition screening of desulfurization sorbent: The static adsorption efficiency of different active components was investigated (Table-1), ZnO showed the highest adsorption desulfurization activity. The desulfurization efficiency of Fe-1 and Fe-2 was better than Fe-3, the reason might be the more amount of acid active. Activated carbon (AC), Al₂O₃ and attapulgite (AT) all had a larger surface area and developed pore structure which not only for desulfurization agent of the carrier, but also for the adsorption components. Although the desulfurization efficiency of TiO₂ was relatively poor, it could be used as additional adsorbent because of the adjustable acidic surface⁵.

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Adsorbents	Desulfurization rate (%)	Adsorbents	Desulfurization rate (%)
Al ₂ O ₃	17.98	Fe-1	18.91
AT	16.17	Fe-2	19.48
AC	20.64	Fe-3	5.10
ZnO	58.90	TiO ₂	4.90

AT = Attapulgite, AC = Activated carbon.

Considering the price of adsorbent, the deep desulphurization adsorbent component was determined as Zn/Fe/AT/Ti.

Ratio optimization of Zn/Fe/AT/Ti of desulfurization sorbent: The influence of content of deep desulphurization adsorbent Zn/Fe/AT/Ti was investigated. The results (Fig. 1) shown that too low or too high attapulgite content would result in low desulfurization rate with the same Zn/Fe ratio, the former had less surface area and pore volume, the latter had less active components. So, 25 % content of attapulgite was selected. Fig. 1b showed desulfurization performance of adsorbents with different Zn and Fe ratio. With the increase of adsorption time, the lowest sulfur-content could be 0.69 mg/L when Zn/Fe was 2:5, which was better than the others. Fig. 1c shows that the increase of adsorption desulfurization rate was not obvious with more Ti content. Adsorption capacity of adsorbents with high Ti content was relatively lower, because the Zn/Fe content was less and desulfurization rate of TiO₂ was only 4.9%. So the deep desulphurization adsorbent component was determined as Zn/Fe/AT with the suitable ratio of 2.1:5.4:2.5.

Expanding agent filter: According to the molecular dynamics diameter (0.6-0.9 nm) of thiophene and its derivatives, increasing the pore size could significantly improve the desulfurization. Methyl cellulose (MC) and ammonium carbonate (NC) were chose to investigate the expanding agent influence and the content was 3 % (wt %). According to the results of TG-DTA of methyl cellulose and ammonium carbonate, baking program C1 was from room temperature to 120 °C (remain 1 h) and then to 390 °C (1 h), C2 was from room temperature to 120 °C (1 h) and then to 250 °C (1 h) with a temperature ramp of 2 °C/min.

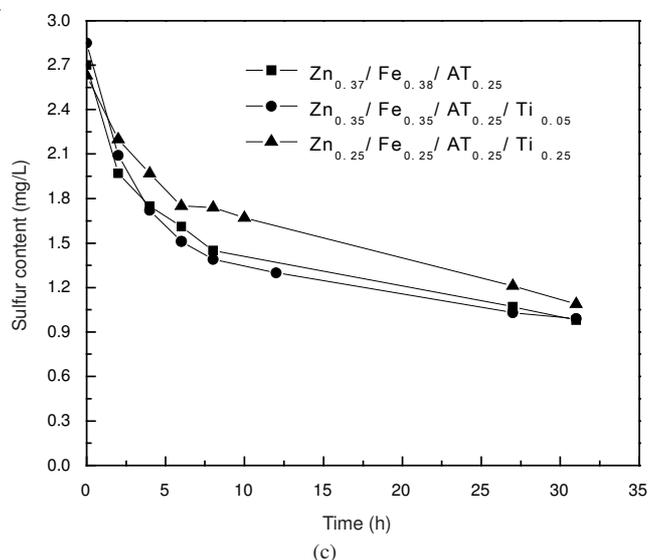
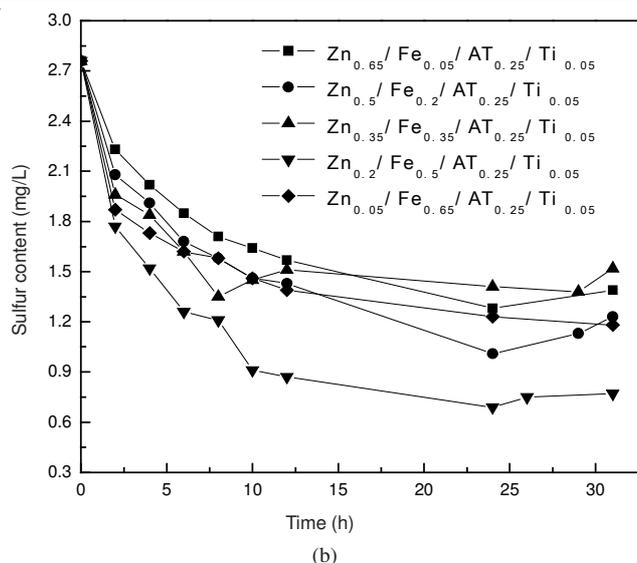
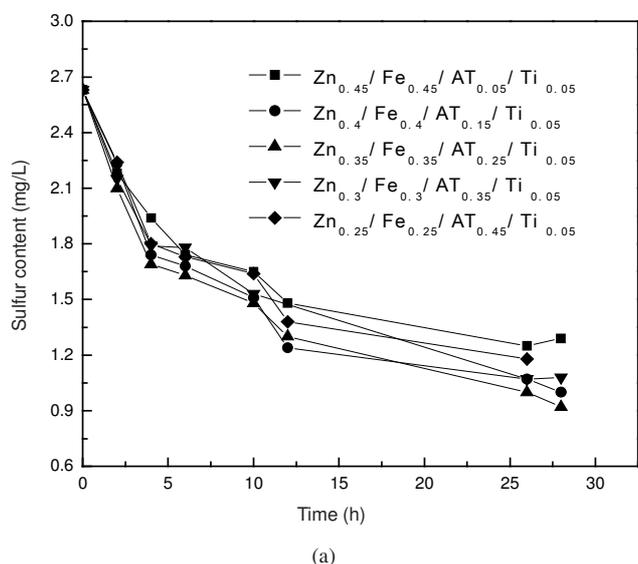


Fig. 1. Desulfurization performance of adsorbents with different Zn/Fe/AT/Ti content

Fig. 2a showed that adsorption rate of XF-1-MC-C1 was significantly higher than XF-1-C1 in the initial stage, while lower than XF-1-MC-C2 and XF-1-C2 in the final stage, because methyl cellulose decomposed of CO₂ and large pore volume and pore diameter led to excellent mass transfer and high temperature could cause structural collapse and reduction of acidic center. Fig. 2a also showed that XF-1-MC-C2 and XF-1-C2 express the similar adsorption performance because methyl cellulose didn't fully decompose.

Because ammonium carbonate decomposition temperature is lower, baking program of XF-1-NC chose C2. Fig. 2b showed that ammonium carbonate would help to produce pores without damaging the active component, which would lead to faster desulphurization rate. The static sulfur capacity of XF-1-NC-C2 was 1.52×10^{-4} g/g, which was 11.7 % higher than that of XF-1-C2.

Table-2 showed the results of BET of three adsorbents with the same prepared condition. Because of the large number of macropore after decomposition of methyl cellulose, pore volume and pore diameter of XF-1-MC were more than

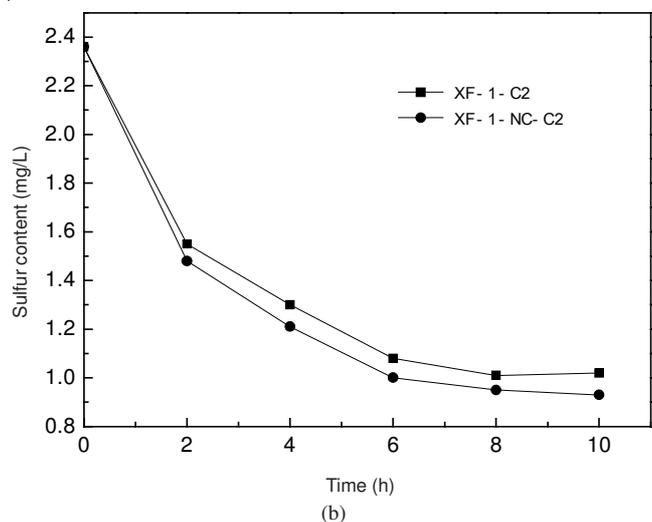
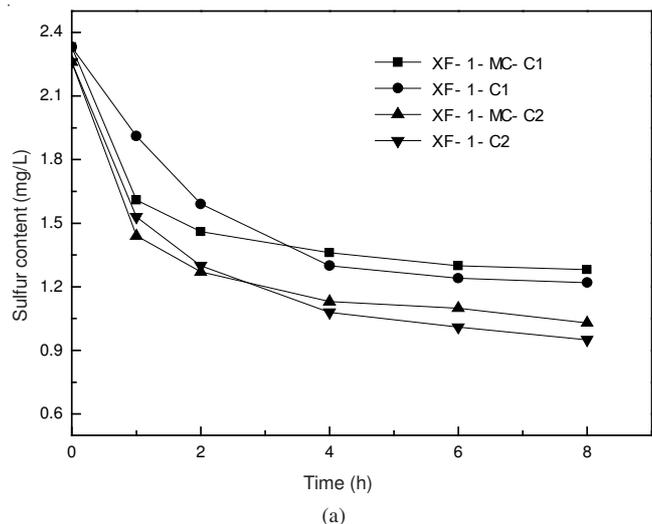


Fig. 2. Effect of desulfurization performance of XF-1 with expanding agent

XF-1, surface area was less than XF-1. It also showed that surface area and pore volume of XF-1-NC was more than XF-1. So, expanding agent with low decomposition temperature could help to improve mass transfer performance and lead to initial faster desulphurization rate.

TABLE-2
SURFACE AREA, PORE VOLUME AND PORE DIAMETER OF ADSORBENTS WITH PORE-EXPANDING AGENT

Adsorbent	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
XF-1	97.39	0.17	7.05
XF-1-MC	80.70	0.19	8.32
XF-1-NC	99.94	0.19	7.01

MC = Methyl cellulose; NC = Ammonium carbonate.

Conclusion

By static adsorption experiment, active component and carrier of the ultra-deep desulphurization adsorbent component were determined as Zn/Fe/AT, with the suitable ratio being 2.1:5.4:2.5(XF-1). Little amount of ammonium carbonate would help to produce pores without damaging the active component, which would lead to faster initial desulphurization rate. The static sulfur capacity of XF-1-NC was 1.52×10^{-4} g/g, which was 11.7 % higher than that of XF-1.

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