



Denitrogenation of raw diesel fuel by lithium-modified mesoporous silica

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ABSTRACT

Lithium-modified mesoporous silica adsorbents (YSP-Li and MCF-Li) were prepared in order to selectively remove nitrogen compounds from residue hydrodesulfurization diesel (RHDS DSL: 271.3 ppmw of nitrogen compounds and 430.2 ppmw of sulfur compounds) provided by a refinery factory. Adsorption properties, such as the adsorption capacity, adsorption rate, and the regeneration ability toward nitrogen and sulfur compounds, were measured through batch experiments at 15 and 45 °C. They were compared with the results of previously reported Si–Zr cogel experiments. The lithium-modified mesoporous silica adsorbents exhibited a much stronger adsorption affinity for nitrogen compounds than for sulfur compounds. With regards to the adsorption capacity and the adsorption rate, the lithium-modified mesoporous silica adsorbents exhibited improved performance when compared to Si–Zr cogel. Furthermore, the Li-modified adsorbents, especially YSP-Li, could be easily regenerated by MIBK, an organic solvent.

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1. Introduction

Due to increasingly stringent environmental regulations for transportation fuels, the desulfurization and denitrogenation of fuels have become very important research topics in the production of clean automotive fuels with ultra-low sulfur levels [1–7]. According to the new environmental protection agency (EPA) Tier II regulations, the maximum allowable sulfur content in US diesel fuel is less than 15 ppmw (parts per million by weight). Refineries are facing major challenges meeting the new fuel sulfur requirements and reducing the content of aromatics because further tightening regulations of sulfur limits are expected for both highway vehicles and off-road diesel fuels in the near future [1,5].

To bring commercial diesel fuels from refineries to the market, fuels from various process streamlines are hydrodesulfurized and then blended with light hydrocarbons and additives. At present, ultra-low sulfur diesel (<10 ppmw of S) is available from many refineries that utilize conventional hydrodesulfurization (HDS) processes at high temperatures and high pressures in order to produce light gas oil with a low sulfur content. However, because of the ongoing consumption of fuels from limited natural resources, petroleum refineries must treat heavy low-quality crude oil so as to comply with tightening regulations.

Heavy low-quality crude oil is rich in highly refractory nitrogen compounds. During catalytic hydrotreating (an integral step in

the refinement of oil), denitrogenation (HDN) and desulfurization (HDS) are performed simultaneously. The ability to adsorb nitrogen compounds is generally higher when compared to aromatic thiophene derivatives, which have to compete with nitrogen compounds for active sites on catalysts during HDS processes [1,6,7]. In addition, the denitrogenation reaction (HDN) is the most difficult hydrotreatment reaction and slower than the desulfurization reaction (HDS). Therefore, nitrogen compound residue remains on active sites longer than sulfur compounds. As a result, refractory sulfur compounds are difficult to convert and, in the treatment of heavy crude oil, using present HDS technologies to reduce the level of sulfur is difficult while complying with ever-tightening regulations [3].

As an alternative method, selective adsorption appears to be a promising approach to ultra-deep desulfurization and denitrogenation because the process can be run at ambient temperature and atmospheric pressure without consuming pressurized hydrogen [8] or oxygen [9] gas. In addition, adsorbents can be regenerated by proper methods. However, for selective adsorption to be viable, an effective adsorbent that can selectively adsorb sulfur and nitrogen compounds must be developed.

Real fuels, which are different from model fuels, consist of many different compounds and their compositions, including the concentration of nitrogen and sulfur compounds, depend on the feedstock and the applied processes. Many researchers experimenting with different adsorbents have reported on the desulfurization and denitrogenation of commercial fuels using zeolite-based materials [10], carbon materials [11,12], activated alumina [13] and aluminosilicate [6,14], silica-based materials [15], and materials

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modified by CoMo [6], Cu [10,14], NiMoS–CoMoS [14], Ni [12], or MV²⁺ (methyl viologen) [14]. Commercially available activated carbon MAXSROB-II (2973 cm²/g) reportedly can adsorb 98 mg of S and 39 mg of N per gram of adsorbent from straight run oil gas (SRGO), which contains 11780 ppmw of S and 260 ppmw of N [11]. It was also reported that CuY zeolite can selectively adsorb sulfur and nitrogen compounds from commercial fuels [10]. We have previously reported on the desulfurization and denitrogenation of light gas oil (LGO) using a silica–zirconia (Si–Zr) cogel [4]. In addition, zirconium–mesoporous silica (YSP-II) [7] and magnetite–mesoporous silica [16] were introduced for the denitrogenation of LGO and for the desulfurization of natural gas.

The selective adsorption and capacity of an adsorbent may be key factors in the development of adsorptive processes. Furthermore, the adsorption rate and regeneration are important in the design of an effective cyclic adsorptive process for bulk treatments at a refinery because of the need for treating large molecules (e.g. dibenzothiophene and carbazoles) in liquid phase.

The purpose of this work is to study the adsorption properties of lithium (Li) modified mesoporous silica adsorbents toward nitrogen and sulfur compounds in fuels. A Li ion has an attraction toward O and N donor atoms, in contrast to a metal–chalcogenide interaction that is much weaker than its oxygen and nitrogen analogues [17]. Therefore, Li ions were selected as a modifier of silica-based materials for the selective adsorption of nitrogen compounds.

In this study, residue hydrodesulfurization diesel (RHDS DSL) was employed as the fuel. RHDS DSL contains about 430.2 ppmw of sulfur compounds, approximately 271.3 ppmw of nitrogen compounds, a certain level of aromatic hydrocarbons, and a trace amount of metals. Before the fuel is subject to HDS and blending, the concentration of nitrogen compounds must be decreased. Thus, YSP developed in previous research [7] was selected as one mesoporous silica-based material, which could effectively adsorb nitrogen and sulfur compounds from LGO. To study the effect of the surface area and the pore size on the adsorption rate and regeneration, mesocellular siliceous foams (MCF) was also employed. MCF has a larger pore size and a smaller surface area than YSP. In the previous Si–Zr cogel study [4], the adsorbed amount of nitrogen compounds from light gas oil increased with an increase in temperature even though the adsorption is exothermic. Since this study focused on the performance evaluation of modified mesoporous silica adsorbents, the adsorption equilibria, kinetics and the regeneration of nitrogen and sulfur compounds in RHDS DSL were measured within the limited temperature conditions. And the results of both YSP–Li and MCF–Li were compared to the performance of Si–Zr cogel supplied from a refinery.

2. Experimental

2.1. Materials

Pluronic P123 (EO₂₀PO₇₀EO₂₀; Kumkamg Chemical Korea Co., South Korea, LTD), cetyltrimethylammonium bromide (Aldrich, USA, 95%), tetrabutylammonium bromide (Junsei Chemical Co., Ltd., Japan, 98%), petroleum benzene (Kanto Chemical Co., Inc., Tokyo, Japan, fraction 50–90 °C–min 90%), tetraethyl orthosilicate (Sigma–Aldrich, USA, 98%), mesitylene (Aldrich, USA, 98%), hydrochloric acid (Sigma–Aldrich, USA, 37%), lithium acetate (Aldrich, USA, 99.99%), toluene (Sigma–Aldrich, USA, 99.9%) and methyl isobutyl ketone (MIBK; Duksan Pharmaceutical Co., LTD, South Korea, boiling range 114–117 °C–95%, v/v% up) were used as received. Milli-Q deionized water was also employed in the experiments.

Table 1

Properties of residue hydrodesulfurization diesel (RHDS DSL) fuel.

Properties	Values
Distillation start point [K]	430.3
5% distilled T [K]	469.5
10% distilled T [K]	500.3
20% distilled T [K]	539.7
30% distilled T [K]	566.5
50% distilled T [K]	603.9
70% distilled T [K]	637.1
90% distilled T [K]	674.1
Distillation end point [K]	714.9
Residues [vol.%]	0.5
Compounds:	
Al [ppmw]	0.3
Cu [ppmw]	0.5
Fe [ppmw]	0.2
Mg [ppmw]	0.1
Di-aromatic hydrocarbon [ppmw]	43.84
Poly-aromatic hydrocarbon [ppmw]	6.9
Other aromatic hydrocarbon [ppmw]	1.62
Content of sulfur [ppmw]	430.2 ± 11.5
Content of nitrogen [ppmw]	271.3 ± 6.1

The residue hydrodesulfurization diesel (RHDS DSL) contained about 430.2 ppmw of sulfur compounds and approximately 271.3 ppmw of nitrogen compounds. Its distillation characteristics with regard to trace metals and aromatics are listed in Table 1.

2.2. Synthesis of lithium-modified adsorbents

The MCF was prepared in aqueous hydrochloric acid using a dilute solution comprised of Pluronic P123 (EO₂₀PO₇₀EO₂₀), a nonionic block copolymer surfactant, and 1,3,5-trimethylbenzene (TMB) as an organic swelling agent [18]. In a typical preparation, P123 (2.0 g, 0.4 mmol) was dissolved in 2 M HCl (75 mL) at room temperature while being stirred in a beaker. TMB (0.7 mL) was then added, and the mixture was heated to 45 °C. After stirring at 600 rpm for 1 h, lithium acetate was added to the solution (198 mg, 3 mmol) for the MCF–Li. And, after 15 min, tetraethyl orthosilicate (TEOS, 4.5 mL) was introduced into the mixture. After stirring (300 rpm) at 45 °C for 20 h, the reaction mixture was aged at 100 °C under static conditions at atmospheric pressure for 24 h. The mixture was then allowed to cool to room temperature. White precipitates from the solution were isolated by filtration, dried, and calcined at 500 °C for 8 h.

In our previous work, the preparation and characteristics of YSP were described in detail [7]. To synthesize YSP–Li, tetrabutylammonium bromide (TBAB: 1.13 g) and cetyltrimethylammonium bromide (CTMAB: 1.275 g) were mixed in an aqueous HCl solution (46.5 mL HCl and 63 mL water) at ambient temperature. First lithium acetate (99 mg, 1.5 mmol), then 6 mL of petroleum benzene, were added to the above solution, and the mixture was held at 4 °C for 1 h. The fabricated solution was then mixed with 4 mL tetraethyl orthosilicate (TEOS) and stored at 4 °C for 12 h. The synthesized particles were recovered by filtration, dried at 50 °C for 24 h, and calcined at 550 °C for 5 h.

2.3. Adsorption and regeneration experiments

To measure the adsorption equilibrium in the batch experiments, adsorbents with a mass of 5, 25, 50, and 75 mg in vials were activated in a vacuum oven at 110 °C for 2 h. Three vials at the same condition were prepared to analyze the experimental error. After 5 mL of fuel was added to each vial, the vials were immediately capped and immersed in a shaking bath (80 rpm) at 15 or 45 °C. After 48 h, fuel was separated from the adsorbent by centrifugation

Table 2
Properties of adsorbents.

Properties	Values
Si–Zr cogel [4]	
Type/size [mesh]	Pellet/16
BET surface area [m ² /g]	502.0
Bulk density [g/cm ³]	0.61
Pellet density [g/cm ³]	1.29
Amount of Zr	3 wt%
YSP-Li	
BET surface area [m ² /g]	815.2
Pore volume (average) ^a [cm ³ /g]	0.53
Pore size [nm] ^a	3.73
Amount of Li	3.846 × 10 ⁻⁴ wt%
MCF-Li	
BET surface area [m ² /g]	551.6
Pore volume (average) ^a [cm ³ /g]	0.78
Cell pore size [nm] ^a	19.6
Amount of Li	1.912 × 10 ⁻⁵ wt%

^a BJH (Barret–Joyner–Halenda) adsorption.

at 15,000 rpm for 10 min (Vision VS-15000N). The fuel was then examined with an N-S analyzer.

To measure the adsorption rate, seven samples (50 mg of adsorbent and 5 mL of fuel) at each temperature (15 or 45 °C) were simultaneously immersed in a shaking bath (80 rpm) and each sample was analyzed at different time interval.

To evaluate the regeneration ability of the adsorbents, an organic solvent (MIBK; methyl isobutyl ketone) with a high polarity (2.8 debayes) was employed. After removing the fuel from the vials, 5 mL solvent (MIBK) was added to each vial at the temperature of its adsorption experiment (15 or 45 °C). After 24 h in a bath, the solvent was removed from the vial and the vial (along with the adsorbents) was held in an oven at 50 °C for 12 h. Readsorption experiments were then performed following the same sequence as the first adsorption experiment. To confirm the effect of polarity on regeneration, the results were compared with those obtained from washing of low-polar solvent, toluene.

The uptake percent of nitrogen and sulfur compounds on the adsorbents (%) was calculated using the following equation:

$$\% \text{Uptake} = \frac{C_0 - C_e}{C_0} \quad (1)$$

where C_0 is the initial concentration of nitrogen or sulfur compounds and C_e is the equilibrium concentration.

2.4. Analytical methods

The size and morphology of the prepared materials were analyzed by TEM and HR-TEM (JEOL model JEM-300) at 300 kV. Samples for TEM analysis were prepared by placing a drop of the particle solution onto a copper grid and evaporating it at room temperature. The lithium content in the synthesized adsorbents was recorded via ICP-AES (ELAN 6100, Perkin-Elmer SCIEX) with an argon plasma (6000 K) source. Surface area, pore volume, and pore size distribution data were obtained from N₂ adsorption/desorption isotherms generated with a BET analyzer (Micromeritics, ASAP2020). The physical characteristics of the adsorbents are listed in Table 2.

The concentration of nitrogen and sulfur compounds was measured with an N-S analyzer (ANTEK, 9000 series). The standard component in the sulfur compounds was dibenzothiophene (DBT); for the nitrogen compounds, it was 9-methyl carbazole. Toluene (Duksan Pure Chemical Co. Ltd., 99.5%) was selected as the base component for calibration. Standard solutions were mixed with toluene for the calibrations.

3. Results and discussion

3.1. Characterization of materials

In a previous study, it was reported that YSP has a surface area of 1331.2 m²/g and a pore size of 2.47 nm [7]. It is also known that MCF has a surface area of 443.5 m²/g and a pore size of 22.1 nm [18]. However, when compared to the original adsorbents detailed in Table 2, the physical properties of the Li-modified adsorbents were slightly different.

Compared to the original YSP, the YSP-Li possessed a smaller surface area (815.16 m²/g) and a larger pore size (3.73 nm). The MCF-Li had a larger surface area (551.59 m²/g) and a smaller pore size (19.62 nm), when compared to the MCF. The pore volume of the YSP-Li (0.53 cm³/g) was smaller than that of the MCF-Li (0.78 cm³/g). From the ICP-AES analysis, the amount of lithium found in the prepared YSP-Li and MCF-Li was 3.846 × 10⁻⁴% (3846.0 ppbw) and 1.912 × 10⁻⁵% (191.2 ppbw), respectively. Even though almost twice the amount of lithium acetate was used in the synthesis of MCF-Li, its Li concentration was about 20 times less than that found in the YSP-Li. The amount of Li that may be doped into the MCF is limited by the above preparation method.

TEM images of the MCF-Li and YSP-Li are shown in Fig. 1. The MCF-Li in Fig. 1(a) and (b) is comprised of large spherical cells that are interconnected by uniform windows so as to create a continuous 3D pore system [18]. The window pore size was found to be around 8.6 nm (BJH adsorption). As shown in Fig. 1(c) and (d), the particle shape of the YSP-Li was different from that of the YSP, which exhibited a spherical shape with a micron scale particle size [7]. Due to the addition of lithium acetate, the aggregation of particles may be altered.

3.2. Effect of temperature and dosage amount on adsorption

Figs. 2 and 3 show the adsorption amounts in the batch experiments at 15 and 45 °C, respectively. The removal of nitrogen compounds at both temperatures increased as the adsorbent amount was increased from 1 to 15 mg/mL. Favorable adsorption characteristics were also observed. As shown in Fig. 2, the removal percent for nitrogen compounds on YSP-Li (~41% at a maximum adsorbent dosage of 15 mg/mL) at 15 °C was higher than that observed with Si–Zr cogel (34.01%) and MCF-Li (25.9%). However, the removal percent for sulfur compounds at 15 °C was negligible for all of the adsorbents (<2% at the maximum adsorbent dosage).

When compared to the results obtained at 15 °C, the removal efficiency for nitrogen compounds on MCF-Li and Si–Zr cogel at 45 °C exhibited a considerable increase (43.9 and 47.2% uptake, respectively). The removal efficiency of YSP-Li at 45 °C (Fig. 3(a)) also showed a slight increase (42.18% at a maximum adsorbent dosage of 15 mg/mL). At 45 °C, the difference in the nitrogen removal efficiency among the adsorbents became small, and the performance of the Si–Zr cogel was slightly better in the range of a high dosage amount. Furthermore, an increase in the temperature led to the improved removal of sulfur compounds, as shown in Fig. 3(b). The adsorption capacity of sulfur compounds on YSP-Li and MCF-Li was nearly the same. Both materials possessed a higher adsorption capacity than the Si–Zr cogel. Therefore, the overall removal capacity of nitrogen and sulfur compounds from RHDS DSL on Li-modified adsorbents was higher than that of Si–Zr cogel at 45 °C. In addition, all of the adsorbents clearly exhibited more favorable adsorption toward nitrogen compounds than sulfur compounds, even though the concentration of sulfur compounds in the RHDS DSL was almost 1.5 times higher than that of nitrogen compounds.

The YSP-Li with a high concentration of lithium and a large surface area exhibited improved adsorption results for nitrogen

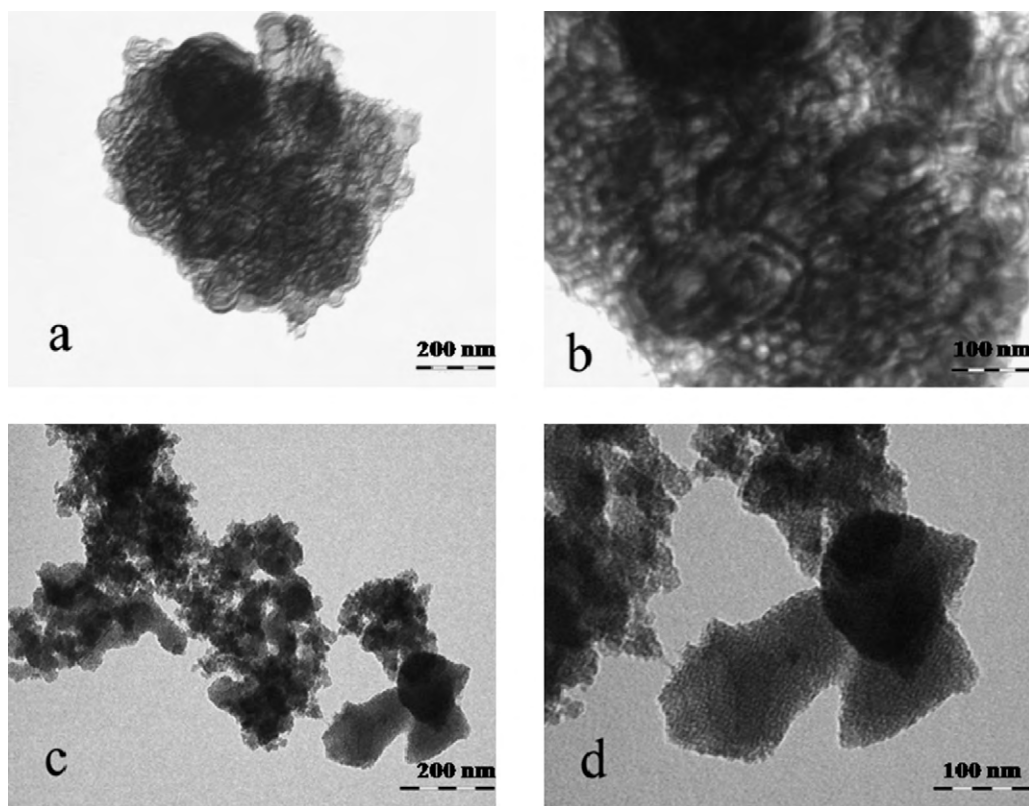


Fig. 1. TEM images of (a and b) MCF-Li and (c and d) YSP-Li.

compounds at 15 °C. The nitrogen adsorption capacity was not significantly affected by the applied temperature. On the other hand, even though the adsorption processes are generally exothermic, the amount of adsorbed nitrogen compounds on MCF-Li and Si-Zr cogel significantly increased at 45 °C. Furthermore, a certain amount of sulfur compounds could be adsorbed on all adsorbents at 45 °C.

The nitrogen compounds in the real fuels typically belong to one of two groups [4]. One group is strongly basic with a pyridine ring, such as pyridines, tetrahydroquinolines, quinolines, and acridines. The other group is weakly acidic with a pyrrole ring, such as indoles, carbazoles, and benzocarbazoles. The representative sulfur compounds are dimethylthiophene, 4-methyldibenzothiophene, 4,6-dimethylthiophene, and 3C-dibenzothiophene. Since the molecules of the nitrogen and sulfur compounds in RHDS DSL could be activated with an increase in temperature, relatively large

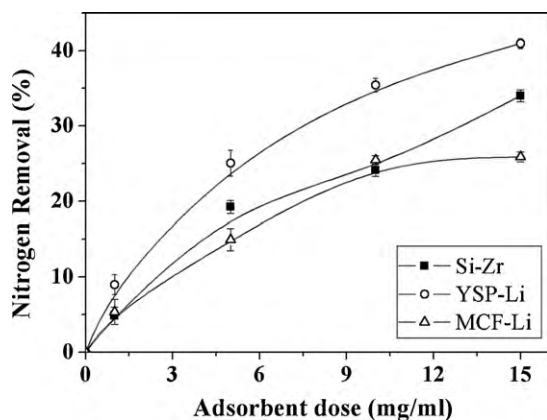


Fig. 2. Effect of adsorbent amount on adsorption of nitrogen compounds at 15 °C for 48 h (80 rpm) in RHDS diesel fuel.

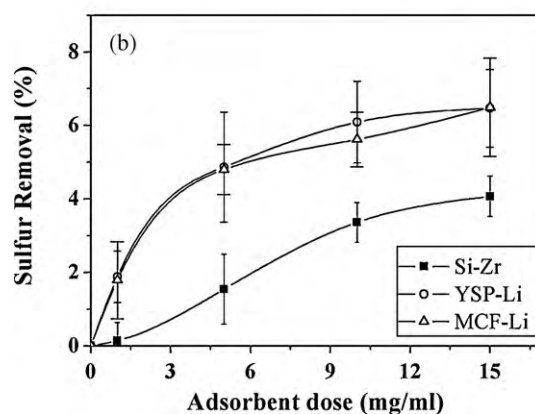
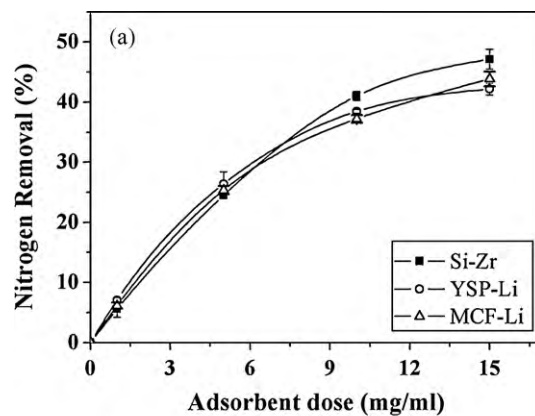


Fig. 3. Effect of adsorbent amount on adsorption of (a) nitrogen and (b) sulfur compounds at 45 °C for 48 h (80 rpm) in RHDS diesel fuel.

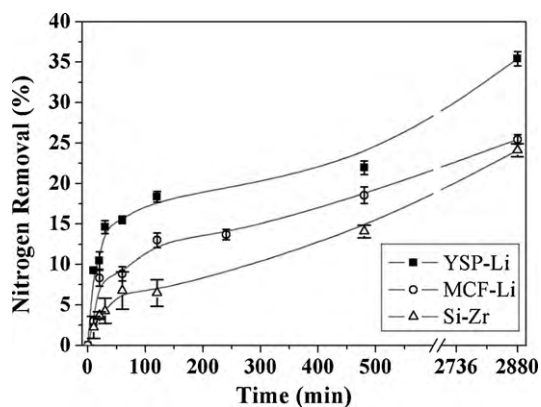


Fig. 4. Adsorption rate of nitrogen compounds at 15 °C (adsorbent concentration: 10 mg/mL; stirring speed: 80 rpm).

molecules could more easily pass through the pores. Therefore, when compared to YSP-Li, MCF-Li and Si-Zr cogel (which have a larger pore size and pore volume) allow more adsorbate to enter the pores at higher temperatures. In addition, some of the nitrogen and sulfur compounds in the pores have a strong affinity to lithium. Such a phenomenon, where the adsorption capacity is affected by a temperature increase, can be confirmed by the results of adsorption rate and regeneration experiments.

3.3. Effect of temperature on adsorption rate

The adsorption rates of nitrogen and sulfur compounds at 15 and 45 °C were measured by batch experiments. At 15 °C, the adsorption rates of all adsorbents (Fig. 4) were initially fast, then slowly increased linearly with time. The initial adsorption rate of YSP-Li was much faster than the others (nitrogen removal% with a 120 min contact time: 18.37% for YSP-Li, 12.99% for MCF-Li, and 6.78% for Si-Zr cogel), even though its pore size is smaller than that of MCF-Li and Si-Zr cogel. However, it should be noted that the adsorption rate of MCF-Li with a large pore diameter is faster than that of the Si-Zr cogel, even though its adsorption capacity is slightly smaller than the Si-Zr cogel in Fig. 2. Therefore, the strong adsorption affinity that stemmed from the lithium may contribute to the adsorption rate.

The trends in the adsorption rate of the adsorbents at 45 °C were different from the aforementioned experiments at 15 °C. When the nitrogen adsorption rates among the adsorbents were compared after a 120 min contact time (Fig. 5(a)), the adsorption rate of MCF-Li (19.88%) was faster than the other adsorbents at 45 °C and its own rate at 15 °C. The nitrogen adsorption rate of Si-Zr cogel at 45 °C increased (12.24%) when compared to the results attained at 15 °C (Fig. 4), while the nitrogen adsorption rate of YSP-Li decreased with an increase in temperature (13.96%). After 120 min, the adsorption rates in all of the adsorbents were not linear with time. Such a scenario may arise from differences in the diffusion of nitrogen compounds because RHDS DSL contains various types of nitrogen compounds.

Shown in Fig. 5(b) is the adsorption rate of sulfur compounds at 45 °C. The adsorption rate of sulfur compounds in YSP-Li and MCF-Li was initially very steep. Because a saturation point was almost reached during this initial period, changes in the amount of adsorption were minor after 60 min. As evident in Fig. 5(b), the sulfur adsorption rate in the Si-Zr cogel was clearly slower than that observed in the other materials.

A hindrance effect due to large adsorbed molecules can be expected in the YSP-Li with a pore size of 3.73 nm. Therefore, due to competitive adsorption between nitrogen and sulfur compounds during the initial testing period, the adsorption rate of nitrogen

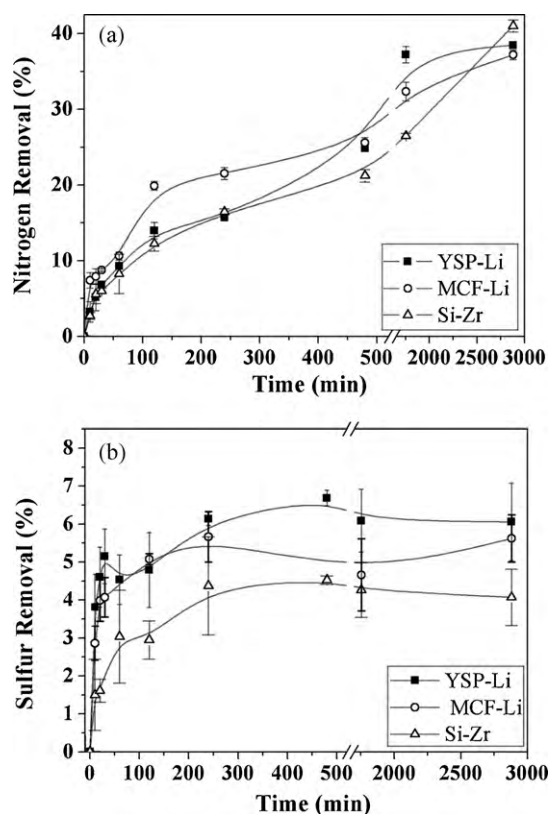


Fig. 5. Adsorption rate of (a) nitrogen and (b) sulfur compounds at 45 °C (adsorbent concentration: 10 mg/mL; stirring speed: 80 rpm).

compounds at 45 °C seems to be slower than that observed at 15 °C. In addition, due to the adsorption of large molecules on the YSP-Li with a smaller pore size, the change in the amount of adsorbed nitrogen compounds with a change in temperature is small. The hindrance effect on the MCF-Li is negligible due to its large pore size (19.62 nm). In addition, when diffused molecules are subjected to a higher temperature, they can adsorb on the active sites within the relatively large interior of the pores.

3.4. Regeneration and re-adsorption

To evaluate regeneration ability, the adsorbents used in the adsorption experiments were washed with two different organic solvents, toluene and methyl isobutyl ketone (MIBK), at the corresponding temperature of the adsorption experiment. The re-adsorption capacity was then studied at the same conditions used in the first adsorption experiment.

For all the adsorbents, the re-adsorption capacity was very close to the initial adsorption capacity at 15 °C (Fig. 6(a)), regardless of the applied solvent. Such a result implies that the low temperature interaction between each adsorbent and nitrogen compounds is weak (otherwise, weak adsorbates from the nitrogen compounds may adsorb mainly on the adsorbents). However, when compared to the results attained at 15 °C (Fig. 6(a)), the re-adsorption capacities at 45 °C (Fig. 6(b)) exhibited significantly different trends. At 45 °C, the re-adsorption capacity of the adsorbents treated by polar MIBK was higher than those treated by toluene. The result implies that high polar solvent (MIBK) works better to desorb the nitrogen compounds from all adsorbents that were adsorbed at this temperature. In addition, this suggests that the aromatic functional group of solvents contribute a little to improving the desorption of nitrogen compounds, which was similar to the previous studies [4,7].

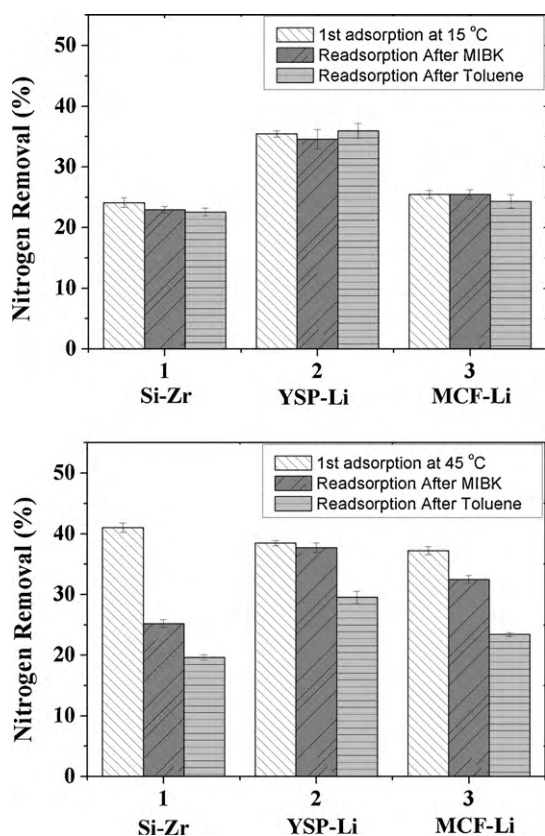


Fig. 6. Readsorption capacity of adsorbent washed by toluene or MIBK of 5 mL at (a) 15 °C and (b) 45 °C (adsorbent concentration: 10 mg/mL; stirring speed at 80 rpm).

The readsorption capacity of the Si-Zr cogel significantly decreased at 45 °C, regardless of the solvent used. In the case of MIBK regeneration, the readsorption capacity of YSP-Li was close to the original adsorption capacity observed at 45 °C (38.5% for adsorption and 37.7% for readsorption), while the readsorption capacity of MCF-Li exhibited a slight decrease (37.2% for adsorption and 32.5% for readsorption). The difference in the regeneration capacity between the adsorbents treated by MIBK and toluene was slightly larger than the adsorption amount of sulfur compounds.

Certain inferences may be derived from the attained results. First, the limited size of the molecules in the nitrogen and sulfur compounds allows them to penetrate into the pores of YSP-Li. Their adsorption affinity is relatively weak regardless of the applied temperature. Therefore, readsorption capacity can nearly be recovered through solvent washing. Other types of molecules (strong adsorbates) can also be adsorbed on the MCF-Li and Si-Zr cogel at higher temperatures due to their large pore sizes. In addition, specific types of molecules (especially those with a large molecular size) adsorbed at a higher temperature interact strongly with highly polar molecules (such as MIBK).

4. Conclusions

Lithium-modified mesoporous silica adsorbents were synthesized for the denitrogenation and desulfurization of refinery fuels (RHDS DSL). The adsorption capacity of nitrogen compounds on YSP-Li at 15 °C was higher than that observed for MCF-Li, but the adsorption capacity of sulfur compounds on both adsorbents was negligible. At 45 °C, the adsorption capacities of both adsorbents with respect to nitrogen were comparable. Furthermore, a certain amount of sulfur compounds was adsorbed on the Li-modified adsorbents at 45 °C, even though the adsorption amount was smaller than that of the nitrogen compounds.

During the initial testing period at 15 °C, the adsorption rate of nitrogen compounds on YSP-Li was faster than that of MCF-Li, even though MCF-Li has a much larger pore size. An opposite result was observed at 45 °C because of a hindrance effect and competitive adsorption on YSP-Li with a relatively small pore size. In addition, the observance of different trends in the adsorption rate at 15 and 45 °C implies the adsorption of different types of nitrogen compounds because of the different diffusion rates of the molecules.

Readsorption capacities for all of the adsorbents were very close to their initial adsorption capacities at 15 °C, regardless of the applied solvent. However, at 45 °C, the readsorption capacity of the adsorbents treated with MIBK was higher than that observed with a toluene treatment. Such a finding implies that molecules which interact strongly with polar molecules (such as MIBK) can be adsorbed at a higher temperature. The limited size of the molecules in nitrogen and sulfur compounds allows them to penetrate into the pores of YSP-Li; their adsorption affinity is relatively weak regardless of the applied temperature. Other types of molecules can be also adsorbed on MCF-Li at higher temperatures due to its large pore size. As such, the regeneration efficiency of YSP-Li was higher than that of MCF-Li.

According to the results of adsorption capacity, adsorption rate, and regeneration experiments, the Li-modified silica adsorbents (YSP-Li and MCF-Li) exhibited improved performance when compared to the Si-Zr cogel. The adsorption capacity of YSP-Li was less sensitive to the applied temperature and its regeneration ability was excellent. The fabricated mesoporous adsorbents can be used to remove nitrogen compounds before or after the hydrodesulfurization of fuel. Furthermore, the adsorbents can be easily regenerated and, therefore, a continuous cyclic process is possible for bulk treatments. In future experiments, the lithium concentration in the adsorbent will need to be optimized.

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