Ultra-Deep Desulfurization Adsorbents for Hydrotreated Diesel with Magnetic Mesoporous Aluminosilicates

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Magnetic mesoporous aluminosilicates (MMAS) were synthesized by hydrothermal method and applied as ultra-deep desulfurization adsorbents for hydrotreated diesel. The size of oleic-coated magnetic Fe_3O_4 nanoparticles prepared by coprecipitation method was about 20 nm. MMAS shows better desulfurization properties for removal of sulfur compounds than NaY and MCM-41. The amount of Fe_3O_4 nanoparticles has significant effects on specific surface area/pore volume and acidic properties, thus, can affect the desulfurization properties of MMAS. Desulfurization properties of MMAS can be improved with the increase of temperature from 30–70°C and decrease the oil to adsorbent ratio. With the increase of Fe_3O_4 content, adsorption capacity first increased and then decreased. The sulfur adsorption of MMAS was due to the synergetic effect of strong molecular affinity of the magnetite to the sulfur compound and large surface area/pore volume of the mesoporous aluminosilicates. © 2009 American Institute of Chemical Engineers *AIChE J,* 56: 1391–1396, 2010

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Introduction

To meet strigent emission standard stipulated by regulatory organics, ultra-deep removal of sulfur from transportation fuels has become very imperative for the petroleum refining industry. Although hydrodesulfurization (HDS) is a conventional method to remove sulfur compounds for industrial purpose, it is difficult to remove some hetercyclic sulfur compounds such as dibenzothiophene (DBT) and substituted DBTs in petroleum.[1] To achieve the ‘‘no sulfur’’ specification, some new technologies such as adsorption desulfurization,[2–4] biodesulfurization,[5] extraction with ionic liquids,[6–8] and complex formation[9,10] were proposed.

Modified Y-type zeolite was popularly used as adsorbents to remove sulfur from fuels via π-complexation. Yang and

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coworkers reported that Cu(I) and Ag-exchanged Y-typed zeolites were effective to remove sulfur compounds from gasoline.[11–13] Song and coworkers proposed the selective adsorption process for removing sulfur (SARS) at ambient temperature to achieve ultra-clean diesel and gasoline with NiY.[14–17] Modified Y zeolites have high adsorption capacity in model solutions and gasoline. But the pore can be blocked by large molecules such as polycyclic aromatics and trace amounts of resins in diesel. Thus, mesoporous materials attracted wide attention for their large pore diameter and specific area. Mesoporous materials Al-MCM-41, Ag^+/SBA-15, and Ag^+/SiO_2 were studied as desulfurization agents in view of its large pore volume and high specific surface area.[18–20] Yang reported that $PdCl_2$/SBA-15 and $PdCl_2$/MCM-41 were excellent adsorbents for desulfurizing very high sulfur commercial jet fuels such as an JP-5 light fraction that contained 847 ppmw S.[19] While, the amorphous interior walls of mesoporous molecular sieves can lead to poor stability and small acidic density. Thus, adsorption capacity is small. Mesoporous aluminosilicates (MAS) were synthesized with zeolite as precursor. MAS have the advantages of microporous zeolite and mesoporous materials. The specific surface area and diameter of MAS are larger than zeolite. The acidic density of MAS is higher than MCM-41. MAS were widely studied for large molecular reaction such as heavy oil cracking and adsorption.[3,21,22] MAS show higher adsorption capacity than MCM-41 and NaY for ultra-deep desulfurization from hydrotreated diesel.[3]

The magnetic materials can be easily separated and applied in many fields such as catalysis,[23] drug delivery,[24] and biodesulfurization.[25] Here, we report magnetite-mesoporous aluminosilicates as a new adsorbent for desulfurization of diesel. The synergetic effect of strong molecular affinity of the magnetite to the sulfur compound and large surface area/pore volume of the mesoporous aluminosilicates was studied.

Materials and Methods

Chemicals

NaY zeolite was kindly provided by Catalyst Plant of Qilu Petrochemical Company CNPC. Hydrotreated diesel was kindly provided by Research Institute of Petroleum Processing (RIPP). Methanol was HPLC grade. Other chemicals were of analytical reagent grade and commercially available.

Adsorbents preparation

The oleic acid-coated magnetic Fe_3O_4 nanoparticles were prepared by a coprecipitation method.[25] Under nitrogen gas, 23.5 g of $FeCl_3{\cdot}6H_2O$ and 8.6 g of $FeCl_2{\cdot}4H_2O$ were dissolved in 500 ml deionized water with mechanical stirring. When the solution was heated to 85°C, 15 ml $NH_3{\cdot}H_2O$ were added. Then, 8 ml oleic acid was added dropwise within 20 min. The reaction was kept at 85°C for 30 min. The black lump-like Fe_3O_4 gel was cooled to room temperature and washed several times with deionized water. Magnetic precipitate was modified with 7.1 mol/l $NH_3{\cdot}H_2O$ to form the hydrophilic magnetic nanoparticles, which in an aqueous solution were monodispersed.

MCM-41 with Si/Al ratio of 50 was synthesized following the method described in the work of Corma et al. (1995).[26] 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 1208C for 24 h. 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.[27] Nanocluster zeolite Y seeds were prepared by reacting 0.088 mol NaOH and 0.10 mol $NaAlO_2$ in 8.5 mol H_2O with 0.9 mol silicate anions in the form of sodium silicate solution. The clear solution was aged overnight. Then the seed solution was added to the 0.27 mol CTAB solution. The pH value was lowered to 10 with sulfuric acid. The mixture was placed at 100°C for 24 h. The MMAS was calcinated in a N_2 atmosphere at 550°C during 1 h followed by 6 h calcinations in the air at the same temperature.

The process of MMAS synthesis was similar to that of MAS. Certain amounts of magnetic nanoparticles were added into the suspension. During the process of synthesis of MMAS-1, 10-ml magnetic suspension was added into 100 ml silica-alumina suspension. For MMAS-2, 10 ml magnetic suspension was added into 100 ml silica-alumina suspension.

Characterization

Powder X-ray diffraction (XRD) patterns were recorded by a Shimadzu XD-3A diffractometer equipped with CuKa radiation ($k = 0.154$ 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 at the temperature of liquid nitrogen using a Micromeritics ASAP2010 analyzer.

The size and morphology of magnetic nanoparticles and magnetic cells were determined by transmission electronic microscopy (TEM) (Hitachi 8100, 200 kV). The Fe_3O_4 nanoparticles were prepared by evaporating a drop of a very dilute nanoparticle suspension on a carbon copper grid.

The size and surface features of MAS and MMAS were investigated by scanning electron microscope (SEM, JSM-6700F, JEOL, Tokyo, Japan).

Magnetic properties were measured with alternating gradient magnetometer (AGM, micromegTM 2900) at room temperature.

Adsorption methods

Adsorption properties of Ag-MAS, Ag-MCM-41, and Ag-Y were tested with hydrotreated diesel at 30°C. Ratio of adsorbents to oil is 20 ml g^{-1}. Table 1 shows the physical properties of hydrotreated diesel. Sulfur concentration of diesel is 36.89 ppm.

Analytical methods

The total sulfur content (by weight) was determined in triplicate for each sample by combustion of samples and measurement of the released sulfur dioxide using a micro-coulomb analyzer (RPA-200, JiangHuan Electroanalysis, China).

Table 1. Texture Properties of MAS, MMAS-1, and MMAS-2

	MAS	MMAS-1	MMAS-2
Pore diameter (nm)	2.90	3.12	2.65
Pore volume (cm^3/g)	0.64	0.62	0.56
Surface area (m^2/g)	916	610	551

Results and Discussions

Characterization of magnetic Fe_3O_4 nanoparticles

Superparamagnetic Fe_3O_4 nanoparticles were prepared by a coprecipitation method. Figure 1 shows the TEM image of the magnetic Fe_3O_4 nanoparticles. It can be seen that the nanoparticles are spherical in shape with an average size of 20 nm. It is known that magnetic particles less than about 25 nm will exhibit superparamagnetism.[28] Figure 2 shows the magnetic properties of iron nanocomposites tested by AGM magnetometer under different magnetic fields. Therefore, the prepared magnetic Fe_3O_4 nanoparticles have superparamagnetic properties.

Characterization of adsorbents

Figure 3 illustrates the X-ray diffraction (XRD) patterns of MAS, MMAS-1, and MMAS-2 after calcination. Figure 3A clearly indicates characteristic low-angle peaks of mesoporous materials. When the amount of magnetic suspension increased, the intensity of XRD patterns of all the samples decreased significantly. From Figure 3B, wide-angle XRD pattern, it can be seen that no diffraction peaks were observed in the region of higher angles 5–70 in XRD of MAS, suggesting that the growth of large microporous crystals was hindered during the process of synthesis, and the aluminosilicate precursors were mainly in the form of zeolite primary building units, which resulted in the formation of a highly ordered and pure phase of MAS. The wide angle peak at $2\theta = 25°$ less well defined and merge into a broad peak similar to amorphous silica ''halo'' peak, which suggests that the calcined materials are largely amorphous.[29] The peaks 2θ at 31.1, 36.6, and 46.2° was referred to hercynite. During the process of calcinations, hercynite can be formed through the reaction of Fe_3O_4 nanoparticles Al species.[30]

The SEM photographs in Figure 4 show the variation in morphology of MAS and MMAS-1. It can be seen that MAS

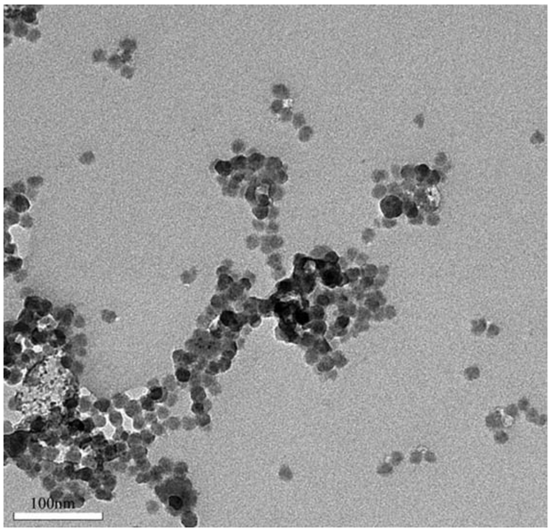

Figure 1. TEM image of magnetic Fe_3O_4 nanoparticles.

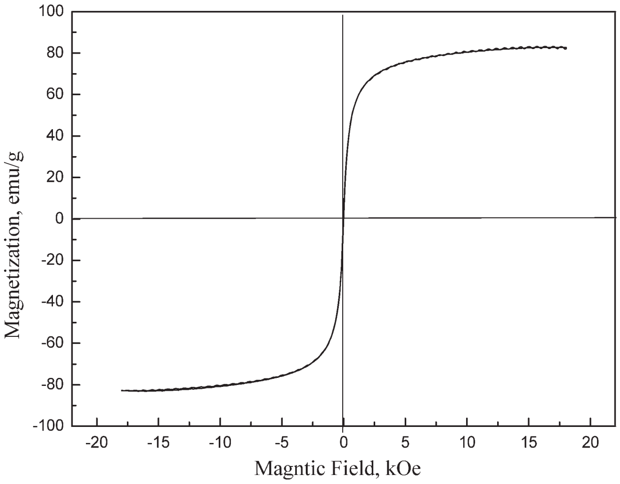

Figure 2. Magnetization curves of Fe_3O_4 nanoparticles determined with alternating gradient.

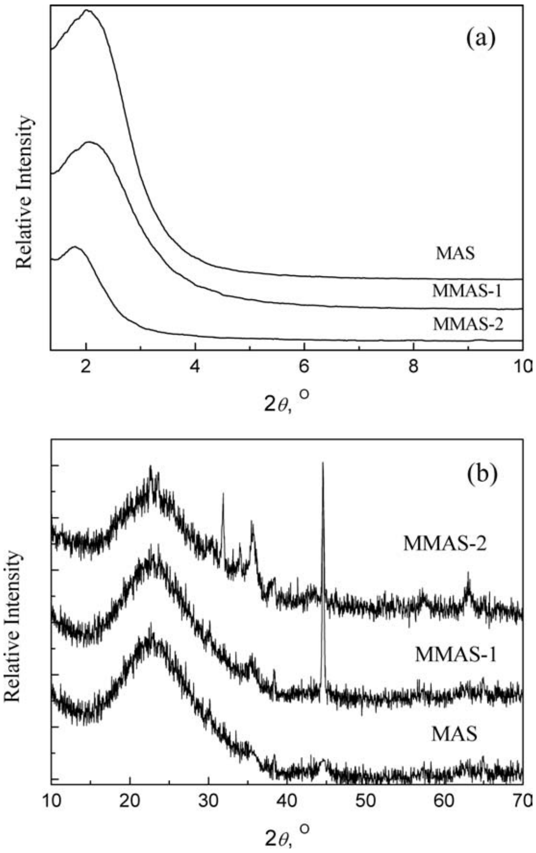

Figure 3. (a) Low-angle and (b) wide-angle X-ray diffraction patterns of MAS, MMAS-1, and MMAS-2.

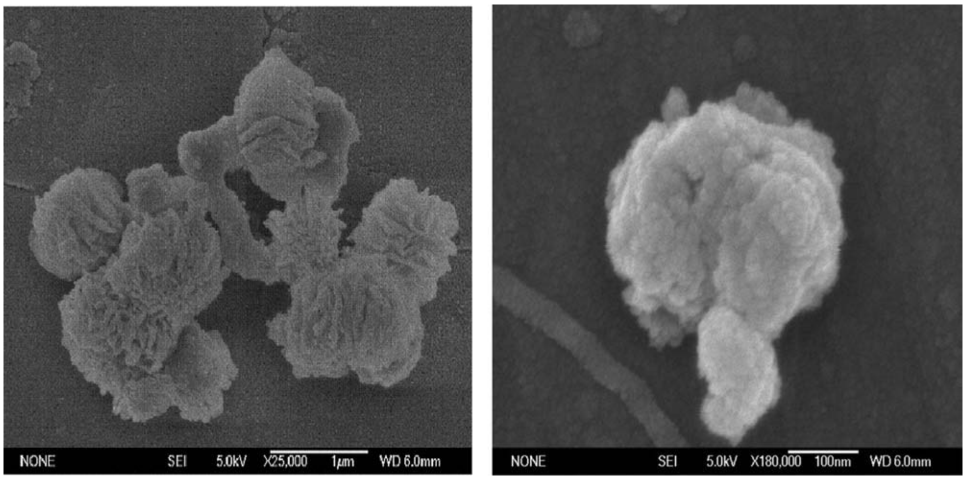

Figure 4. SEM images of MAS and MMAS-1.

and MMAS-1 was irregular spherical. The diameter of MAS and MMAS-1 was about 200–400 nm. The surface of MAS was smooth. While, the surface of MMAS-1 was seemed to be covered by nanoparticles.

FTIR of adsorbed pyridine was conducted to elucidate the nature and relative amounts of Brønsted and Lewis acid sites in the adsorbents. Generally, bands around 1540–1548 and 1445–1460 cm^{-1} are characteristic of Brønsted ($Py\text{-}H^+$) and Lewis (L-Py) acid sites, respectively.[31] Accordingly, Lewis-bonded pyridine can be properly determined from a record of the infrared spectra at sufficiently high temperatures, to character the acid sites of adsorbents. From Figure 5, it can be seen that the Lewis and Brönsted acids of MCM-41 is the weakest among the adsorbents. The intensity of the peak at 1540 cm^{-1} of MMAS is higher than that of MAS. Therefore, it can be concluded that the density of Lewis acid sites of MMAS is much higher than MAS. Part of the Lewis acid sites can be provided by magnetic nanoparticles. The density of Lewis and Brönsted acids of NaY zeolite is the highest which is in accordance with our previous study.[3]

Desulfurization properties of MMAS, MCM-41, and NaY

Adsorption of sulfur compounds from diesel is dependent on temperature. The effect of temperature on the adsorptions of sulfur compounds was investigated with MMAS-1 as adsorbent. The temperature was chosen as 30, 40, 50, and 70°C. Ratio of oil to adsorbents was chosen as 20 mL g^{-1}. As shown in Figure 6, for MMAS-1, when the temperature was 30, 40, 50, and 70°C, the sulfur concentration of the product is 11.98, 10.01, 8.79, 7.23, and 6.52 ppm, respectively. It can be concluded that desulfurization can be improved with the increase of temperature.

Oil to adsorbents ratio is an important factor in adsorption desulfurization, which cannot only influence on desulfurization content but also on operation cost. The effect of oil to adsorbents ratio on the desulfurization properties of MMAS-1 was studied with the ratio as 10, 20, 30, and 40 ml g^{-1}. As shown in Figure 7, for MMAS-1 adsorbents, when the ratio was 40, 30, 20, and10 ml g^{-1} the sulfur concentration of the diesel is 17.34, 15.63, 11.98, and 6.17 ppm, respectively. With the decrease of oil to adsorbents ratio, the concentration of sulfur decreased sharply.

Adsorption properties of NaY, MCM-41 MAS, and MMAS-1 for hydrotreated diesel were studied at 30°C. Oil to adsorbents ratio was 20 ml g^{-1}. As shown in Figure 8, by the adsorption of NaY, MCM-41, MAS, and MMAS-1, the sulfur concentration of diesel decreased from 36.89 to 24.46, 13.17, 6.89, and 9.67 ppm within 20 min, respectively. Adsorption desulfurization properties of MMAS-1, MAS, and MCM-41 are much better than microporous molecular sieves 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 of NaY is much smaller than mesoporous materials and can be blocked easily. The pore diameters of MAS, MMAS-1, and MCM-41 are much larger than NaY zeolite. Therefore, adsorption capacity of NaY is less than MCM-41, MAS, and MMAS. The acidic sites density of MAS and MMAS-1 is higher than MCM-41, which provides acitve adsorption sites. Thus, MAS and MMAS-1 have better adsorption properties than MCM-41.

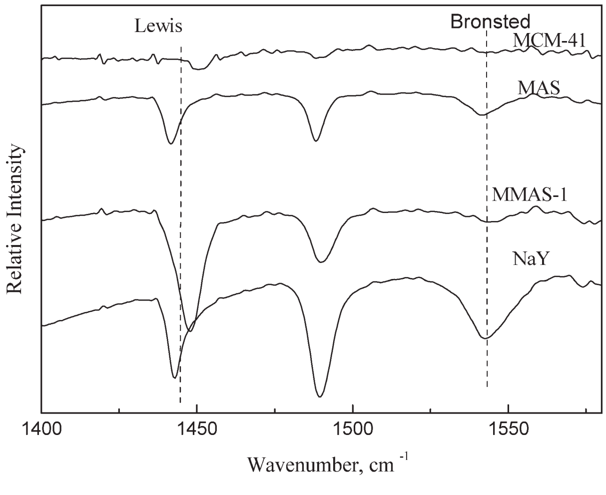

Figure 5. FTIR spectra of adsorbed pyridine on adsorbents.

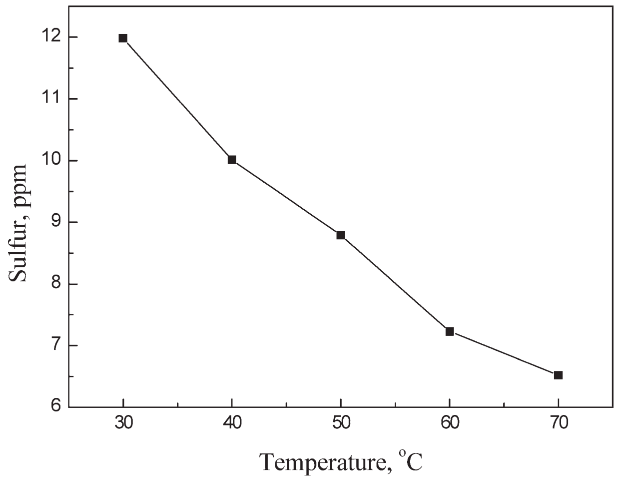

Figure 6. Effect of temperature on the desulfurization properties of MMAS-1.

MMAS-1 has better adsorption ability than MAS because of its more active sites provided by ferric species. Modification of ferric species can improve the adsorption desulfurization properties because of π complexation interaction.[32]

Synergetic effect of magnetite

The amounts of Fe_3O_4 in adsorbents can determine the superparamagnetic properties of adsorbents. While, it also can destroy the ordered structures of MAS. Thus, Fe_3O_4 nanoparticles have significant influence on the specific surface areas and pore volume. As shown in Table 1, surface areas and pore volume decrease with the increase of Fe_3O_4 nanoparticles. The effect of the amounts of magnetic nanoparticles added on adsorption desulfurization properties was studied. During the process of preparation, 5, 10, 15, and 20 ml magnetic suspension was added to 100 ml Si/Al suspension. As shown in Figure 9, the optimal content of magnetic nanoparticles was 10 ml per 100 ml Si/Al suspension. Magnetites act as additional active adsorption sites. The MCM-4 works as a weak adsorbent to sulfur compounds. On the other hand, adsorption sites of magnetite in the composite supply to more adsorptive potential to the MCM-41, more molecules can be filled to the pore volume. As a result, the modification of composite nanostructures enables the removal of sulfur species due to the synergetic effect of strong molecular affinity of the magnetite and large surface area/pore volume of the mesoporous silica.

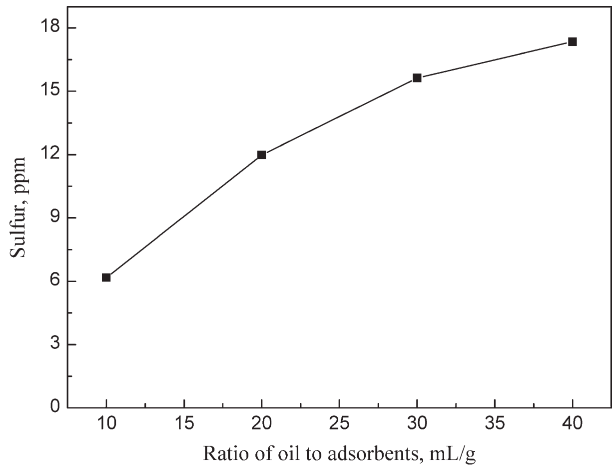

Figure 7. Effects of the ratio of oil to adsorbents on the desulfurization properties of MMAS-1.

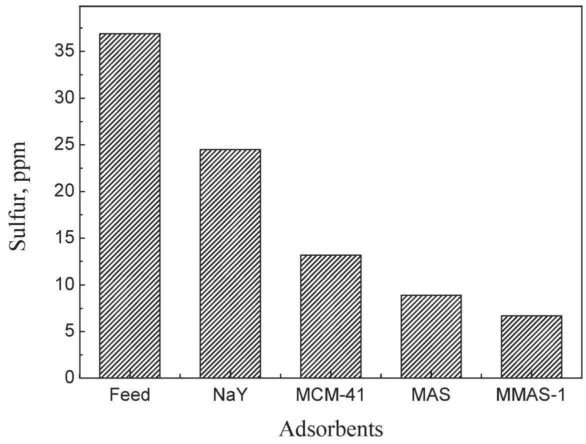

Figure 8. Adsorption properties of adsorbents with different supports.

Conclusion

Magnetic mesoporous aluminosilicates (MMAS) were synthesized with hydrothermal method and applied in ultra-deep desulfurization of hydrotreated diesel. Adsorbent MMAS, about 200 nm, exhibits superparamagnetic property. Addition of Fe_3O_4 nanoparticles has significant effects on specific surface area/pore volume and acidic properties. The sequence of acidic sites density of the adsorbents is NaY > MMAS-1 > MAS > MCM-41. MMAS shows better desulfurization properties for removal of sulfur compounds than NaY and MCM-

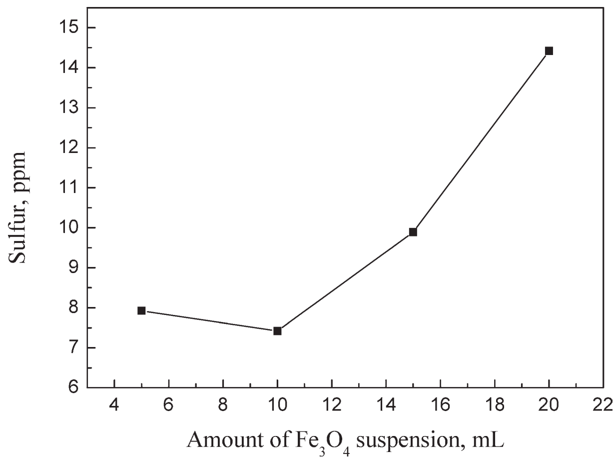

Figure 9. Effect of the amounts of magnetic nanoparticles added on adsorption desulfurization properties.

41. The amount of Fe_3O_4 has significant influence on the desulfurization properties of MMAS. With the increase of Fe_3O_4 content, adsorption capacity first increased and then decreased. The sulfur adsorption of MMAS was due to the synergetic effect of strong molecular affinity of the magnetite to the sulfur compound and large surface area/pore volume of the mesoporous aluminosilicates.

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