Enhanced adsorption desulfurization performance over hierarchically structured zeolite Y

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ABSTRACT

Hierarchically structured zeolite Y (meso-Y) was successfully achieved by treating parent NaY (Si/Al = 2.6) by sequential dealumination-desilication. The obtained sample was characterized by X-ray diffraction, N_2 sorption, Transmission electron microscopy, X-ray fluorescence, pyridine-Fourier transform infrared and ^{29}Si Magic angle spinning nuclear magnetic resonance techniques. The mesopore surface area up to 110 $m^2 g^{-1}$ was obtained for meso-Y when the parent zeolite Y was subjected to sequential treatment by ethylenediaminetetraacetic acid and NaOH, with the preserving of the intrinsic crystallinity. The adsorption desulfurization results showed that hierarchically structured CeY (meso-CeY) exhibited much higher desulfurization performance than microporous CeY in the presence of large amount of toluene or cyclohexene, even in fluid catalytic cracking gasoline. FTIR studies and structure characterization indicate that the mesopore of the adsorbent is benefit to the selective adsorption desulfurization, possibly because the enlarged pore size weakens the micropore-filling effect of the microporous adsorbent, and thus depresses the non-selective adsorption of toluene and cyclohexene.

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1. Introduction

Deep desulfurization for ultra-clean transportation fuels has become a crucial important subject worldwide owing to the more stringent environmental legislations in many countries [1–3]. Conventional hydrodesulfurization (HDS) is effective in the removal of reactive (di) sulfides and mercaptans, but less efficient for refractory molecules such as thiophene (TP), benzothiophene (BTP), dibenzothiophene (DBTP) and their derivatives. As for gasoline distillate, ultra-deep desulfurization by HDS required substantial hydrogen consumption and inevitably lead to a significant loss in octane number due to olefin saturation [4,5]. To avoid the above problems, several new technologies [6–9] have been explored to meet the urgent needs for ultra-clean fuels. Among these, adsorption desulfurization is regarded as a promising method in the selective removal of thiophenic sulfur compounds under moderate conditions.

So far, various types of adsorbents [1,10–19] have been reported for the desulfurization of fuels, and ion-exchanged FAU zeolites, as a kind of promising adsorbents, have been widely investigated. It is worth noting that the interaction modes between the sulfur compounds and the active sites in adsorbents has been considered as a crucial factor in sulfur removal, more efforts have been made to study the interaction

modes [1,15,17,20], and based on which two mechanisms including π-complexation and direct S-Metal interaction are proposed. Compared with that, the role of the pore size of adsorbent in desulfurization performance has been neglected. Though some research investigated the desulfurization of mesoporous materials [18,21–23], most emphasis has been put on the adsorption desulfurization of BTP, DBTP and their derivatives with larger molecular sizes, from the viewpoint of circumventing the steric hindrance and diffusion limitation in microporous zeolite. An good example for this case is that mesoporous $AgNO_3$/MCM-41 represented a better performance in the desulfurization of JP-5 light fraction (841 ppmw-S) with alkylated benzothiophenes, but exhibited a much lower sulfur capacity than CuY in model jet fuel containing only benzothiophene and metylbenzothiophene with smaller molecular sizes [23]. This indicates that the adsorbent with larger pore size doesn't always mean a better desulfurization performance. In other words, more attention should be paid to the role of the pore size of the adsorbent in adsorption desulfurization.

Hierarchically structured zeolite is a kind of ideal material to investigate the role of the pore size of the adsorbent in adsorption desulfurization, since it possesses similar properties as its microporous counterpart, except for the pore structure. Our previous work [24] studied desulfurization performance of cerium ion-exchanged hierarchical zeolite beta and found that the newly created mesopore to some extent improved the desulfurization performance, especially for DBTP with larger molecular diameter. But the SiO_2/Al_2O_3 ratio of zeolite beta is higher than that of Y, which limits the amount of metal ions in beta introduced by ion exchange. In this paper, the desulfurization performances of hierarchical

CeY (meso-CeY) have been evaluated and compared with those of microporous CeY in order to shed light on the role of the pore structure of adsorbents in desulfurization.

2. Experimental

2.1. Adsorbents and fuels

The parent zeolite NaY used in this study was described elsewhere [20,25]. Hierarchical Y zeolite (labeled as meso-Y) was prepared as follows [26,27]. First, 5.845 g ethylenediaminetetraacetic acid (EDTA) and 6.7 g parent NaY zeolite were added into three-neck round-bottom flask with 100 mL deionized water. The obtained suspension was then stirred at 373 K for 6 h. After that, the slurry was filtered and washed thoroughly with deionized water. The solid product was collected, dried at 393 K for 6 h in oven, and calcined at 773 K. The dealuminated sample was then treated with 0.8 M NaOH aqueous solution at 338 K for 0.5 h. After filtration, washing, drying and calcination, the meso-Y was obtained. Both parent NaY and meso-Y were ion exchanged with $Ce(NO_3)_3$ solution according to our previous description [25], and the obtained adsorbents were labeled as CeY and meso-CeY.

Three kinds of sulfur compounds, TP, 3-methylthiophene (3-MTP), and BTP, were employed as model organic sulfur compounds and dissolved into cyclohexane respectively to make three model gasolines (MGs). Toluene and cyclohexene were selected as aromatic and olefin competitors. The sulfur contents of different MGs were ca. 100 mg/L. Detailed compositions of the MGs are listed in Table 1.

The compositions of fluid catalytic cracking (FCC) gasoline are n-alkanes (9.4 wt.%), isoalkanes (45.8 wt.%), cycloalkanes (7.4 wt.%), olefins (21.6 wt.%) and aromatics (15.8 wt.%). The sulfur content of the FCC gasoline is initially 52.0 mg/L, and it is doubled to 113.3 mg/L by adding TP for convenient comparison. The main sulfur compounds in the FCC gasoline are TP, 2-MTP, 3-MTP, dimethylthiophene, ethylthiophene, BTP and its derivatives, thioethers and mercaptans.

2.2. Characterizations

The X-ray diffraction (XRD) patterns of NaY and meso-Y were collected in the 2θ range of 5-35° using a Rigaku D/Max-RB diffractometer with Cu K$_\alpha$ radiation (λ = 1.5418 Å), operated at 40 kV and 40 mA. N_2 adsorption-desorption isotherms of the samples were measured on an ASAP-2020 apparatus at 77 K. Prior to the measurements, the samples were evacuated at 573 K for 3 h. The total surface areas were determined by BET method. The micropore volumes and the micropore surface areas were obtained by t-plot method. The BJH model applied to the adsorption branch of the isotherm was used to obtain the mesopore size distribution. Fourier transform infrared spectra of pyridine (Py-FTIR) adsorption were obtained on Nicolet Avatar 360 spectrometer by scans of 64 with a resolution of 4 cm^{-1}. The samples were pressed into a self-supporting wafer (15–20 mg) and placed in a quartz IR cell with CaF$_2$ windows. Then it was purged with N_2 flow at

673 K for 1 h and subsequently cooled down to room temperature (RT) for pyridine adsorption. The IR spectra of the samples before adsorption were recorded at RT, and after adsorbing pyridine for 10 s, the samples were purged with N_2 flow for 10 min. Then the IR spectra of pyridine adsorption were recorded at RT. Desorption was performed by sweeping the wafer with N_2 flow at elevated temperatures. The spectra were recorded at 423 and 723 K, respectively. Transmission electron microcopy (TEM) was carried out in a Hitachi HT7700 microscope operated at 100 kV and equipped with a AMT41B camera. A few drops of the sample suspended in ethanol were placed on a carbon-coated copper grid followed by evaporation at ambient conditions. ^{29}Si Magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were measured by a Bruker Avance-500 MHz spectrometer with single-pulse experiments, spinning rate ca. 12 kHz, and the spectra were recorded at 99.36 MHz, pulse width 1.23 μs (22.5°), and the time interval between pulse sequences was 4 s. Chemical shifts were referred to external kaolin. The content of cerium in the adsorbents was measured by SRS-3400 (BRUKER) X ray fluorescence (XRF).

2.3. IR study on adsorbent – adsorbate interaction

IR spectra of TP (cyclohexene or toluene) adsorption were obtained on Nicolet Avatar 360 spectrometer by scans of 64 with a resolution of 4 cm^{-1}. The pretreatment of the samples and adsorption procedures are the same as pyridine adsorption, and the spectra were recorded at RT. All the spectra given in this paper were difference spectra.

2.4. Desulfurization and regeneration

Prior to desulfurization experiment, the adsorbents were dried in oven at 393 K overnight in order to remove the physically adsorbed water. The adsorption experiment was carried out in a batch system at RT and atmospheric pressure. The dried adsorbents (0.250 g) were mixed rapidly with 5.00 mL of MG or 2.50 mL of FCC gasoline in flasks for 3 h. The adsorption time was determined by monitoring the variance of sulfur content of MG with time, and the results showed that a period of three hours was enough for the adsorption to achieve equilibrium. The desulfurized MG was separated by filtration, and the sulfur content of MG before and after adsorption was analyzed by microcoulometry. The sulfur removal ($R\%$) and adsorption capacity (q) were calculated according to the following two formulae:

$$R\% = \frac{c_0 - c_e}{c_0} \times 100\%$$
$$q(\text{mg S/g Ad}) = \frac{(c_0 - c_e)V}{m}$$

Where c_0 and c_e are the sulfur content in the fuels before and after desulfurization (mg/L), respectively, V is the volume of the fuel (mL), and m the mass of the adsorbent (g).

Table 1
The compositions of MG distillates.

MG	Sulfur content (mg/L)	Component	$n_{Cyclohexene}/n_{TP}$	Cyclohexene (vol.%)	$n_{Toluene}/n_{TP}$	Toluene (vol.%)
MG1	93.2	TP/cyclohexane				
MG2	101.3	3-MTP/cyclohexane				
MG3	96.8	BT/cyclohexane				
MG4	99.5	TP + toluene/cyclohexane			1	0.033
MG5	98.5				10	0.330
MG6	101.9				100	3.300
MG7	92.5				500	16.600
MG8	97.7	TP + cyclohexene/cyclohexane	1	0.032		
MG9	96.5		10	0.320		
MG10	100.4		100	3.200		
MG11	93.5		500	15.800		