Ultra-deep adsorptive desulfurization of a model diesel fuel on regenerable Ni–Cu/γ-Al₂O₃ at low temperatures in absence of hydrogen

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**HIGHLIGHTS**

- Ni–Cu/γ-Al₂O₃ sorbents show high activity in adsorptive desulfurization of diesel fuel.
- Reduction temperature decreases significantly by adding Cu to Ni/γ-Al₂O₃ sorbent.
- Desulfurization temperature is considerably improved by adding Cu to Ni/γ-Al₂O₃ sorbent.
- Selectivity of Ni–Cu sorbents to sulfur in the presence of aromatics is improved.
- Decrease in loss of adsorption capacity after regeneration of spent Ni–Cu sorbents.

**ABSTRACT**

A model diesel fuel containing 250 ppmw sulfur (as dibenzothiophene) in n-hexadecane was desulfurized at low temperatures in absence of hydrogen, down to about zero ppmw S on a novel adsorbent of well dispersed 3–12 nm Niₓ–Cu₁₀₋ₓ (ₓ Ni wt%) nanoparticles formed by impregnation on γ-Al₂O₃ and reduced in H₂ at 275 or 450 °C. The sorbents were characterized by XRD, TEM–EDX, FESEM–EDS, H₂–TPR, TPO, BJH and BET surface area measurement techniques. Effects of various parameters comprising Cu content, reduction and desulfurization temperatures, inhibition by naphthalene, and regeneration of spent sorbents were investigated. As copper is added to nickel: (a) the sorbent reduction temperature shifts to dramatically lower values, (b) sulfur adsorption capacity of the sorbents at lower reduction and desulfurization temperatures is significantly improved, and when 14 wt% Ni5Cu5 sorbent is added to the fuel, the sulfur content reduces from 250 ppmw S to about zero in less than 1 min, (c) loss of adsorption capacity after the regeneration of the spent sorbent reduced at 275 °C is significantly diminished, and (d) the selectivity of the sorbents to dibenzothiophene in the presence of naphthalene is improved. A higher reduction temperature tends to agglomerate nickel nanoparticles and reduce the sulfur adsorption capacity.

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1. Introduction

Environmental protection regulations tend to further reduce allowed sulfur content in the transportation fuels across the world. The U.S. Environmental Protection Agency (EPA) restricted the total sulfur content of diesel to 15 and that of gasoline to 30 ppmw S. European standard organization also limited the total sulfur content of diesel and gasoline to 10 ppmw S [1,2]. Sulfur compounds in the fuels also poison the catalytic converter in automobiles and contribute to acid rain by producing SO₂ compounds. Therefore, deep desulfurization of fuels has become an important process in the petroleum refineries [1].

Hydrodesulfurization (HDS) is the conventional method for desulfurization of the fuels in petroleum refinery carried out in the presence of sulfided Co(Ni)Mo/γ-Al₂O₃ catalysts at elevated operating temperatures (300–400 °C) and H₂ pressure (30–100 bar) [3,4]. HDS is efficient for removing sulfides, disulfides, mercaptans and thiophenes but is less effective for removing refractory sulfur compounds such as benzothiophene (BT), dibenzothiophene (DBT) and their alkyl derivatives such as 4,6-DMDDBT [5].

Desulfurization of refractory sulfur compounds with HDS requires severe operating condition [6,7]. To reduce total sulfur content of diesel from 500 to less than 15 ppmw S using
conventional HDS technology, the reactor volume or catalyst activity should be at least three times greater than those used ordinarily in the petroleum refinery. This is a very costly and energy consuming process at severe operating conditions and might also contribute to undesirable changes in fuel quality [8,9].

Recently, a wide variety of studies done to find alternative processes such as oxidation, extraction and adsorption for ultra-deep desulfurization of fuels, instead of using HDS at severe operating conditions [10]. Adsorptive desulfurization is one of the new economical and attractive methods which does not need H2 as the reaction media and can be carried out at even room operating conditions [10–12].

It has been reported that Ni and Cu sorbents supported on alumina, activated carbon and zeolite are effective for desulfurization of transportation fuels [9,13]. Song et al. have reported that among the different types of adsorbents such as metals, metal oxides, metal halides, metal sulfides and zeolites, nickel based adsorbents shown high desulfurization capacity and selectivity without using H2 gas [11]. Ma et al. have used the Ni/Al2O3 sorbent for desulfurization of gasoline in a temperature range of 25–200 °C under ambient pressure without H2 gas. They have also found that the nickel based adsorbents had the high capacity and selectivity toward sulfur compounds. It has been reported that the sulfur adsorption capacity (SAC) increases significantly with increasing temperature up to 200 °C [14].

It has also been reported that the breakthrough adsorption capacity of Ni-based adsorbents to less than 1 ppmw S was 0.37 mg S/g. Adsorbent at room temperature, which was higher than Cu(II)/Y-Zeolite (0.22 mg S/g) for commercial gasoline with 305 ppmw S [13]. In addition, Sarda et al. have reported that Ni based sorbent and alumina support are more effective compared with Cu sorbent and ZSM-5 support [9].

In spite of positive aspects, sorbents become inactive gradually and need to be regenerated. Under mild operating conditions, sulfidation of nickel active sites is irreversible and requires a separate regeneration process [14]. The regeneration of spent sorbents is usually done with oxidation of spent ones in air, and then reduction by H2 in temperature range of 300–400 °C [3,7,13]. In addition, several literatures have shown that SAC of sorbents decreased in the presence of olefins and aromatic compounds [15–17]. Therefore, developing sorbent which can selectively remove sulfur compounds is a challenging issue in adsorptive desulfurization process.

Changes in activity and selectivity of nickel catalysts with the addition of Cu has been reported [18]. The activity of Ni–Cu catalysts compared to Ni one is much higher for many reactions such as ethylene and styrene hydrogenation and hydrogcnolysis of ethane to methane [19,20]. Ni and Cu, formed by reduction of a mixture of nickel and copper oxides under hydrogen, have the same crystaline structure and can form a continuous series of substitution solid solutions in a cubic close-packed lattice structure, based on Ni–Cu phase diagram [20].

In this work, novel Ni–Cu/γ-Al2O3 sorbents are used for desulfurization of a synthetic diesel fuel containing 250 ppmw S as dibenzothiophene in n-hexadecane at low temperature in the absence of hydrogen. To the best of our knowledge, it is the first reported results of Ni–Cu sorbents for desulfurization of a model diesel fuel. The effects of copper content, reduction and desulfurization temperature, aromatic content of diesel fuel, and regeneration of spent sorbents are investigated. Copper significantly decreases the reduction and desulfurization temperature of sorbents and improves the performance of sorbents after regeneration, compared to the conventional Ni sorbents. Moreover, selectivity of sorbents toward sulfur compounds in the presence of aromatics is improved.

2. Experimental methods

2.1. Sorbents preparation

A series of x wt% Ni and (10–x) wt% Cu on γ-Al2O3, where x = 0, 2.5, 5, 7.5, 10 were synthesized via incipient wetness impregnation method. γ-Al2O3 (Sasol) with BET surface area of 195 m2/g and a pore volume of 0.75 ml/g was used as the support and Ni(NO3)2·6H2O and Cu(NO3)2·3H2O (both Merck) were used as the sorbents precursors. Following the impregnation, the sorbents dried overnight at 100 °C and calcined at 450 °C for 5 h, and then grounded and sieved to obtain a particle size of 63–100 μm for desulfurization.

2.2. Sorbents characterization

The BET surface areas of the samples were determined by N2 adsorption–desorption at the liquid nitrogen temperature, using a Micromeritics-TriStar II apparatus equipped with a thermal conductivity detector (TCD). Prior to the measurements, the sorbents were degassed by Ar at 300 °C for 2 h. The pore size distribution was calculated from desorption branch of the isotherm by Barrett–Joyner–Halenda (BJH) method.

Samples were also characterized by X-ray powder diffraction (XRD) technique to get information about the structural properties of the sorbents before and after the desulfurization, using Philips powder diffractometer (PW-1800) with Cu Kα radiation (λ = 1.54 Å), which operates at 40 kV. The data were collected in the range of 2θ value between 20° and 70° with the step size of 0.02° s⁻¹.

H2-Temperature programmed reduction (H2-TPR) analyses were carried out using a Quantachrome CHEMBET-3000 apparatus equipped with a TCD detector. About 25 mg of sorbent was loaded in the quartz U-tube reactor and degassed by Ar at 300 °C for 2 h. After cooling down to room temperature, H2-TPR analysis was performed using a 10 ml/min flow rate of 7 mol% H2/Ar at the heating rate of 10°C/min from room temperature up to 900°C.

Field emission scanning electron microscopy (FESEM) images were recorded on a H3TACHİ S-4160 instrument in order to study the morphology of the sorbents. Samples were coated with gold before measurement. The chemical analysis of Al, Ni, Cu, O, sulfur and carbon in the spent sorbent was performed using Oxford Instrument Energy dispersive X-ray spectroscopy (EDS).

Transmission electron microscopy (TEM) with EDX, operating at accelerating voltage of 200 kV, was obtained using a TEM Philips (CM200 FEG). The samples were prepared by dispersing the sorbent powder as slurry in methanol and then was deposited and dried on a lacey carbon film on an Au grid.

After desulfurization tests, spent sorbents which washed with pure toluene at 80°C and dried at 100 °C were characterized by temperature programmed oxidation (TPO) in a tubular quartz reactor. In the TPO experiments, the sulfur compounds and coke formed during desulfurization tests were burnt in air (100 ml/min), while the temperature was increased from room temperature up to 800 °C with a ramp rate of 10°C/min. TPO effluent gases including CO, CO2 and SO2 were passed through a gas cell in a Fourier transform infrared spectroscopy (FTIR) for analysis (Bruker-Vector 22).

2.3. Desulfurization tests

Fig. 1 (a) and (b) shows schematic diagrams of the sorbent reduction and the desulfurization setups, respectively. A solution of 250 ppmw S as dibenzothiophene (DBT) in n-hexadecane (both 99% Merck) was used as the model diesel fuel. Before desulfurization tests, 0.5 g of sorbent was loaded into a tubular quartz...
reactor (Fig. 1(a)) and reduced at either 275 or 450 °C for 4 h using 20 ml/min of high purity H₂ gas, and then the sorbent was cooled down under the same flow rate of H₂. The reactor was also purged with H₂ gas before introducing the sorbent into a batch reactor containing 10 ml of diesel fuel solution. As shown in Fig. 1(b), the reactor was equipped with the condenser, sampling line, sorbent inlet, and magnetic stirrer and PID temperature controller.

The influence of aromatics on the performance of sorbents was also studied by adding 0.4 wt% of naphthalene to the model diesel fuel.

For regeneration tests, the spent sorbents were washed five times with pure toluene at 80 °C and dried at 100 °C overnight. Then the sorbent was loaded into the quartz reactor, and heated to the reduction temperature of 275 or 450 °C in 20 ml/min of air or Ar flow, and finally cooled down to room temperature. The sorbent was then reduced under the same conditions as the fresh sorbent and used in desulfurization test.

The quantitative analysis of DBT was performed using Varian-CP 3800 gas chromatograph (GC) equipped with DB-1 capillary column (Teknokroma, 30 m, 0.25 mm, 1 μm film thickness) with high purity He as carrier gas and flame photometric detector (FPD). The injector and detector temperatures were maintained at 300 °C and column temperature was kept at 100 °C for 5 min, then increased at a 10 °C/min rate to 290 °C and held for 10 min at this temperature. 1 μl of the diesel fuel was injected to the GC for analysis.

3. Results and discussion

3.1. Sorbents characterization

3.1.1. BET

Ni and Cu contents, BET surface areas, pore volume and H₂-reduction results of the calcined samples are presented in Table 1. As the γ-Al₂O₃ of 195 m²/g BET surface area is loaded with 10 wt% Ni and/or Cu, the areas of the sorbents decrease by 25–35 m²/g. Ni and/or Cu oxides may deposit onto the γ-Al₂O₃ micro-pores and result in the pore volume and surface area reduction [21].

3.1.2. XRD

Fig. 2 shows the XRD patterns of Ni10 and Ni5Cu5 sorbents calcined at 450 °C and the ones reduced and used in the desulfurization tests at 150 °C. NiO crystalline phase is observed for the calcined Ni10 sorbent, while after desulfurization test, the most prominent diffractions are assigned to γ-Al₂O₃ and metallic Ni phase formed during the reduction. For the calcined Ni5Cu5 sorbent, only γ-Al₂O₃ phase can be observed, due probably to low loadings or high dispersion of NiO and CuO phases. Broad peaks of γ-Al₂O₃ with low intensities after reduction and desulfurization tests could correspond to the formation of highly dispersed particles or change in surface morphology of sorbents [21,22]. Also, the peaks corresponding to nickel/copper sulfides or nickel/copper carbides were not detected in the spent sorbents.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ni loading (wt%)</th>
<th>Cu loading (wt%)</th>
<th>BET area (m²/g)</th>
<th>Pore volume (ml/g)</th>
<th>TPR peak 1 (°C)</th>
<th>TPR peak 2 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al₂O₃</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ni10</td>
<td>10</td>
<td>–</td>
<td>195</td>
<td>0.75</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ni₇.₅Cu₂.₅</td>
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<td>2.5</td>
<td>195</td>
<td>0.64</td>
<td>513</td>
<td>–</td>
</tr>
<tr>
<td>Ni₅Cu₅</td>
<td>5</td>
<td>5</td>
<td>170</td>
<td>0.64</td>
<td>279</td>
<td>462</td>
</tr>
<tr>
<td>Ni₂.₅Cu₇.₅</td>
<td>2.5</td>
<td>7.5</td>
<td>160</td>
<td>0.59</td>
<td>258</td>
<td>462</td>
</tr>
<tr>
<td>Cu₁₀</td>
<td>–</td>
<td>10</td>
<td>160</td>
<td>0.64</td>
<td>250</td>
<td>376</td>
</tr>
</tbody>
</table>

Table 1: Physicochemical characteristics of fresh samples used in this work.
3.1.3. H$_2$-TPR

H$_2$-TPR profiles of sorbents calcined at 450 °C are shown in the Fig. 3. For the Ni10 sorbent, a main broad peak is observed in the temperature range of 400–600 °C with a maximum at 515 °C. This may be attributed to the reduction of well-dispersed nickel oxide particles with different metal-support interactions [23]. Fig. 3 also shows the TPR of unsupported nickel oxide prepared by calcination of nickel nitrate salt at 450 °C. The main reduction peak occurs at around 420 °C. The interactions with γ-Al$_2$O$_3$ shift the reduction peak of nickel oxide on alumina to significantly higher temperature of 515 °C [23–25].

TPR analysis of sorbents containing copper oxide suggests the presence of two different types of copper oxides. For Cu10 sorbent, the first peak at 250 °C and the second one at 376 °C may be ascribed to the reduction of well-dispersed small and bulk large copper oxide particles, respectively [22,25–27]. The reduction peak of bulk copper oxide prepared by calcination of copper nitrate salt at 450 °C occurs in the temperature range of 310–520 °C with a maximum at 355 °C (Fig. 3). The minor peak at 290 °C in the TPR of Cu10, after the first peak, can be explained by the presence of well-dispersed copper oxide particles with stronger interaction with the support [28,29].

Adding Cu to Ni can lead to the formation of dispersed Ni–Cu oxide solid solution particles with lower metal-support interaction [20,28,29]. The first peak in Ni7.5Cu2.5 sorbent TPR may be assigned the copper oxide reduction. The second peak is related to the reduction of nickel oxide and/or a nickel-rich Ni–Cu oxides solid solution [12]. The first and second TPR peak, temperatures of Ni7.5Cu2.5 sample increases and decreases by 28 °C and 51 °C, as compared to Cu10 and Ni10, respectively. The TPR profile of Ni2.5Cu7.5 is nearly similar to that of Cu10. In the second peak, in addition to the reduction of bulk copper oxides, the solid solution of copper and nickel oxides may also reduce [12,30].
3.1.4. FESEM

The SEM–EDS micrographs of N10 and Ni5Cu5 sorbents after 3 h of desulfurization test at 150°C are shown in Fig. 4(a–f). Ni10 and Ni5Cu5 sorbent reduced at 450°C (shown by Ni10-450 and Ni5Cu5-450 in this work) in Fig. 4(a and e) shows the formation of filamentous carbons, while no such carbons are observed on the Ni5Cu5-275 (Ni5Cu5 sorbent reduced at 275°C). The filamentous carbons on Ni5Cu5-450 are much thicker than the ones on Ni10-450. This may be due to the excessive sintering of Ni5Cu5 nanoparticles at the high reduction temperature of 450°C, which in turn results in thicker filamentous carbons [31].

3.1.5. TEM

TEM images of Fig. 5 shows that Ni–Cu nanoparticles of ca. 3–12 nm are well-dispersed on the Al2O3 support. Energy dispersive X-ray spectrometry (EDX) analysis results (not shown here) reveal the presence of both Ni and Cu in the nanoparticles. The average nanoparticle sizes of Ni2.5Cu7.5 and Ni5Cu5 samples are 5.5 and 6 nm, respectively.

3.1.6. Temperature Programed Oxidation

Fig. 6(a) and (b) shows the TPO profiles of spent Ni10-450 and Ni5Cu5-450 sorbents after 3 h of desulfurization at 150°C and consequently washed with toluene and dried at 100°C. CO2
evaluation profiles show two peaks at around 220 and 260 °C for Ni5Cu5 and Ni10, respectively. Oxidation at such low temperatures may be due to the formation of coke on the metals or metal-support interfaces [32].

In SO2 evaluation profiles, the two peaks at around 180 and 700 °C may be attributed to the oxidation of nickel sulfides and partial decomposition of metal sulfates formed during the TPO, respectively, based on Yoshimura et al. report [33]. They have reported that during TPO test, nickel sulfates are formed from nickel sulfides at low oxidation temperature up to 380 °C. They are stable below 700 °C and highly protective for oxygen diffusion to the bulk of sulfides. It has also been reported that most sulfur removal occurred in the temperature range of 150–350 °C.

3.2. Desulfurization of the model diesel fuel

Fig. 7(a) and (b) shows the desulfurization results of the model diesel fuel on sorbents reduced at 450 and 275 °C, respectively. Two regions of desulfurization can be distinguished for all sorbents: a remarkable reduction in the sulfur content of the fuel occurs in less than 5 min, followed by a gradual decrease of the sulfur content up to 3 h. For example, Ni10-450 sorbent, the sulfur content of the fuel declines from 250 ppmw S to about 80 ppmw S in 5 min and then slowly decreases to about 6 ppmw S after 100 min. Obviously, by increasing the Ni5Cu5-450 sorbent mass in desulfurization test from 0.5 g to about 1.25 g, the sulfur content decreased from 250 ppmw S to nearly zero in less than one minute (not shown here). This way, increased the sorption sites and provided enough time for sulfur compounds to diffuse into the pores of the adsorbent [9].

Thiophenic compounds can interact with metal atoms or ions by either direct S–M bonds formation or π-electrons located in their aromatic ring to form π-complexation. Co-presence of these bonding bonding is extremely possible [34–36]. Baeza et al. [37] have reported that Cu(II) and Cu2+ species do not adsorb thiophenic compounds, and the active sites in desulfurization is Cu1+ which adsorb DBT with forming π-complexation bonds. Ma et al. [14] have reported that during desulfurization of thiophenic compounds, dissociative chemisorptions of sulfur compounds at the surface of metallic nickel crystal planes occurred. This may involve hydrogenolysis of C–S bonds to form sulfur and hydrocarbon radicals and result in nickel sulfides formation by saturation with active hydrogen atoms, which may be adsorbed on the Ni surface during reduction of the sorbents. Furthermore, in the absence of hydrogen flow, coke formation on the Ni surface by radical dimerization and disproportionation may take place [14,38,39]. This is in agreement with results of CO2 evaluation profile during the TPO of the spent sorbents. Therefore, the sharp desulfurization trend in the first zone may be due to the adsorption of DBT on the large
quantity of Ni\(^{2+}\) surface active sites through the sulfur atom or insertion of Ni atom in the thiophenic ring and/or partial adsorption of DBT on the exposed Cu\(^{2+}\) cation with \(\pi\)-complexation interactions in aromatic rings \[37,38,40\].

Comparing the heat of adsorption of sulfur on the Ni (\(\Delta H_{\text{ads}} = -150\, \text{kJ/mol}\)) with that of bulk nickel sulfide formation (\(\Delta H = -75\, \text{kJ/mol}\)), one may conclude that sulfur adsorption on the nickel surface is most favorable. As different kinds of nickel sulfides passive layers are formed on the surface of active sites, the diffusion of S into the bulk of the nickel through the surface sulfide layer is suppressed and the feed desulfurizes with much slower rate in the second zone \[38,41\]. Whereas, the presence of hydrogen can increase the mobility of adsorbed sulfur species at the surface of metallic nickel nanocrystals and favoring the formation of bulk nickel sulfides by thermally induced restructuring of the sulfur species \[38\].

3.3. Effects of reduction temperature on the SAC

Fig. 8 shows the SAC of the sorbents containing various proportions of Cu and reduced at either 275 or 450 °C after first 5 min and 3 h of desulfurization at 150 °C. For the samples reduced at 275 °C, the SAC in first 5 min desulfurization sharply increases to 1.9 mg S/g A for the sample containing 2.5 wt% Cu and then levels off for higher copper contents. The SAC after 3 h desulfurization for the samples reduced at the same temperature shows a maximum of 3.4 mg S/g A at 7.5 wt% Cu in the sorbents. However, for the sorbents reduced at 450 °C, the SAC after first 5 min and 3 h desulfurization test significantly decrease, particularly at higher Cu contents of the sorbents. SAC of sorbents may be modified by changing adsorption stoichiometry of sulfur compounds related to the geometric and electronic effects of Ni–Cu solid solution \[18,42,43\]. Cunha et al. \[42\] have reported that the change in catalytic properties of Ni–Cu solid solution is due to the dilution of nickel surface atoms (geometric effect) rather than electronic effect related to the occupation of Ni \(d\)-band by Cu according to the Dowden theory \[18\]. According to TPR results, the reduction temperature of 450 °C is more favorable for higher degree of reduction of NiO particles than 275 °C. Therefore, for the sorbents reduced at 450 °C, as the Ni content increases, more Ni active sites are available for sulfur removal, which result in higher adsorption capacity.

![Fig. 8. Effects of reduction temperature on SAC of sorbents after 5 min (a) and 180 min (b) of desulfurization at 150 °C.](image-url)
Significantly, higher SAC of Cu10–275 sorbent, as compared to Cu–450, can be explained by sintering of copper particles at the higher reduction temperature. Moreover, it can be due to the partial reduction of CuO to Cu2O, rather than Cu, and desulfurization by \( \pi \)-complexation mechanism [40,44].

\( \text{H}_2 \)-TPR results indicate the facilitative effects of Cu on the NiO reduction. For the sorbents reduced at 275 \( ^\circ \text{C} \), SAC increases as more Cu is added to the sorbent. In addition, the dispersion of Ni active sites increases with proportion of Cu in Ni–Cu samples [28,29]. NiO and CuO reduction and Ni–Cu alloy formation occur within two fast and thermodynamically favorable steps as follows [25]:

\[
\begin{align*}
\text{Step 1:} & \quad \text{CuO} + \text{H}_2 \rightarrow \text{Cu}^0 + \text{H}_2\text{O} \\
\text{Step 2:} & \quad 2\text{Cu}^0 + \text{NiO} \rightarrow \text{CuO} + \text{Cu} + \text{Ni}
\end{align*}
\]

In this mechanism, CuO formed in step 1 diffuses to the NiO by Cu/NiO molar ratio 2:1 and incorporated to the Ni lattice to form Ni–Cu alloy and CuO formed in step 2 is reduced once more through step 1. High dispersion of nickel particles has been reported as the main reason for higher initial SAC of sorbents [45]. Therefore, further addition of Cu to the sorbents reduced at 275 \( ^\circ \text{C} \) can lead to increase in highly dispersed Ni active sites for desulfurization by increasing the reduction of NiO in the presence of Cu. Whereas, Ni–Cu particles with higher Cu contents may agglomerate at the higher reduction temperature of 450 \( ^\circ \text{C} \). Moreover, Cu lattice parameter is higher than that of Ni and the surface free energy of Cu (1.85 J/m\(^2\)) is less than that of Ni (2.45 J/m\(^2\)) leading to excess Cu atoms on the surface of Cu–Ni alloy which decreases the SAC [18,46]. Therefore, larger particles and Cu segregation on the surface may be the main reasons for lower adsorption capacity of sorbents with Cu contents higher than 2.5 wt% reduced at 450 \( ^\circ \text{C} \).

### 3.4. Effects of desulfurization temperature

Fig. 9 shows the desulfurization at various temperatures in the range of 50–200 \( ^\circ \text{C} \), on Ni5Cu5–450 sorbent. The desulfurization rate in both zones of sharp decline in the sulfur content and the gradual one are significantly enhanced by increasing the temperature. The same trend is observed for the other sorbents (not shown here). Fig. 10(a) and (b) shows that SAC of all sorbents increases with temperature. The SAC of Ni10–450 sharply increases from 0.6 mg S/g A at 50 \( ^\circ \text{C} \) to 3.9 at 150 \( ^\circ \text{C} \) and then levels off at 200 \( ^\circ \text{C} \). At lower temperatures, bimetallic Ni–Cu sorbents have higher SAC than nickel one.

Several researches have reported that the desulfurization activity of sorbents increases with temperature [14,47]. This is due to the supply of activation energy needed for adsorption, diffusion and chemical interaction between the sulfur compound and active sites [34,48]. In addition, from the viewpoint of kinetic study, surface reaction rates of sulfur compounds with nickel particles increases with temperature in the absence of hydrogen in reaction media, which lead to the formation of additional sulfide layers [14,41].

### 3.5. Effects of aromatic compounds

Fig. 11(a) shows that the naphthalene decreases the sulfur removal in both zones of adsorption and surface reaction for Ni5Cu5–450 sorbent. The same trend is observed for other sorbents (not shown here). Fig. 11(b) shows that the SAC for Ni10 sorbent is dramatically inhibited in the presence of aromatic. Hernan-dez et al. [17] have reported a significant loss, from 18 to about 4 g fuel/g A, in the amount of treated fuel on Ni Sud-Chemie commercial sorbent for removing DBT in the presence of aromatics. Moreover, a decline in SAC of bimetallic Ni–Ce sorbent has been reported [49], while minor to no effect is observed for the Ni–Cu sorbents, due possibly to the Ni–Cu interaction (synergism).

Zhang et al. [34] have reported that both S–M bonding and \( \pi \)-type complex of DBT can significantly be hindered by a competitive adsorption between DBT and aromatics on active sites, especially when the interaction between the sulfur compounds and active sites is through \( \pi \)-electrons in aromatic ring and \( \pi \)-complexation [8,17,49]. This way, a part of the sorbent active sites is occupied by aromatic compounds, which results in a decrease in the SAC [14].

3.6. Regeneration of spent sorbents

The effects of regeneration gas on Ni5Cu5-450 sample regenerated in either air or Ar is presented in Fig. 12. Both fresh and regenerated sample are reduced at 450°C before desulfurization test at 150°C. For the spent Ni5Cu5-450 sorbent regenerated at 450°C in air, the final sulfur content of desulfurized fuel after 180 min is about 86 ppmw S, compared to 140 ppmw S for the sample regenerated in inert Ar at the same temperature. SEM–EDS results indicate the presence of deposited carbon and sulfur in the spent samples. During the desulfurization process, various sulfide layers form on the surface of active sites with different binding energies as well as coke formation which block the metallic and carbonaceous active phases [38]. Regeneration in air may destruct various forms of sulfide compounds formed in the desulfurization test based on the TPO evaluation profiles. In addition, some nickel sulfate compounds may form during regeneration in air [33]. However, a part of sulfides such as NiS remains unchanged at this temperature, according to the Ni–S phase diagram, and the sorbent will not achieve its initial activity [38].

The results shown in Fig. 13 indicates that the decline in the initial SAC of fresh sorbents reduced and regenerated at the lower temperature of 275°C is lower than the ones reduced at 450°C. For Ni5Cu5 sorbent, the loss in initial SAC is about 36% for regeneration temperature of 450°C and is about 6% for 275°C. One of the reasons for lower SAC of the Ni5Cu5-450 sorbent regenerated at 450°C than that of Ni5Cu5-275 regenerated at 275°C could be due to the presence of more surface nickel active sites blocked with sulfur atoms and deposited carbon during desulfurization tests. During oxidative regeneration of sorbents up to 380°C, nickel would be covered with the oxide/sulfate layers. Above 380°C, partial decomposition of sulfates would occur since decomposition rate of NiSO₄ at temperatures lower than 700°C is insignificant. Therefore, the amount of deposited S in the regenerated sorbents increases with regeneration temperature [33]. Moreover, at higher reduction and regeneration temperatures, the possibility of agglomeration and growth of Ni or Ni–Cu crystals increase with Cu contents. As can be seen in the SEM images of used sorbents (Fig. 4), the presence of thicker carbon fibers in the used Ni5Cu5-450 may be due to the presence of larger Ni particles. Besides, sulfidation of metallic nickel particles could lead to an increase in crystallite size which changes the adsorption stoichiometry of sulfur compounds [50].

Fig. 13 shows that the reduction in SAC of Ni5Cu5-450 regenerated at 450°C is more than Ni10-450 regenerated at the same temperature. Therefore, sintering of the metals nanoparticles during the regeneration may also partly contribute to the diminished SAC.

4. Conclusion

In this study, effects of Cu content of 10 wt% Ni–Cu/γ-Al₂O₃ sorbents on ultra-deep desulfurization of a model diesel fuel containing 250 ppmwS as dibenzothiophene in n-hexadecane in absence of hydrogen are investigated. The desulfurization occurs in two distinguished steps of a sharp sulfur removal in less than 5 min followed by gradual desulfurization in 3 h examined.
The reducibility of NiO dramatically enhances as CuO is partially replaced with NiO, and change the electronic properties of Ni by formation of a solid solution with Cu. In addition, an increase in Ni dispersion has been observed for the sorbents reduced at 275 °C, as the Cu content increase, whereas, agglomeration may occur at 450 °C as the reduction temperature leading to decreases in sulfur adsorption capacity (SAC).

For the samples reduced at 275 °C, the SAC maximizes at 3.4 mg S/g A for Ni2.5Cu7.5 sorbent, while for 450 °C reduction temperature, SAC sharply increases with the nickel content up to about 3.6 mg S/g A for Ni5Cu5 and then levels off for higher nickel contents. The sulfur content of the model diesel fuel is reduced to 6 and 34 ppmwS for desulfurization at 150 °C on Ni10-450 and Ni2.5Cu7.5-275 sorbents, respectively. As more sorbent is used in the desulfurization the sulfur content decreases to about zero in less than 1 min.

SAC of all sorbents increase with temperature since the activation energy for adsorptive desulfurization is provided at higher temperature. However, at lower temperatures, SAC of sorbents increases with Cu content. As naphthalene is added to the feed, SAC slightly decreases for the bimetallic sorbents, while a significant decrease is observed for the Ni sorbent.

SAC is higher for the sorbents regenerated in air than in Ar, due possibly to removal of passive surface sulfide layers in air. Significantly lower decline in SAC is observed for the sorbents regenerated at the lower temperature of 275 °C. Sintering and blockage of some active phases by carbon and sulfur may be the main cause of a significant decline of SAC of the sorbents regenerated at 450 °C.

References


