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Deep desulfurization of model gasoline by selective adsorption on Ag^+/Al-MSU-S

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ABSTRACT

The desulfurization of model gasoline containing 600 ppmw thiophene or dibenzothiophene (DBT) by selective adsorption over Ag^+ exchanged mesoporous material Al-MSU-S was studied in a fixed adsorbent bed at ambient temperature and pressure. The results showed that the sulfur capacity increased with Al content incorporated in the silicate framework and Ag^+ exchange can effectively improve the desulfurization performance. The best adsorbent, Ag^+/20%Al-MSU-S, has adsorption capacity of 5 or 20 ml model gasoline containing thiophene or DBT per gram adsorbent, respectively, before the detection limit in our experiments, as a result of π-complexation. The adsorbent can be regenerated more than six times by simple calcination in air at 350 °C without obvious losing the sulfur adsorption capacity.

1. Introduction

Ultra-deep desulfurization of transportation fuels has aroused much attention ever since government worldwide mandated further stringent specifications for sulfur in fuel oils from the environmental concern [1,2]. Moreover, interest in ultra-low-sulfur fuels is also driven by fuel cell applications [3]. Conventional hydrodesulfurization (HDS) is highly effective for the removal of thiol, sulfides and disulfides, but less effective for thiophene and thiophene derivatives [4,5]. To produce ultra-low-sulfur gasoline to meet the new regulations, the reactor size needs to be 5–15 times increased in comparison with those currently used [6].

In recent years, other desulfurization processes including adsorption [7], extraction [8], oxidation [9,10], and bioprocesses [11] have been developed. Among these methods, selectively removing sulfur compounds from transportation fuels by the π-complexation adsorption is currently the most promising alternative because adsorption can be accomplished at ambient temperature and pressure. Molecular orbital (MO) calculations and experiments have shown that the refractory compounds (4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene) bind strongly through π-complexation because of a better electron donation/back-donation ability [12]. Commercially available adsorbents including zeolites [13], activated carbon [14], activated alumina [15], etc., however, show low selectivity or sulfur capacity. In the π-complexation mechanism, the cations can form usual σ-bonds with their s-orbitals while their d-orbitals can back-donate electron density to the antibonding π-orbitals of the sulfur rings. The metals that can form strong π-complexation bonding are those that possess empty s-orbitals and the electron density available at the d-orbitals necessary for back donation [16], especially the copper Cu(I) electronic configuration. Based on π-complexation concept, Yang and co-workers have developed a new kind of high-sulfur-selectivity and high sulfur-capacity adsorbents, Cu^+ and Ag^+ exchanged zeolites or other materials [17–19]. It was reported that sulfur selectivity and capacity over Cu^+ or Ag^+ exchanged zeolite Y were orders of magnitude higher than those obtained by other previously known adsorbents [20].

With the discovery of mesoporous MCM-41 molecular sieves [21], the synthesis and application of ordered mesoporous material has drawn sensitive research interests owing to its faster transfer ability. Some mesoporous materials like MCM-41, SBA-15 were modified by Cu^+ or Ag^+, etc., for desulfurization [22–26]. However, the weak acidity and poor hydrothermal stability induced by the amorphous pore wall structure limit their potential applications in petroleum refining. To overcome the limitations, Liu et al. [27] synthesized the mesoporous molecular sieves Al-MSU-S derived from faujasitic zeolite type Y seeds, and found that these molecular sieves had better characters including strong hydrothermal stability, strong acidity and high ion exchange ability. It is expected that such novel structure with characters of zeolite and ordered mesoporous material will be an ideally parent material for deep desulfurization adsorbent. Here, in the paper, Ag^+ exchanged mesoporous material Al-MSU-S were prepared and

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used for the desulfurization of model gasoline containing thiophene (TP) or dibenzothiophene (DBT) by selective adsorption in a fixed adsorbent bed at ambient temperature and pressure, and its regeneration ability was also examined.

2. Experimental

2.1. Preparation of Ag^+/Al-MSU-S

Al-MSU-S was synthesized by direct assembly of nanosized zeolite Y according to the reported method [27]. Briefly, nanoclustered zeolite Y seeds were prepared by reaction of 0.088 mol NaOH and 0.10 mol $NaAlO_2$ in 8.5 mol H_2O with 0.90 mol silicate anions in the form of a sodium silicate solution containing 27 wt% SiO_2 and 14 wt% NaOH under stirring at 100 °C overnight. The formation of a hexagonal mesostructure, rather than a zeolite, was achieved by lowering the pH of the seeds solution to 9 and introducing a surfactant after the initial aging period. Thus, 0.20 mol cetyltrimethylammonium bromide, 0.52 mol sulfuric acid and 127 mol water were added to the seeds solution, followed by another aging period of 20 h at 100 °C afforded a hexagonal aluminosilicate. Three Al-MSU-S samples with molar ratio of Si/Al being 99, 9 and 4 were synthesized and labeled as 1%Al-MSU-S, 10%Al-MSU-S and 20%Al-MSU-S, respectively.

The adsorbents Ag^+/Al-MSU-S were prepared by Ag^+ exchange as follows: as-synthesized Al-MSU-S were exchanged using a 5-fold excess $AgNO_3$ (0.1 M) at room temperature for 48 h. After that, the molecular sieves suspension were filtered and washed with deionized water. The products were dried at 100 °C overnight, and then calcined in air at 450 °C for 2 h. The samples were labeled as Ag^+/1%Al-MSU-S, Ag^+/10%Al-MSU-S and Ag^+/20%Al-MSU-S, respectively.

2.2. Adsorbent characterization

The powder X-ray diffraction (XRD) patterns of the samples were carried out using a Riguku 2400 instrument. Fourier transform infrared (FT-IR) spectra were recorded on an EQUINOX55 spectrometer using the KBr pellet technique. Nitrogen adsorption/desorption isotherms at −196 °C were obtained on Surface Area and Porosity Analyzer ASAP 2020. Prior to the adsorption measurements, the samples were degassed at 300 °C for at least 5 h. TEM micrographs were acquired with a Tecnai G220 microscope. The contents of Ag^+ in the samples were analyzed by inductively coupled plasma spectroscopy (ICP) on an ICP1014 instrument.

2.3. Adsorption/breakthrough experiments

TP or DBT was diluted in sulfur-free n-octane with sulfur concentrations both being 600 ppmw (0.06 wt%) and used as model gasoline. The adsorption/breakthrough experiments were performed in a fixed-bed stainless-steel adsorber (10 mm i.d., 300 mm long). A layer of quartz sand (about 7.4 g) was used as guard-bed, and about 0.5 g adsorbent was loaded inside the adsorber. Prior to each experiment, the adsorbent was activated in flowing dry nitrogen at 350 °C for 1 h to remove physically adsorbed water. After activation treatment, the adsorbent was allowed to cool down to the room-temperature under nitrogen. At room-temperature and atmospheric pressure, model gasoline was pumped by a liquid metering pump into the adsorber at a flow rate of 10 ml/h. After wetting the adsorber for about 12 min, the effluent samples were collected at regular intervals and analyzed with GC7890II gas chromatograph equipped with a SE-54 capillary column (15 m × 0.25 mm × 0.33 μm) and a flame photometric detector (FPD). The detection limitation of the instrument is 1 ppmw. In the paper, C_t is the sulfur concentration at time t and C_0 is the initial sulfur concentration of model gasoline (600 ppmw sulfur).

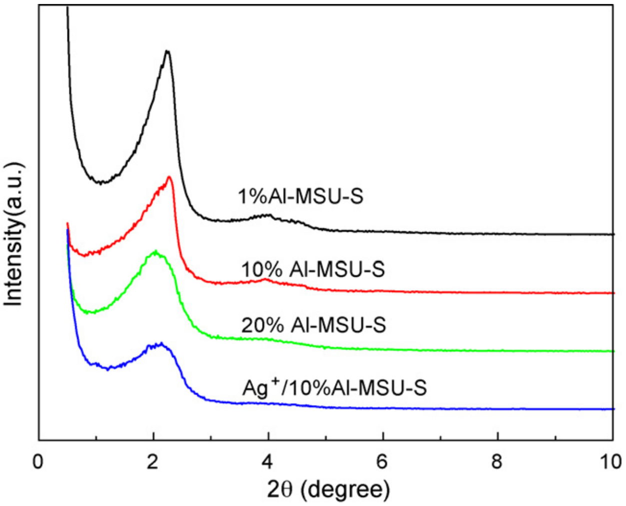

Fig. 1. XRD patterns of mesoporous aluminosilicate molecular sieves with different Al contents.

3. Results and discussion

Fig. 1 shows XRD patterns of Al-MSU-S samples with different Al contents in the silicate framework. The existence of diffraction reflections in the small angle region indicates that the produced samples have ordered structure in mesopore scale. And there are no diffraction reflections in wide angle, confirming the formation of pure mesostructure phase. It was also found that the quality of the patterns decreased with the increase of Al content from 1% to 20%. FT-IR spectra of the mesostructure Al-MSU-S as well as reference Y zeolite are shown in Fig. 2. Bands around 1000–1100 cm^{-1}, which is considered as characteristic of faujasitic zeolite Y, can be found in the patterns of Al-MSU-S. TEM images of Al-MSU-S shown in Fig. 3a and b also indicate that the Al-MSU-S was high-quality hexagonal structured material. The mesopore nature of as-synthesized Al-MSU-S and Ag^+/Al-MSU-S samples was verified by nitrogen adsorption. From the isotherms in Fig. 4(a), it can be seen that there exists high uptake at very low partial

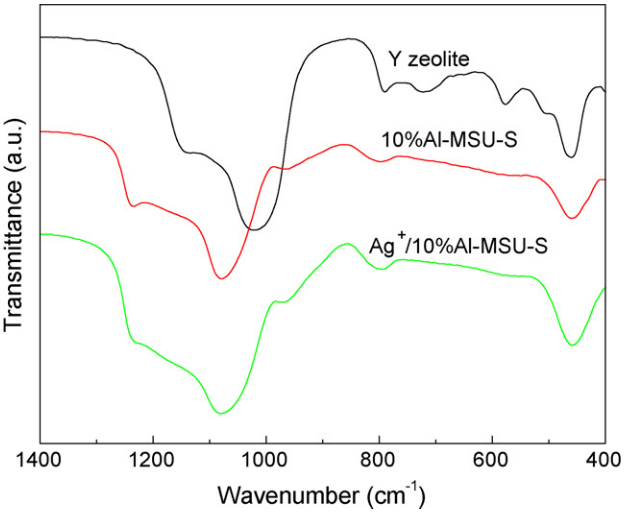

Fig. 2. FT-IR spectra of Y zeolite, 10%Al-MSU-S and Ag^+/10%Al-MSU-S.

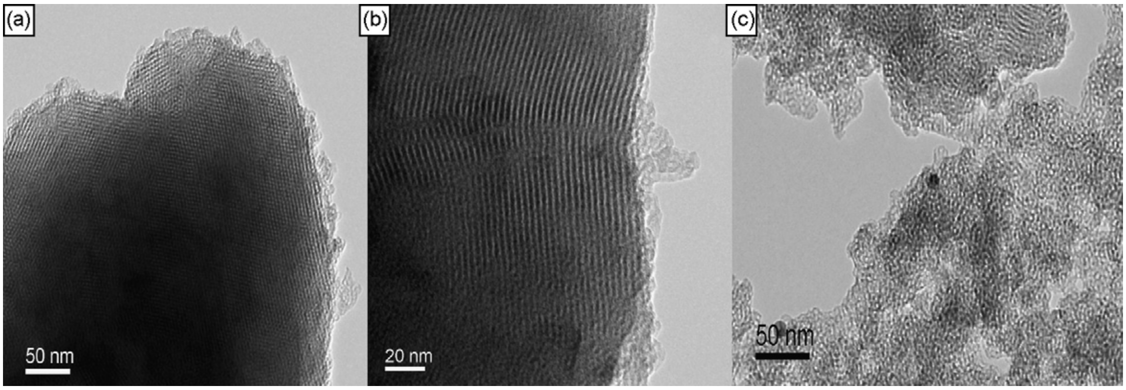

Fig. 3. TEM images of Al-MSU-S (a and b) and Ag^+ exchanged Al-MSU-S (c).

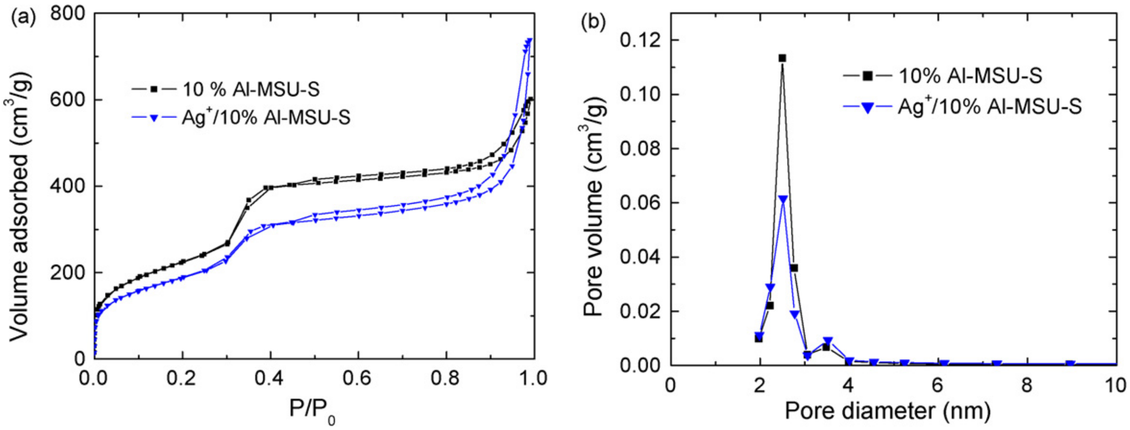

Fig. 4. Nitrogen adsorption/desorption isotherms at −196 °C (a) and pore distribution (b) of 10%Al-MSU-S and Ag^+/10%Al-MSU-S.

pressure and hysteresis loop above P/P_0 being 0.4, which are the characteristics of microporous and mesoporous materials. According to BJH analysis of the desorption branch of isotherms, the mesopore distribution was very uniform and centered at about 2.5 nm, as shown in Fig. 4(b).

ICP analyses were carried out to determine the exchange ratio of Al-MSU-S samples. The content of silver in the exchanged sample Ag^+/10%Al-MSU-S is 11.34 wt%, indicating that the Ag^+ exchange is almost 100%. After Ag^+ exchange, the reflections in XRD pattern of Ag^+ exchanged Al-MSU-S (shown in Fig. 1) are broader than that of corresponding Al-MSU-S, illuminating the decrease of structural order, which was further confirmed by TEM image shown in Fig. 3c. The Ag^+ exchanged Al-MSU-S sample only showed wormlike mesopore, similar to the mesoporous molecular sieve with low structure symmetry. However, the decrease of structural order had little influence on the pore structure of Ag^+ exchanged Al-MSU-S. As shown in Fig. 4, Ag^+/10%Al-MSU-S shows similar character in N_2 sorption isotherms and pore size distributions to 10%Al-MSU-S. The decrease of BET surface area from 819 to 685 m^2/g is in accord with the increase of sample density after Ag^+ exchanged.

The samples were tested for selective desulfurization of TP or DBT containing model gasoline by adsorption. Fig. 5 shows adsorption capacities of TP and DBT from model gasoline with

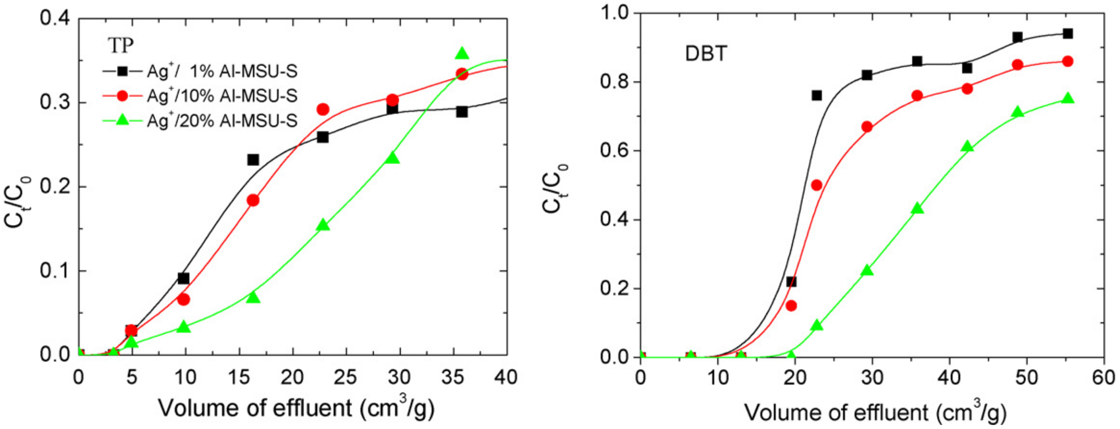

Fig. 5. Breakthrough curves of thiophene (TP) and dibenzothiophene (DBT) with different adsorbents in a fixed-bed adsorber for model gasoline at room temperature.

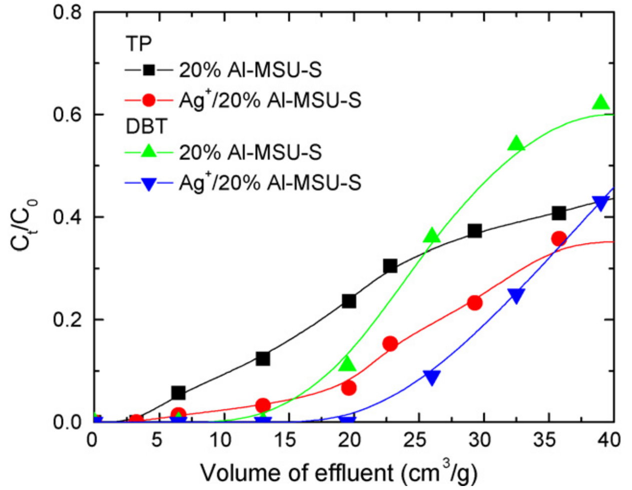

Fig. 6. Breakthrough curves of TP and DBT with 20%Al-MSU-S and Ag^+/20%Al-MSU-S in a fixed-bed adsorber for model gasoline at room temperature.

cumulative effluent volume. The sulfur capacity of the adsorbents increased with the incorporation of Al contents into the framework. Compared with DBT, the smaller molecular TP easily and early broke through the detection limitation, following that of molecular weights (or polarizabilities) [28]. The TP or DBT removal by three Ag^+/Al-MSU-S samples is 100% at the beginning, but for TP, the sulfur content is below the GC-FPD detection limitation in our experiments after a cumulative effluent volume of 5 ml/g for Ag^+/20%Al-MSU-S, 3.5 ml/g for Ag^+/10%Al-MSU-S and Ag^+/1%Al-MSU-S; for DBT, the sulfur content still remains below the GC-FPD detection limitation after a cumulative effluent volume of 20 ml/g for Ag^+/20%Al-MSU-S, 13 ml/g for Ag^+/10%Al-MSU-S and Ag^+/1%Al-MSU-S. All these indicate that mesopore material Ag^+/Al-MSU-S is promising for removal of larger molecular thiophenic derivatives because of stronger π-complexation interaction besides its geometric structure.

To better understand the effect of Ag^+ exchange and the guard bed on the selective adsorption, it is necessary to investigate the breakthrough curves of TP and DBT for the Ag^+/Al-MSU-S and Al-MSU-S or quartz sand bed individually. As shown in Fig. 6, for Ag^+/20%Al-MSU-S, the sulfur adsorption capacity for TP or DBT is almost twice as that of 20%Al-MSU-S. It is thought that the long delay of the breakthrough of the thiophenic compounds is the result of π-complexation type interactions with the sulfur species.

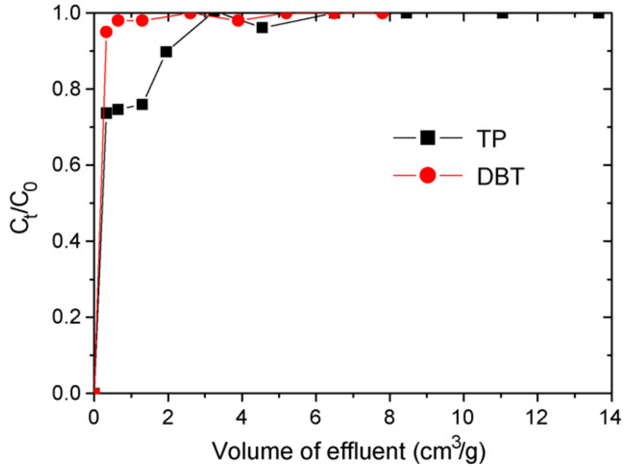

Fig. 7. Breakthrough curves of TP and DBT with the quartz sand in a fixed-bed adsorber at room temperature.

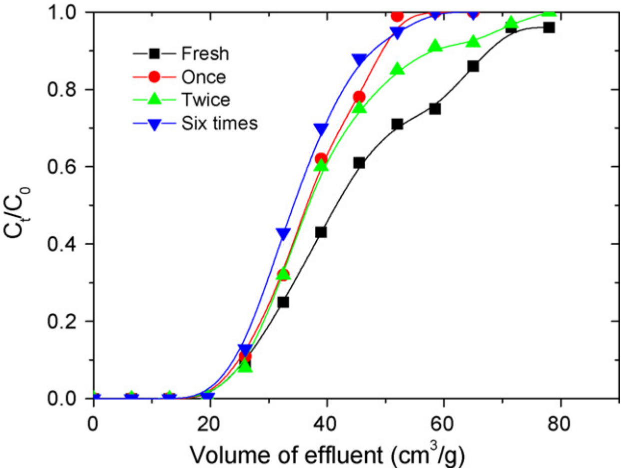

Fig. 8. Breakthrough curves of DBT with fresh and regenerated adsorbents Ag^+/20%Al-MSU-S in a fixed-bed adsorber at room temperature.

For quartz sand, the breakthroughs of thiophenic compounds occur quickly because there is no selectivity to the thiophenic compounds in the model gasoline (see Fig. 7). Therefore, the guard bed did not influence the concentration of sulfur in the effluent before sulfur breakthrough.

The regeneration performance of the adsorbent is important for economical utility. The adsorbent, Ag^+/20%Al-MSU-S, saturated with the organosulfur molecules was regenerated by calcination using dry air at 350 °C to completely remove the sulfur species. Then the regenerated adsorbent was cooled to room temperature and used to adsorb DBT from model gasoline. The results are shown in Fig. 8. It can be seen that the regenerated Ag^+/20%Al-MSU-S has no obvious loss of DBT adsorption capacity after regeneration for six times, although it has a little decrease in the later effluent, suggesting that the adsorbent provided in the experiment has good regeneration performance.

4. Conclusion

The adsorption performance for sulfur removal from the model gasoline including TP or DBT can obviously be improved with the increase of Al content in the silicate framework of Al-MSU-S. And Ag^+ exchange can effectively improve the sulfur containing compounds adsorption capacity of mesoporous Al-MSU-S because of π-complexation. The best adsorbent, Ag^+/20%Al-MSU-S, has adsorption capacity of 5 ml model gasoline containing TP and 20 ml model gasoline containing DBT per gram adsorbent below the GC-FPD detection limitation, respectively. The effective removal of bulk thiophenic derivatives is ascribed to their strong π-complexation interaction with adsorbent besides the geometric structure. The prepared adsorbents have good regeneration ability. All the results show that mesostructural Ag^+/Al-MSU-S is suitable for removal of sulfur containing compounds, especially for the bulk thiophenic derivatives, and a promise for deep desulfurization of transportation fuels.

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