High-Efficiency Desulfurization by Adsorption with Mesoporous Aluminosilicates

Wangliang Li, Qingfen Liu, Jianmin Xing, Hongshuai Gao, Xiaochao Xiong, Yuguang Li, Xin Li, and Huizhou Liu
National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences,
P.O. Box 353, Beijing 100080, China

DOI 10.1002/aic.11319

Mesoporous aluminosilicate (MAS) was synthesized by hydrothermal method with zeolite NaY as precursor and CTMAB (cetyltrimethylammonium bromide) as structure directing agent. Desulfurization adsorbents were characterized with XRD, BET, FTIR and NH_3-TPD. FTIR results showed that Lewis acid sites act as adsorption centers for dibenzothiophene (DBT) molecules. The adsorption desulfurization ability of MAS was studied in model and hydrotreated diesel. For model oil containing 10mmol/L DBT, the adsorption capacity of adsorbents is NaY > MAS > MCM-41. For hydrotreated diesel, MAS shows the largest adsorption capacity, MCM-41 the second, and NaY shows the least adsorption capacity. The improvement of desulfurization ability of improvement of MAS by Cu(I) is more significant than that of MCM-41. The physicochemical properties of fuels, such as viscosity and aromatics concentration had great influence on the desulfurization property of adsorbents. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 3263–3268, 2007

Keywords: desulfurization, adsorption, dibenzothiophene, aluminosilicates, acidity

Introduction

Vast amounts of sulfur oxides released into the atmosphere by combustion of fossil fuels are the principal source of acid rain. Ultra-deep removal of sulfur from transportation fuels has become very imperative for the petroleum refining industry due to the increasing stringent environmental regulations. Hydrodesulfurization (HDS) is a conventional method to remove sulfur compounds for industrial purpose. The main drawbacks of HDS include high-temperature (>300°C), high-pressure (>4MPa), high-energy cost and difficulty to remove aromatic heterocyclic sulfur compounds, such as substituted dibenzothiophenes (DBTs).[1] In order to achieve the "no sulfur" specification, some new technologies, such as adsorption desulfurization,[2–4] biodesulfurization,[5] extraction with ionic liquids,[6,7] and complex formation[8,9] were proposed to remove sulfur compounds from fuels.

Modified Y-type zeolite was popularly used as adsorbents to remove sulfur and nitrogen compounds from fuels. Yang et al. reported that Cu(I) and Ag-exchanged Y-type zeolites were very effective to remove thiophenes, including 4,6-dimethyldibenzothiophene (4,6-DMDBT). The used adsorbents could be regenerated by heating at 350°C under flowing air.[10–13] Song et al. reported the selective adsorption process for removing sulfur at ambient temperature (SARS) to achieve ultraclean diesel and gasoline.[14–17] Mekinley et al. reported selective removal of DBT and 4,6-DMDBT from simulated feedstock with Ag^+/SBA-15 and Ag^+/SiO_2 as adsorbents. Adsorption properties have close relationship with acidic properties of adsorbents.[18]

Modified Y-typed zeolite and mesoporous molecular sieves, such as MCM-41 and SBA-15 can effectively remove sulfur compounds from hydrotreated gasoline and model fuels. The amorphous interior walls which lead to poor

---

Correspondence concerning this article should be addressed to J. Xing at jmxing@home.ipe.cn and H. Liu at hzliu@home.ipe.ac.cn

stability and weak acidity inhibit the application of mesoporous molecular sieves. The relatively weak acidity of mesoporous materials, such as MCM-41 compared with zeolite can be attribute to the amorphous nature of the pore walls. To improve the stability and acidity of mesoporous molecular sieves, much effort has been made including post-synthesis grafting of aluminum to the silica wall,[19] conversion of the amorphous matrix to nanosize zeolite phase partially and synthesis of mesoporous molecular sieves with zeolite precursor, such as MAS series.[20–22] The improvement of acidity was due to the introduction of micropouous zeolite precursor. The comparison of adsorption desulfurization properties of micro- and mesoporous materials, and the desulfurization properties of mesoporous aluminosilicates has not been reported.

Here MAS was synthesized by hydrothermal method and characterized by XRD, BET and NH_3-TPD. The desulfurization properties of MAS, MCM-41 and NaY, and the effects of Cu(I) modification were tested with model and hydrotreated diesel.

Experimental

Materials

NaY zeolite and sodium silicate solution (27 wt % SiO_2 and 14 wt % NaOH) were obtained from Catalyst Plant of Qilu Petrochemical Company CNPC. DBT and naphthalene were purchased from Acros Organics, USA. *n*-Octane was purchased from Shanghai Reagents Co., China National Pharmaceutical Group Corporation. Methanol was HPLC grade; sodium chloride and ethanol was analytical reagent grade.

Preparation of molecular sieves MCM-41 and MAS

MCM-41 with Si/Al ratio of 50 was synthesized following the method as in ref. 23. CTABr (cetyltrimethylammonium bromide, purity = 99%) was used as structure directing agent, sodium silicate solution as silica source and pseudobohemite (Catapal B) as aluminum source. The sol-gel was crystallized under 120°C for 24h. The as-synthesized material was calcinated under N_2 atmosphere at 550°C for 1 h, and then in the air at the same temperature for 6 h.

MAS was synthesized by two-step method.[24] Nanocluster zeolite Y seeds were prepared through the reaction of NaOH (0.088 mol) and $NaAlO_2$ (0.10 mol) in H_2O (8.5 mol) with silicate anions (0.9 mol) in the form of sodium silicate solution. The solution was aged overnight. Then, the seed solution was added to CTMAB (0.27 mol) solution. The pH value was lowered to 10 with sulfuric acid. The mixture was placed at 100°C for 24 h. The as-synthesized MAS was calcinated under N_2 atmosphere at 550°C for 1 h, and then in the air at the same temperature for 6 h.

Ion-exchanging process

Cu(I)-MAS, Cu(I)-MCM-41 and Cu(I)-Y were prepared by ion exchanging of MAS, MCM-41 and NaY with $Cu(NO_3)_2$ aqueous solution (0.5 mol·L^{-1}) for 24 h, and followed by reduction of Cu^{2+} to Cu^{+} in He atmosphere. The amount of copper in the solution was equivalent to a five- to 10-fold cation exchange capacity. The ion exchange process was operated at room-temperature. Then the adsorbents were dried at 100°C for 24 h, and reduced in He atmosphere at 450°C for 3 h.

Characterization

Powder X-ray diffraction (XRD) patterns were recorded by a Shimadzu XD-3A diffractometer equipped with Cu Ka radiation (k = 0.154168 nm), and Ni filter and operated at 40 kV and 40 mA.

The Brunauer-Emmett-Teller (BET) surface areas and N_2 sorption isotherms were measured with liquid nitrogen using a Micromeritics ASAP2010 analyzer. The samples were degassed at 573 K until a vacuum of 10^{-3} Torr before analysis. The pore-size distribution was calculated using the Barrett-Joyner-Halenda (BJH) model from absorption data.

Temperature-programmed desorption of ammonia (NH3-TPD) was carried out to evaluate the total acidity of the supports. Catalysts were reduced at 400°C in a hydrogen flow (50 mL/min) for 40 min. After cleaning with helium and adsorption of ammonia at 100°C, the NH3-TPD was performed between 100 and 550°C, with a heating rate of 10°C/min by using a helium flow. The evolved ammonia was analyzed by online gas chromatography (Shimadzu GC-14A) provided with a thermal conductivity detector (TCD).

Nature and strength of the acidity of the adsorbents were determined by pyridine adsorption. The sample was heated to 400°C in flow of inert gas (N_2) for 2 h. It was cooled to 100°C and pyridine was adsorbed on the sample. The physisorbed pyridine was removed by flushing the adsorbents with N2 for 30 min at 100°C. The spectra were recorded after maintaining the temperature for 30 min. FTIR spectra of the adsorbents were collected on a Vector 22 instrument (Bruker Corporation, Germany) using the KBr pellet technique. About 10 mg of the sample was ground with 200 mg of spectral grade KBr to form a pellet to record the IR spectrum in the range of 1,400–1,700 cm^{-1}.

Adsorption Process

The adsorption capacity of adsorbents MAS, MCM-41 and NaY were tested with DBT as model compound. The concentration of DBT in *n*-octane is 10 mmol/L. Ratio of oil to adsorbents was 40 mL/g.

The ability to remove sulfur compounds from hydrotreated diesel was tested with 207 and 315ppm diesel as feedstocks.

Analytical methods

High-performance liquid chromatography (HPLC) was used for the quantitative assay of DBT in the *n*-octane phase. HPLC was performed on a Agilent 1100 (HP1100, Agilent, USA) liquid chromatography equipped with an autosampler, a reversed- phase Zorbax SB-C18 column (4.6 mm × 150 mm; 3.6 μm), and a diode array detector. The mobile phase was 90% of methanol in water (v/v, %) with a flow rate of 1.0 mL·min^{-1}. For the quantification of DBT, the external standard method was used at 280 nm.

The total sulfur content (by weight) in diesel was measured in triplicate for each sample by combustion of samples and measurement of the released sulfur dioxide with a micro-

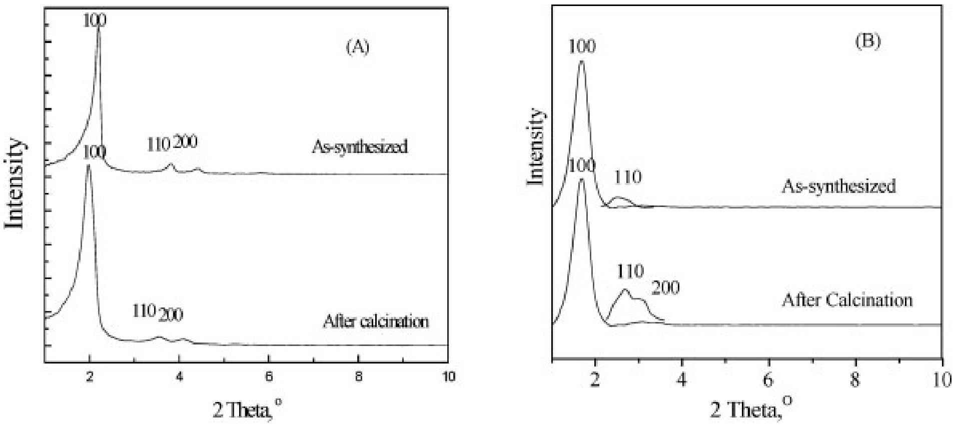

Figure 1. XRD patterns of molecular sieves.

(A) MCM-41; (B) MAS.

coulomb analyzer (RPA-200, JiangHuan Electroanalysis, China).

Results and Discussion

Characterization of adsorbents

The XRD patterns of mesoporous molecular sieves MCM-41 and MAS are shown in Figure 1. There are three resolved peaks at 2θ from 0.5 to 5 that can be indexed to 100, 110 and 200. It can be concluded that MCM-41 and MAS exhibit hexagonal arrays with uniform pore size.[25]

The texture properties were characterized by nitrogen adsorption-desorption analysis. The texture results are summarized in Table 1. MCM-41 and MAS possess mesoporous structure. The pore diameter of MCM-41 and MAS are 3.51 nm and 3.27 nm, repectively, which are much larger than that of NaY zeolite. BET surface area of MCM-41 and MAS are 940 m^2/g and 906 m^2/g, repectively, while it is 647 m^2/g for NaY zeolite.

NH_3-TPD is frequently used to characterize the acid strength, as well as the amount of acid sites on a solid surface. Due to its strong basicity and small molecular dimension (3.70 Å × 3.99 Å × 3.11 Å), ammonia is a suitable probe molecule for all acid sites on zeolite. Figure 2 reports the NH_3-TPD for three adsorbents used in this work. It can be seen that the NaY sample gives a spectrum composed of four desorption peaks with maxium at about 140, 185, 230 and 320°C. The spectrum of MCM-41 sample has only two peaks with maxium at about 140 and 180 °C. The spectrum of MAS has four desorption peak with maxium at about 130, 170, 220 and 310°C. The number of acid sites can be determined by the areas under the NH_3-TPD curve. The amount of desorbed ammonia directly related to the number of acid sites on the sample. NaY curve shows the largest area. MCM-41 curve shows the least area. It can be deduced that the of acid sites of the adsorbents is NaY > MAS > MCM-41.

Table 1. Textural Properties of Adsorbents MAS, MCM-41 and NaY

	MCM-41	MAS	NaY
Pore diameter (nm)	3.51	3.27	0.79
Pore volume (cm^3/g)	0.79	0.82	0.34
Surface area (m^2/g)	940	906	647

FT-IR characterization of adsorbents acidity

FTIR analysis of adsorbed pyridine was conducted to elucidate the nature and relative amounts of Brønsted and Lewis acid sites in the adsorbents. Generally, the bands around 1,540–1,548, and 1,445–1,460 cm^{-1} are characteristic of Brønsted (Py-H^+) and Lewis (L-Py) acid sites, respectively.[26] Accordingly, Lewis-bonded pyridine can be properly determined from a record of the infrared spectra at sufficiently high-temperatures. As shown in Figure 3, the strength of the peak at 1,540 cm^{-1} of fresh and spent adsorbents is similar. The peak at 1,450 cm^{-1} is very strong, which means that fresh adsorbent Cu(I)-MAS shows strong Lewis acid. When the adsorbent is saturated with DBT molecules, the strong peak at 1450 cm^{-1} disappeared. It can be deduced that the Lewis acid sites act as active centers for DBT molecules.

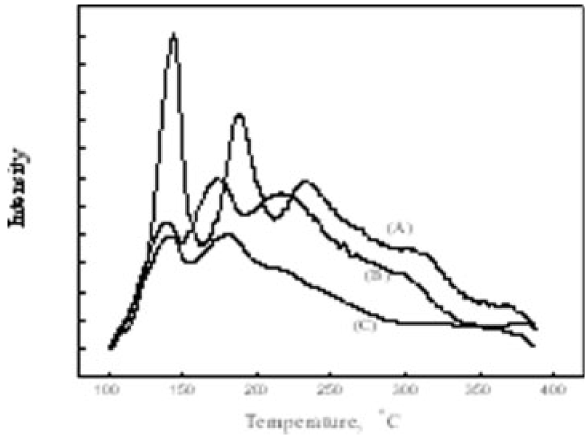

Figure 2. NH_3-TPD curves of adsorbents.

(A) NaY; (B) MAS, and (C) MCM-41.

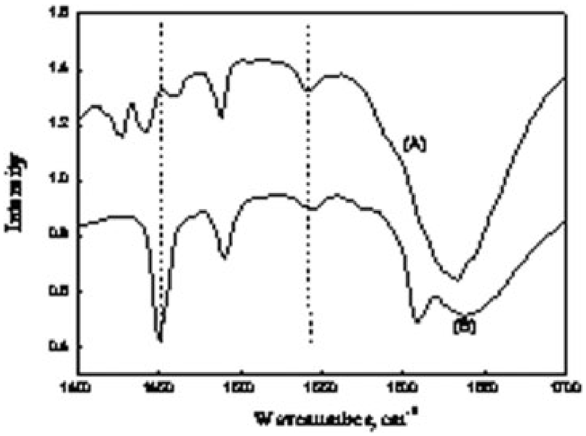

Figure 3. FTIR spectra of adsorbed pyridine on fresh and DBT saturated adsorbents NaY.

(A) adsorbents first saturated with DBT, and then with pyridine, and (B) adsorbents saturated with pyridine.

Desulfurization ability from model oil. The adsorption desulfurization properties of NaY, MCM-41 and MAS were studied with model oil of 10.07 mmol/L DBT in octane. The ratio of oil to adsorbents was 40 mL/g. Figure 4 shows the adsorption desulfurization patterns of the adsorbents. The adsorption desulfurization process reached equilibrium within 6 min. NaY shows the best adsorption capacity, MAS the second and MCM-41 the least. DBT was adsorbed on the acid sites of adsorbents. It can be deduced that the adsorption capacity has close relationship with acidity of the adsorbents.[18]

Viscosity of diesel is much higher than that of model oil, which can decrease the adsorption capacity. Liquid paraffin, a mixture of heavier alkane hydrocarbons, was used to change the viscosity of diesel. Paraffin, compared with olefin, aromatics and sulfur compounds, seldom can be adsorbed on π complexation adsorbents. Paraffin is often used as solvent in desulfurization studies.[3,27] The effects of viscosity on the adsorption capacity was sutided with NaY as adsorbents, and 8.0 mmol/L DBT as a model oil. Oil to adsorbents ratio was 60 mL/g. As shown in Figure 5, concentration of DBT in the products increases with the increase of liquid paraffin concentration. It can be concluded that adsorption capacity of NaY decreases with the increase of viscosity of diesel.

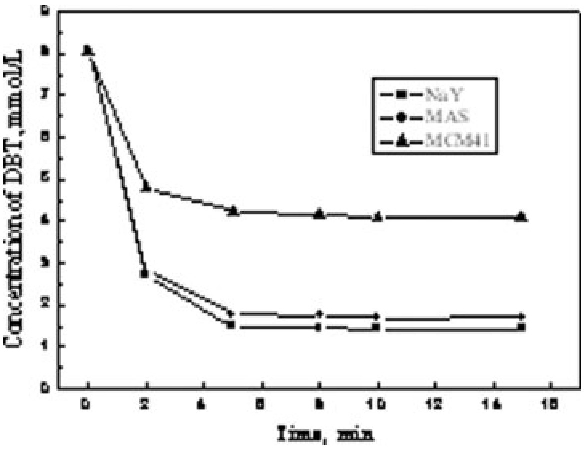

Figure 4. Desulfurization of model fuel with NaY, MCM-41 and MAS.

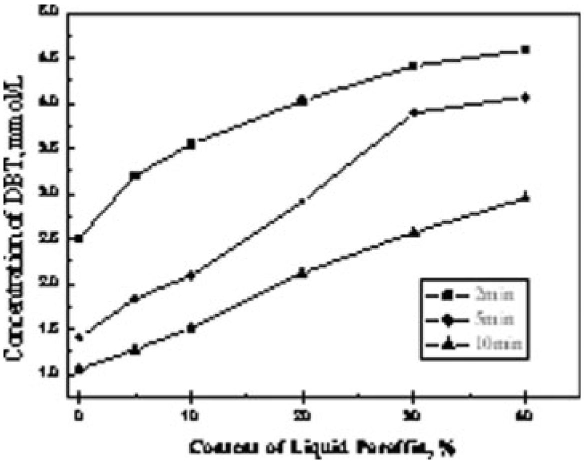

Figure 5. Effects of viscosity on adsorption desulfurization properties.

Desulfurization ability from hydrotreated diesel

Adsorption properties of NaY, MCM-41 and MAS for hydrotreated diesel were studied at 30°C. Oil to adsorbents ratio was 20 mL/g. As shown in Figure 6, the sulfur concentration of diesel decreased from 207 ppm to 93, 98 and 135 ppm, respectively, within 10 min by the adsorption of MAS, MCM-41 and NaY. Adsorption desulfurization properties of MAS and MCM-41 are much better than microporous molecular sieves NaY. It can be concluded that adsorption desulfurization capacity is MAS > MCM-41 > NaY. There are large amounts of polycyclic aromatics and trace amounts of resins in diesel. The compounds can competitively adsorbed on the adsorbents and have significant influence on adsorption capacity. The pore diameter is small, which can be blocked easier than MAS and MCM-41. The pore dia-

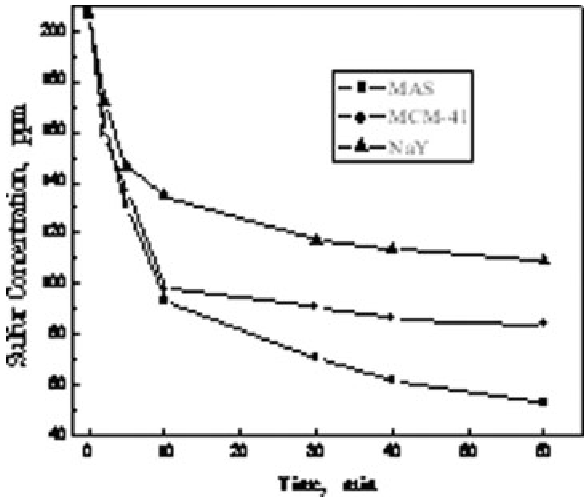

Figure 6. Adsorption desulfurization properties of different adsorbents.

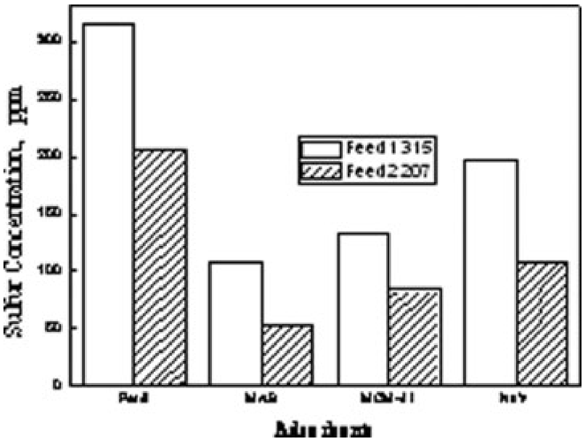

Figure 7. Adsorption properties of NaY, MCM-41 and MAS toward hydrotreated diesel.

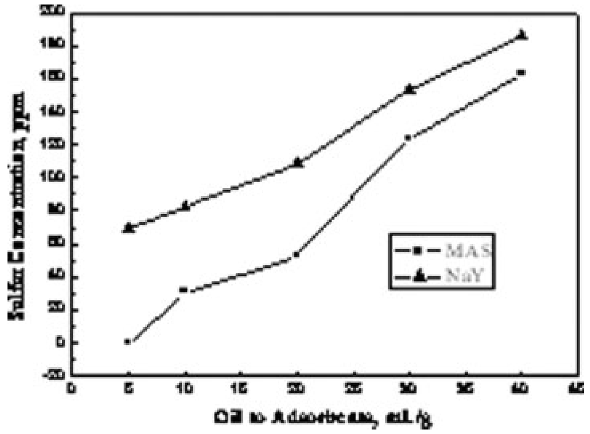

Figure 8. Effects of oil to adsorbents ratio on the adsorption desulfurization.

meters of MAS and MCM-41 are much larger than NaY zeolite. Desulfurization ability of MAS and MCM-41 are better than NaY zeolite. The number of acid sites of MAS is larger than that of MCM-41. Desulfurization capacity of MAS is better than that of MCM-41.

Adsorption desulfurization properties were influenced by sulfur and aromatics concentrations in the diesel, which is determined by the hydrotreated extent. Adsorption desulfurization properties for diesel with sulfur concentration of 315 and 207 ppm were studied with equilibrium method. Oil to adsorbents ratio was 20 mL/g. As shown in Figure 7, for adsorbents MAS, MCM-41 and NaY, the sulfur concentration was decreased from 315 to 109, 133 and 196 ppm, respectively. For the 207 ppm diesel, the sulfur concentration of the treated diesel was 53, 84 and 109 ppm. It can be seen that mesoporous molecular sieves MAS showed better desulfurization activity than MCM-41 and NaY.

Oil to adsorbents ratio is an important factor in adsorption desulfurization, which can have significant influence not only on desulfurization content but also on operation cost. The effects of oil to adsorbents ratio on the desulfurization properties of MAS and NaY were studied with hydrotrated diesel at 30°C. Oil to adsorbent ratio selected were 5, 10, 20, 30 and 40. As shown in Figure 8, for MAS adsorbents, when the ratio was 40, 30, 20, 10 and 5, the sulfur concentration of the diesel after treated with MAS are 163, 124, 53, 31 and 0ppm, respectively. The sulfur concentrations of the diesel treated with NaY are 186, 156, 109, 83 and 69 ppm. With the decrease of oil to adsorbents ratio, sulfur concentration decreased sharply, especially for MAS as adsorbents.

Adsorption desulfurization properties can be improved by modification with transitional metals through ion-exchanging and impregnation methods. For ion-exchanging method, the modification was determined by the amount of exchangeable ions in the framework of molecular sieves. The adsorption properties of the adsorbents were studied with equilibrium method. As shown in Figure 9, for 315 ppm diesel, with the adsorption of MAS and Cu(I)-MAS, the sulfur concentration was decreased from 315 ppm to 109 ppm and 54 ppm and for 207 ppm, the sulfur concentration decreased to 53 ppm and 30 ppm. After adsorption with MCM-41, the sulfur concentration is 133 and 71 ppm, while treated with Cu(I)-MCM-41, the sulfur content is 117 and 71 ppm.

Adsorption properties can be significantly improved by Cu(I) modification. The improvement of MAS is more significant than that of MCM-41. The main reason is due to the NaY nanocrystaline on the surface of MAS, which provides large amounts of ion-exchangable ions Na^+.

Conclusions

The physicochemical and texture properties and ions status of adsorbents have great influence on the adsorption properties in the process of desulfurization. For model diesel, the adsorption capacity of adsorbents is NaY > MAS > MCM-41. Adsorption capacity has close relationship with acidity of the adsorbents. MAS and MCM-41 show better efficiency in removal sulfur compounds from hydrotreated diesel than NaY. For 207 ppm hydrotreated diesel, the adsorption desulfurization activity of adsorbents is MAS > MCM-41 > NaY. The improvement of desulfurization ability of improvement of MAS by Cu(I) is more significant than that of MCM-41. MAS show more excellent adsorption properties than popularly used Y typed-zeolite and mesoporous molecular sieves in sulfur removal of hydrotreated diesel.

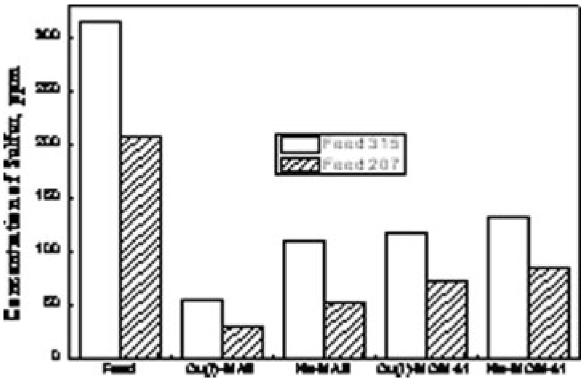

Figure 9. Adsorption desulfurization properties of the adsorbents modified with Cu(I).

Acknowledgments

This work was supported by the financial support of the National High Technology Research and Development Program of China (20060102Z2042) and State Major Basic Research Development Program of China (Grant No. 2006CB202507).

Literature Cited

1. Dhar GM, Srinivas BN, Rana MS, Maity SK. Mixed oxide supported hydrodesulfurization catalysts-a review. *Catalysis Today*. 2003;86:45–60.
2. Yang RT, Herna'ndez-Maldonado AJ, Cannella W. Desulfurization of transportation fuels with zeolite under ambient conditions. *Science*. 2003;301:79–81.
3. Shan G, Liu H, Xing J, Zhang G, Wang K. Separation of polycyclic aromatic compounds from model gasoline by magnetic alumina sorbent based on π-complexation. *Ind Eng Chem Res*. 2004;43(3):758–761.
4. Song C, Ma X. New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization. *Appl Catal B: Environ*. 2003;41(1–2):207–238.
5. Gray KA, Pogrebinsky OS, Mrachlko GT, Xi L, Monticello DJ, Squires CH. Molecular mechanisms of biocatalytic desulfurization of fossil fuels. *Nat Biotechnol*. 1996;14:1705–1709.
6. Zhang S, Zhang Q, Zhang Z. Extractive desulfurization and denitrogenation of fuels using ionic liquids. *Ind Eng Chem Res*. 2004;43: 614–622.
7. Huang C, Chen B, Zhang J, Liu Z, Li Y. Desulfurization of gasoline by extraction with new ionic liquids. *Energy & Fuels*. 2004;18:1862–1864.
8. Vicic DA, Jones WD. Room-temperature desulfurization of dibenzothiophene mediated by [(i-Pr2PCH2)2NiH]2. *J Am Chem Soc*. 1997; 119:10855–10856.
9. Garcia JJ, Mann BE, Adams H. Equilibria of the thiametallacycles with tris(triethylphosphine)-platinum(0) and dibenzothiophene, benzothiophene, or thiophene: the hydridesulfurization Reaction. *J Am Chem Soc*. 1995;117:2179–2186.
10. Herna'ndez-Maldonado AJ, Yang RT. Desulfurization of diesel fuels by adsorption via π-complexation with vapor-phase exchanged Cu(I)-Y zeolites. *J Am Chem Soc*. 2004;126:992–993.
11. Herna'ndez-Maldonado AJ, Yang RT. Desulfurization of commercial liquids fuels by adsorption via π-complexation with Cu(I)-Y. *Ind Eng Chem Res* 2003;42(13):3103–3110.
12. Herna'ndez-Maldonado AJ, Yang RT. New sorbents for desulfurization of diesel fuels via π-complexation. *AIChE J*. 2004;50(4):791–801.
13. Herna'ndez-Maldonado AJ, Yang RT, Cannella W. Desulfurization of commercial jet fuels by adsorption via π-complexation with vapor phase ion exchanged Cu(I)-Y zeolites. *Ind Eng Chem Res*. 2004;43: 6142–6149.
14. Ma X, Sun L, Song C. A new approach to deep desulfurization of gasoline, diesel fuel and jet fuel by selective adsorption for ultra-clean fuels and for fuel cell applications. *Catal Today*. 2002;77:107–116.
15. Song C. An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. *Catal Today*. 2003;86: 211–263.
16. Ma X, Sprague M, Song C. Deep desulfurization of gasoline by selective adsorption over nickel-based adsorbent for fuel cell applications. *Ind Eng Chem Res*. 2005;44(15):5768–5775.
17. Velu S, Ma X, Song C, Namazian M, Sethuraman S, Venkataraman G. Desulfurization of JP-8 jet fuel by selective adsorption over a Ni-based adsorbent for micro solid oxide fuel cells. *Energy & Fuels*. 2005;19:1116–1125.
18. McKinley SG, Angelici RJ. Deep desulfurization by selective adsorption of dibenzothiophenes on Ag+/SBA-15 and Ag+/SiO2. *Chem Commun*. 2003;20:2620–2621.
19. Chen L, Horiuchi T, Mori T, Maeda K. Post-synthesis hydrothermal restructuring of M41S mesoporous molecular sieves in water. *J Phys Chem B*. 1999;10:1216–1222.
20. Han Y, Wu S, Sun Y, Li D, Xiao F. Hydrothermally stable ordered hexagonal mesoporous aluminosilicates assembled from a triblock copolymer and preformed aluminosilicate precursors in strongly acidic media. *Chem Mater*. 2002;14:1144–1148.
21. Lee C, Lang J, Yen C, Shih P, Lin T, Mou C. Enhancing stability and oxidation activity of cytochrome *c* by immobilization in the nanochannels of mesoporous aluminosilicates. *J PhysChem B*. 2005; 109:12277–12286.
22. Zhang Z, Han Y, Xiao F, Qiu S, Zhu L. Mesoporous aluminosilicates with ordered hexagonal structure, strong acidity, and extraordinary hydrothermal stability at high temperatures. *J AmChem Soc*. 2001;123:5014–5021.
23. Corma A, Martinez A, Martinez-Soria V, Monoton J B. Hydrocracking of vacuum gasoline on the novel mesoporous MCM-41 aluminosilicate catalyst. *J Catal*. 1995;153:25–31.
24. Liu Y, Zhang W, Pinnavaia T J. Steam-stable aluminosilicate mesostructures assembled from zeolite type Y seeds. *J Am Chem Soc*. 2000;122:8791–8792.
25. Kresge CT, Leonowica ME, Roth WJ, Vartuli JC, Beck JS. Ordered mesoporous molecular sieves synthesized by liquid-crystal template mechanism. *Nature*. 1992;359:710–712.
26. Tarafdar A, Panda A B, Pramanik P. Synthesis of ZrO2-SiO2 mesocomposite with high ZrO2 content via a novel sol-gel method. *Micropor Mesopor Mater*. 2005;79:101–110.
27. Herna'ndez-Maldonado AJ, Yang RT. Desulfurization of commercial jet fuels by adsorption via π-complexation with Cu(I)-Y zeolite. *Ind Eng Chem Res*. 2003;42:123–129.

Manuscript received Dec. 11, 2006, and revision received Aug. 10, 2007.