Adsorption Desulfurization Performance and Mechanism over Nanocrystalline NiO/Al$_2$O$_3$-1 Adsorbent[1]

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Abstract—Desulfurization performance was evaluated by an adsorption model or real oil (diesel and kerosene) at low temperature using nanocrystalline NiO/Al$_2$O$_3$-1 adsorbent in static equipment. The properties of the NiO/Al$_2$O$_3$ adsorbent samples were characterized by BET surface areas, transmission electron microscopy, FTIR spectra, and TG-DTG curves. Desulfurization experimental results indicated that the desulfurization efficiency for kerosene is much higher than that for diesel due to the π-electronic interaction and S–M bonds with NiO/Al$_2$O$_3$-1 adsorbent. Also, a performance of adsorbent regeneration was kept well for multiple cycles.

INTRODUCTION

Since S-compounds in transportation fuels, such as diesel, gasoline, and kerosene, are the main group of SO$_x$ emission sources, which results in health damage and air pollution [1], more stringent standards of sulfur content in transportation fuels are continuously being offered by governments [2, 3]. Therefore, deep desulfurization of fuels has been one of the most important research topics in recent years [4]. Hydrodesulfurization (HDS) is the major method of desulfurization, the disadvantages of HDS are higher temperature, higher pressure, larger reactor volume, and more active catalysts, which can result in plenty of cost and difficult to remove DBT and their alkyl derivatives efficiently [5, 6]. Many efforts have been made by researchers to obtain the effective desulfurization methods of non-HDS desulfurization [7–10], such as oxidative desulfurization (ODS), adsorption desulfurization (ADS), extractive desulfurization (EDS), etc.

ADS is one of the most attractive complementary methods to HDS [11]. On the one hand, adsorption can avoid solvent residual in transportation fuels, on the other hand, most of the adsorbents also show excellent desulfurization efficiency [12–14]. Various adsorbents such as zeolites, activated carbons (ACs), metal oxides, and clays have been studied for deep desulfurization. Zn, Ni, and Ag etc. have been reported to use as active components on various adsorbent supporters to get higher efficiency [15, 16]. Among the different types of adsorbents, Ni^{2+} based adsorbents have recently attracted attention because of its π-complexation ability [17].

The RADS of Ni/ZnO nano-sorbent can produce a cleaner gasoline and has been successfully applied. The nano material for adsorption desulfurization is a promising research direction. Only few studies focused on nano material as adsorbent for the adsorption desulfurization of transportation fuels. In this paper, NiO supported on nanoscale Al$_2$O$_3$ was used for adsorption desulfurization. Particularly comparing the real oil with the model fuel including kerosene, diesel, DBT, 1-heptanethiol was a new point. Besides, effects of various parameters on a sulfur adsorption capacity (SAC) and selectivity of NiO/Al$_2$O$_3$-1 adsorbent were investigated.

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[1] The text was submitted by the authors in English.

Textural properties of adsorbents

Adsorbents	Surface area, $m^2\ g^{-1}$	Pore volume, $cm^3\ g^{-1}$	Pore diameter, nm
Al_2O_3-1	266	0.34	3.424
Al_2O_3-2	247	0.26	14.00
Al_2O_3-3	230	0.21	18.00
10 wt % NiO/Al_2O_3-1	220	0.27	3.419
15 wt % NiO/Al_2O_3-1	216	0.25	3.415
20 wt % NiO/Al_2O_3-1	186	0.23	3.410
25 wt % NiO/Al_2O_3-1	178	0.22	3.389

EXPERIMENTAL

Chemical Materials and Instrument

Nanoscale alumina (GC, 9.99%), activated alumina (GC, 99.99%) were purchased from Aladin. Aluminum isopropoxide (AR, 99%), toluene (AR, 99.5%), nickel nitrate (AR, 98%), naphthalene, N-octane, DBT, 1-heptanethiol were purchased from ChengDu Kelong chemical Co., Ltd. N-octane mixed with DBT or 1-heptanethiol was used as model fuel, the total sulfur content was 330 ± 5 ppm. The real diesel (S-content: 560 ppm; Bluestar Wuxi Petrochemical Co, Ltd.), kerosene (S-content: 180 ppm; Petrochina Qingyang Petrochemical Company) were used. WK-3000 sulfur analyzer (Taizhou Guochang Analytical Instruments Co, Ltd.) was applied.

Adsorbent Preparation

The nanoscale Al_2O_3-1 sorbents and NiO supported on nanoscale Al_2O_3-1 were prepared by a xerogel process [19]. First, aluminum isopropoxide (4.08 g) was dissolved in a certain amount of the mixture of toluene (130 mL) and ethanol (80 mL), then mixed with pure water or nickel nitrate (98%) solution for hydrolysis. The synthetic process was conducted with vigorous stirring at room temperature for 12 h. Afterwards, the gel was vacuum dried at around 70°C and then calcined at 550°C for 4 h. A series of x wt % NiO/Al_2O_3-1, where $x = 10, 15, 20, 25$ were synthesized.

Three prepared adsorbents (Al_2O_3-1, Al_2O_3-2, and Al_2O_3-3) were implemented in adsorption experiments for discussing the role of support firstly. The samples prepared by this xerogel process without nickel nitrate were defined as Al_2O_3-1. Nanoscale alumina and alumina activated in muffle furnace at temperature 550°C for 4 h were named as Al_2O_3-2 and Al_2O_3-3, respectively.

Desulfurization Experiments

The desulfurization performance of the prepared Al_2O_3-1 and NiO/Al_2O_3-1 was evaluated by adsorption model or real feed (diesel and kerosene) in static equipment. Model fuel oil (10 mL) and adsorbent (0.6 g) were put in a three neck flask, and then heated in a water bath with stirring and temperature controlled at 30°C. Further, 0.4 wt % naphthalene was dissolved in model fuel to investigate the selectivity of the adsorbent. After adsorption, the desulfurized model fuel product was sampled with a syringe and analyzed periodically over a period of 3 h to confirm the adsorption equilibrium has reached. The sulfur content was measured by WK-3000 sulfur analyzer.

Characterization

The surface areas data and pore diameters of all the samples were measured by N_2 adsorption-desorption at the liquid nitrogen temperature, using a Quadrasorb SI-MP equipped with flovac. The pore diameters of all the samples were calculated by BJH method. Transmission electron microscopy (TEM) measurements were made with a Tecnal G^2 F20. TEM operated at accelerating voltage of 200 kV. FTIR spectra of sorbents before and after adsorption of S-compounds were performed on BIO-RAD FTS 3000 spectrophotometer. The TG-DTG curves of sorbents after adsorbing S-compounds were collected on TGA/SDTA85 instrument. The adsorbents after adsorbing of S-compounds were purged with N_2 under the flow rate of 50 mL min^{-1}. The rate of temperature increase was 10°C min^{-1}, it was increased up to 700°C finally.
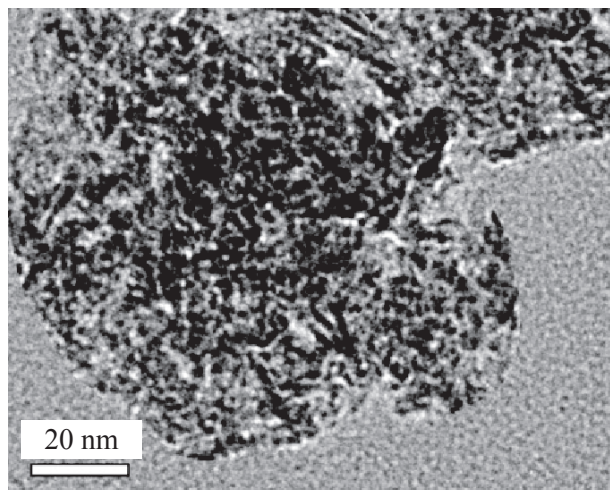
Fig. 1. TEM images of fresh 20 wt % NiO/Al$_2$O$_3$-1 adsorbent.

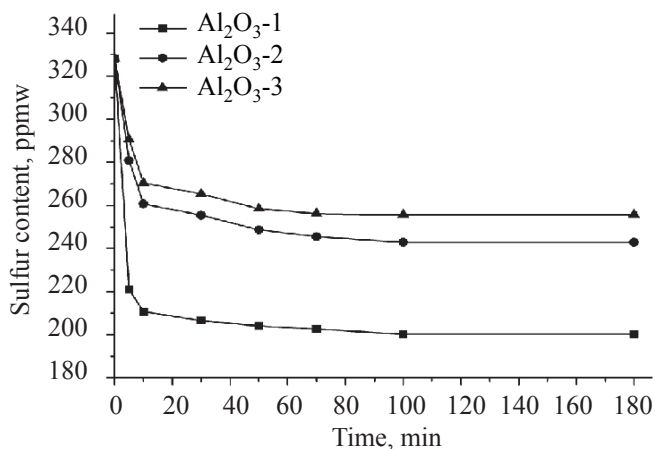**Fig. 2.** Effect of different alumina supports for DBT removal. Conditions: stirring time = 180 min; T = 30°C.

RESULTS AND DISCUSSION

Characterization of the Sorbents

The specific surface areas, pore volume, pore diameter of the three supported alumina and Ni-supported alumina were given in the table. Al$_2$O$_3$-1 had smaller pore size, the largest surface area and pore volume compared with Al$_2$O$_3$-2 and Al$_2$O$_3$-3. NiO loading had a profound influence on the textural properties, the surface area and pore volume decreased with increasing loading of the NiO. This indicated the presence of some guest materials (or probably NiO) filling the pores of Al$_2$O$_3$-1 framework.

Figure 1 displayed the TEM images of fresh 20 wt % NiO/Al$_2$O$_3$-1 adsorbent sample. It can be seen that NiO/Al$_2$O$_3$-1 belongs to nano adsorbent, there were many NiO species in the surface of the NiO/Al$_2$O$_3$-1. Due to the smaller size of the Al$_2$O$_3$-1 nanoparticles, the NiO was well dispersed on the surface of Al$_2$O$_3$-1 nanoparticle.

Effect of Different Sorbents on Sulfur Adsorption

Figure 2 demonstrates an effect of different supported alumina for DBT removal. In the first 10 min all of the three Al$_2$O$_3$ supports showed remarkable reduction in the sulfur content followed by a gradual decrease in the sulfur content for 3 h. Among the adsorbents, Al$_2$O$_3$-1 had the highest desulfurization efficiency. It is obvious from data in the table there is no great difference in the surface areas of the three Al$_2$O$_3$ adsobents. Instead, the most significant property is the pore diameter,

which is 3 nm for one and more than a dozen for others. Kang et al. [20] considered that the target molecules can be adsorbed more easily into porous structure material of small pore size. Their point of view is consistent with our results.

Effect of NiO Content on Desulfurization Efficiency

To investigate the effect of NiO content on the desulfurization of adsorbent, the adsorbing experiments in which NiO/Al$_2$O$_3$-1 (from 10 to 25 wt %) was thoroughly exposed to DBT model fuel, were carried out at 30°C and atmospheric pressure. As can be noted from Fig. 3, 20 wt % NiO/Al$_2$O$_3$-1 adsorbents showed the highest desulfurization efficiencies. The SAC of the 20 wt % NiO/Al$_2$O$_3$-1 sorbent was 2.8 mg g^{-1} whereas it was only 1.2 mg g^{-1} for Al$_2$O$_3$-1 adsorbent. The introduction of NiO not only enhances the ability of ADS but also reduces the adsorption time. The results demonstrated that adding NiO on Al$_2$O$_3$-1 change the adsorption to reactive adsorption greatly enhancing the desulfurization efficiency.

Adsorptive Desulfurization Model Fuel

In this part, DBT and 1-heptanethiol were selected to research the adsorption property of 20 wt % NiO/Al$_2$O$_3$-1 adsorbent, since they represent thiophene and mercaptan, respectively, which are the major S-compounds in diesel and kerosene, respectively. It is definitely (Fig. 4) that the adsorbent worked well at the first 10 min and the content of 1-heptanethiol and DBT dropped in both cases: from
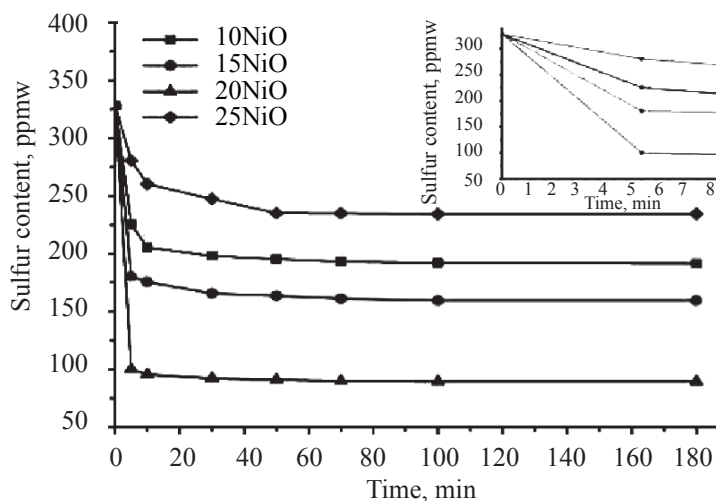
Fig. 3. Effect of NiO content loading on alumina support for DBT removal. Conditions: stirring time=180min; $T = 30°C$.

328 to 15 ppm and to 95 ppm, respectively. Then the sulfur content no longer changed until 180 min. This means that there are certain forces between the NiO/Al$_2$O$_3$-1 and DBT and 1-heptanethiol. These are two different forces, which are one of the reasons why 1-heptanethiol is easier removed than DBT.

Desulfurization Mechanism

TG-DTG curves for the 20 wt % NiO/Al$_2$O$_3$-1 adsorbent saturated with 1-heptanethiol and DBT were shown as Figs. 5a and 5b. Generally, the first weight loss in the range of 30–120°C in TG curves is ascribed to adsorbing impurities (mostly water) [21]. Both DTG curves showed a huge peak in the range of 120–310°C, which indicates a substantial weight loss. There is no
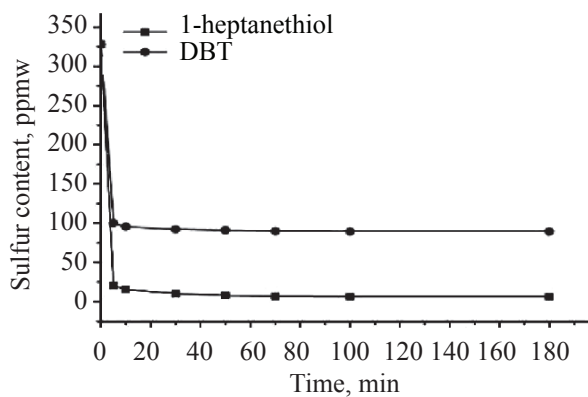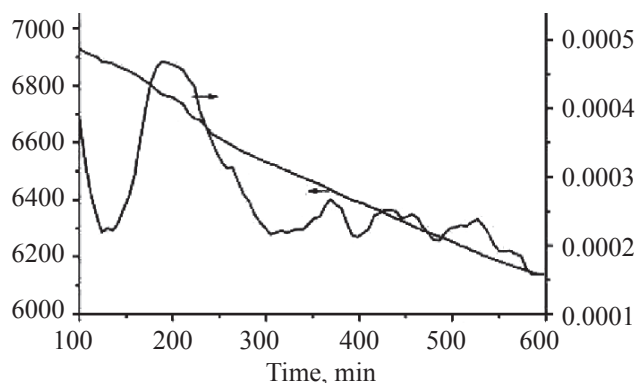
distinct peak observed in the tange of 310–570°C for each sample. The first observation was that both 1-heptanethiol and DBT could be desorbed at temperatures lower than 310°C, which indicates that the chemical interactions
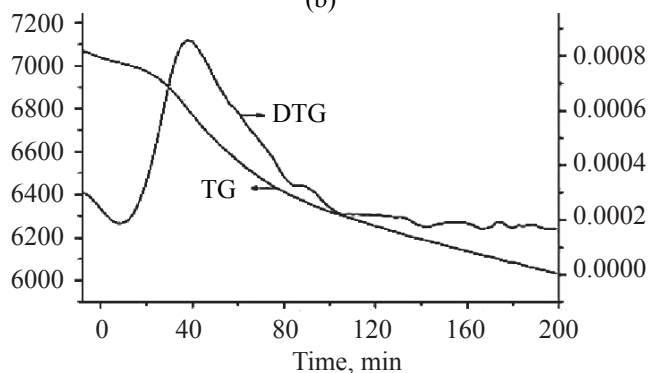
(a)

(b)

Fig. 5. TG and DTG cures of 1-heptanethiol and DBT from 20 wt % NiO/Al$_2$O$_3$-1 adsorbents: (a) 1-heptanethiol and (b) DBT.

Fig. 4. Removed different model fuels over 20 wt % NiO/Al$_2$O$_3$-1. Conditions: stirring time = 180 min; $T = 30°C$.

existed between the adsorbates and adsorbents are not very strong. The second observation was about the temperatures corresponding to the peaks maxima. The weight loss temperature of DBT (~200°C) is higher than that of 1-heptanethiol (~188°C). It can be inferred that the order of adsorption affinity of 1-heptanethiol and DBT onto the 20 wt % NiO/Al_2O_3-1 adsorbent is 1-heptanethiol > DBT. It has reported that the σ-bond dissociation energy is stronger than that of the π-complex bond [22]. The result of the TG-DTG is consistent with this theory.

The S-compounds adsorbed on 20 wt % NiO/Al_2O_3-1 was analyzed by FTIR to discuss the interaction and adsorption mechanism. In Fig. 6b C=C bonds in the fundamental ring a perturbed symmetric stretching vibration caused by π-complexation, which should be around 1384 cm^{-1}, was shifted by 5 cm^{-1} to lower wavenumbers 1379 cm^{-1} in accordance with saturated CH_2 bands deformation vibration. Due to the peak moving to lower wavenumber the electron density in the entire DBT ring have decreased indicating that the adsorbed DBT molecule ring is parallel to the adsorbent surface [23]. That is to say, DBT was adsorbed onto NiO in Al_2O_3-1 by π-electronic interaction. In Fig. 6a we can not find the peak of the S–H bond. The NiO prefers to unite 1-heptanethiol by S–M σ bond. According to the research of organometallic complexes FTIR band of the S–M bond interaction should be at around 1438 cm^{-1}. While in this NiO/Al_2O_3-1 S-compounds system, FTIR band of S–M bond interaction is shifted to 1455 cm^{-1} approaching thereby the band of saturated CH_3 deformation vibration [24], DBT and 1-heptanethiol are adsorbed onto NiO in Al_2O_3 by π-electronic interaction and S–M bond, respectively (Scheme 1).
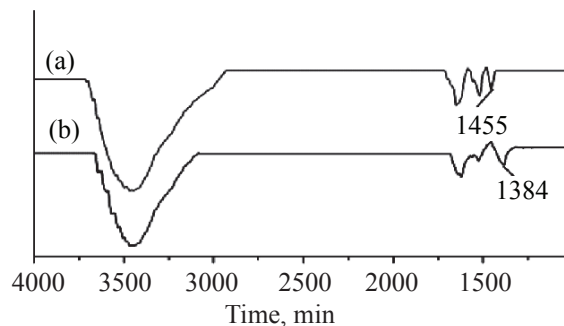

Fig. 6. FTIR spectra of fresh and spent 20 wt % NiO/Al_2O_3-1: adsorbed 1-heptanethiol and (b) adsorbed DBT.

Adsorptive Desulfurization Diesel and Kerosene

Figure 7 showed that the desulfurization efficiency of 20 wt % NiO/Al_2O_3-1 for diesel, DBT, kerosene and 1-heptanethiol were 60, 71, 89, and 95%, respectively. On the one hand, the desulfurization efficiency of 20 wt % NiO/Al_2O_3-1 for DBT was higher than that for diesel and that for 1-heptanethiol was higher than for kerosene, thus, that was the competitive adsorption of aromatic hydrocarbons between diesel and kerosene. On the other hand, the desulfurization efficiency of 20 wt % NiO/Al_2O_3-1 for 1-heptanethiol was significant higher than that for DBT due to the fact that the S–M dissociation energy was stronger than that of the π-complex bond. DBT is the main S-compounds of diesel, 1-heptanethiol is the main S-compounds of kerosene. Therefore, the desulfurization efficiency for kerosene is much higher than that for diesel.

Effects of Aromatic Compounds

In commercial fuels, additives and aromatic hydrocarbons could form competitive adsorption with

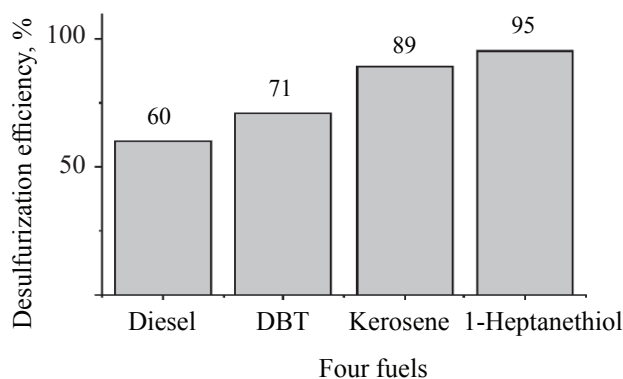**Scheme 1.** Schematic presentations of sulfur-compounds with NiO/Al_2O_3-1.
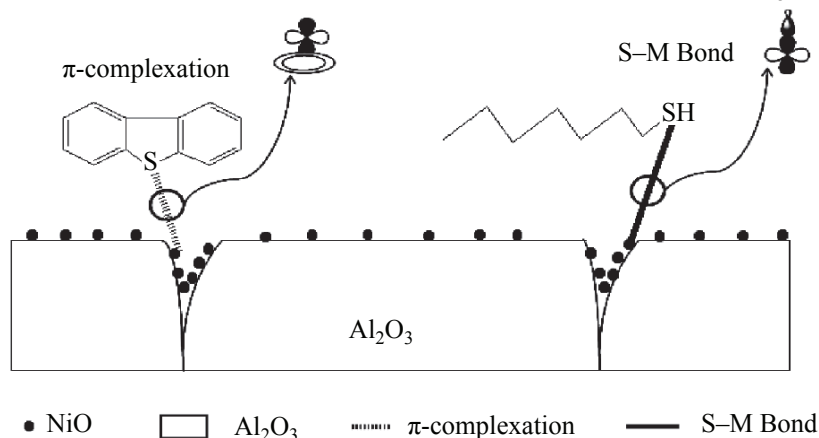
Fig. 7. Desulfurization efficiency of 20 wt % NiO/Al$_2$O$_3$-1 for variety fuels. Conditions: stirring time 180 min; T = 30°C.
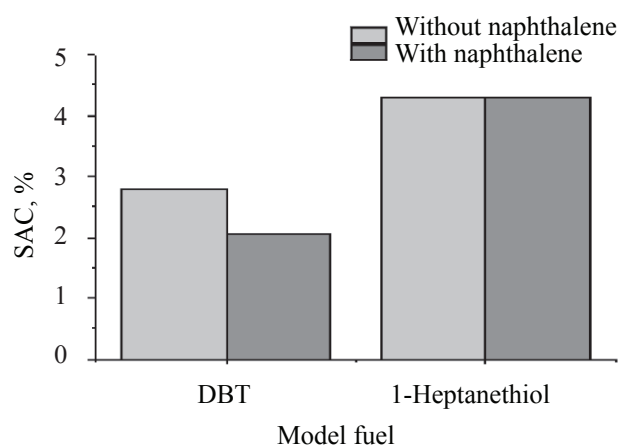

Fig. 8. Naphthalene affected the SAC of 20 wt % NiO/Al$_2$O$_3$-1 in model fuels. Conditions: stirring time 180 min; T = 30°C.
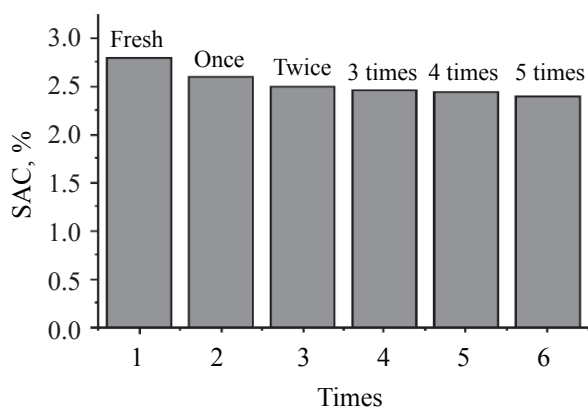

Fig. 9. Effect of regeneration time on SAC of 20 wt % NiO/ Al$_2$O$_3$-1 for adsorbing DBT. Conditions: stirring time 180 min; T = 30°C.

the S-compounds on the adsorbents. These non-sulfur heterocyclic compounds may have a remarkable impact on SAC. In this part, naphthalene was used to discuss its effects on the selectivity of 20 wt % NiO/Al$_2$O$_3$-1

adsorbent (Fig. 8). For the 1-heptanethiol model fuel, the SAC of 20 wt % NiO/Al$_2$O$_3$-1 has not been disturbed: the naphthalene presence did not affect the SAC. For the DBT model fuel, the presence of naphthalene dramatically reduced the SAC. It can assume the S−M bond made the selectivity of 20 wt % NiO/Al$_2$O$_3$-1 for 1-heptanethiol is much higher than for DBT.

Regeneration

In this study, regenerability of 20 wt % NiO/Al$_2$O$_3$-1 was tested by heating the spent adsorbent at 500°C in flowing air. After 3 h, adsorbent was cooled down and collected for the next adsorbing experiment. Figure 9 illustrated the effect of regeneration time on SAC of 20 wt % NiO/Al$_2$O$_3$-1 for adsorbing DBT. The adsorption performance was kept well for multiple cycles (five cycle). It demonstrated that NiO/Al$_2$O$_3$ has stability in repeated heat treatments. Generally, metal in supported metal catalysts (especially supported on γ-alumina) may sinter after repeated heat treatments thereby reducing activity, but sintering did not occur suggesting that NiO can stably interact with alumina [25].

CONCLUSIONS

Nanoscale Al$_2$O$_3$-1 sorbent was prepared through a xerogel process. It was of larger surface area and pore volume than commercial Al$_2$O$_3$-2 and Al$_2$O$_3$-3. Smaller pore size of Al$_2$O$_3$-1 facilitates attaching the target molecules more quickly. The NiO could be well dispersed on the surface of Al$_2$O$_3$-1 nanoparticle, so the 20 wt % NiO/Al$_2$O$_3$-1 sorbent provides the highest desulfurization efficiencies with the most surface adsorption sites. FTIR data indicate that DBT and 1-heptanethiol adsorbed onto NiO in Al$_2$O$_3$ by π-electronic interaction and S–M bond, respectively. It is the reason why the selectivity of 20 wt % NiO/ Al$_2$O$_3$-1 for 1-heptanethiol is much higher than DBT and the desulfurization efficiency for kerosene is much higher than that of diesel. The competitive adsorption experiment indicates that SAC of 20 wt % NiO/ Al$_2$O$_3$-1 for 1-heptanethiol is much higher than that of DBT in the presence of naphthalene. Besides, the heat regeneration multicycle test showed that the regenerability of nanoscale NiO/Al$_2$O$_3$-1 is stable and favorable.

ACKNOWLEDGMENTS

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