



Enhanced sulfur capacity of durable and regenerable mesoporous sorbents for the deep desulfurization of diesel



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HIGHLIGHTS

- Active sites of mesoporous sorbents were increased.
- Desulfurization capability of sorbents was enhanced 250%.
- Sorbents was completely regenerated in deep desulfurization of commercial diesel.
- Active Ni ions on sorbents were intact after desulfurization and regeneration.

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ABSTRACT

The adsorptive desulfurization of a model diesel (300 ppmw S) and a commercial diesel (187.2 ppmw S) using the durable and regenerable Ag/Al-SBA-15, Ni/Al-SBA-15 and Ce/Al-SBA-15 sorbents was investigated in fixed-bed tests. The desulfurization capability of the sorbents was remarkably enhanced by elevating metal ion-exchanging temperature, increasing metal ion-exchanging number of times and using large pore SBA-15 (~11.55 nm) as the support. Ni/ASL60-4 sorbent, which was prepared by exchanging Ni ions onto the aluminized large pore SBA-15 (~11.55 nm) at 60 °C with 4 of times, exhibited the highest desulfurization capability. For the desulfurization of the model diesel, Ni/ASL60-4 can remove 0.228 mmol of total sulfur per gram at saturation. For desulfurization of commercial diesel, 7.0 ml of clean diesel (less than 1.0 ppmw S) can be produced over 1.0 g of Ni/ASL60-4. The desulfurization capability of Ni/ASL60-4 can be enhanced a total of 250% compared to Ni/AS20-1. The saturated Ni/ASL60-4 was regenerated in situ by heating in dry air at 350 °C. After generation, the desulfurization capability of Ni/ASL60-4 can be completely recovered even after 3 cycles. The NiO particles were not found on the fresh and regenerated Ni-based sorbents by XRD test. This showed that metal Ni was in the form of Ni ions after the desulfurization and regeneration. This was mainly because the Ni ions can be firmly anchored on the aluminized SBA-15 by ion-exchanging.

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1. Introduction

Considering of the demand in protecting environment, zero sulfur emissions from the diesel engine will become increasingly stricter in the future [1]. Therefore, extensive study has been carried out about the desulfurization of diesel. Conventional hydrodesulfurization process would require heavy expenditure in capital and operation though this method cannot produce zero sulfur fuel [2]. It was well known that the deep desulfurization of diesel should be an energy efficient, low cost and greener process [3]. Therefore, adsorptive desulfurization of diesel has received

much attention due to the sulfur concentration can be reduced to below 1.0 ppmw even at room-temperature without octane loss [3,4]. Many studies have been made on developing sorbents for deep desulfurization of diesel [5–12]. Yang's group investigated various sorbents for the adsorptive desulfurization of transportation fuels at room temperature and ambient pressure [13]. They thought that the high sulfur selectivity and high desulfurization capability of the sorbents were due to the π -complexation between the sulfur compounds and the active metal of the sorbents. Song's group studied metal ion-exchanged zeolites for removing sulfur compounds from transportation fuels [5]. They thought that the sulfur compounds were adsorbed over the metal-exchanged zeolites mainly via direct sulfur–metal (S–M) interaction. In addition, according to Lewis acid–base theory, most thiophene sulfur

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compounds in transportation fuels are Lewis base which are easy to be adsorbed at Lewis acid sites [8].

It is also known that the desulfurization capability is not the only measurement for an appropriate sorbent. The multi-cycle operability and good durability are perhaps more potentially useful. Therefore, the regeneration property of sorbents should also be considered in developing a sorbent. The sorbent supports reported in literatures mainly included metal oxides [14], zeolites [9], activated carbon [15], and other mesoporous materials etc [10,11]. Take both desulfurization and regeneration into consideration, mesoporous materials can serve as the optimum supports on account of the large specific surface area and large pore volume. Using mesoporous materials as support to prepare the sorbents by wet impregnating, the obtained sorbents usually exhibited a higher desulfurization capability [10–12]. However, the regeneration performance of these sorbents was unsatisfactory. In our previous work, it was found that the sorbents of aluminized SBA-15 grafted with Ag, Ni, Ce metal ions can be completely regenerated after saturating the sulfur compounds in the desulfurization of a model jet fuel [16]. And, it was testified that the sorbents of Ag/Al-SBA-15, Ni/Al-SBA-15 and Ce/Al-SBA-15 were durable and regenerable. The major reason was that the active metal ions were firmly anchored on aluminized SBA-15 by ion-exchanging. However, the desulfurization capability of these durable and regenerable sorbents is not prominent in comparison with some sorbents reported in the literatures [8,11,13,17].

In present work, the objective was to enhance the desulfurization capability of the durable and regenerable Ag/Al-SBA-15, Ni/Al-SBA-15 and Ce/Al-SBA-15 sorbents reported in our previous work [16]. Elevating temperatures and increasing number of times in exchanging Ag, Ni or Ce ions onto the support were applied in preparing the durable and regenerable sorbents. Meanwhile, the large pore SBA-15 (~11.55 nm) was also used as the support to enhance the desulfurization capability of sorbents. The desulfurization capability of the improved sorbents was tested in adsorptive removal of sulfur compounds from a model diesel (300 ppmw S) and a commercial diesel (187.2 ppmw S).

2. Experimental

2.1. Sorbent preparation

SBA-15 was synthesized according to the literature [18] and was signed as S in this work. The aluminized SBA-15, Al-SBA-15, was prepared by post-synthesis [19] and was labeled as AS. The objective of introducing Al to SBA-15 is to enhance the exchanging degree of metal ions onto the supports [16,19]. The sorbents containing Ag, Ni or Ce ions were produced by exchanging the metal ions onto Al-SBA-15 [16]. Two methods were applied to increase the loadings of metal ions. One is to elevate the ion-exchanging temperature and the other one is to increase the ion-exchanging number of times. The exchanging of Ag ion was carried out at 20, 30, 40 and 50 °C, respectively. The typical procedure was as follows: 0.5 g of Al-SBA-15 was dispersed in 50 ml of dry THF with 0.1 mol/l of AgNO₃ solution and stirred for 24 h. After filtration and washed with THF, the products were dried at 130 °C for 2 h under vacuum. The prepared Ag/Al-SBA-15 sorbents were labeled as Ag/AS20-1, Ag/AS30-1, Ag/AS40-1 and Ag/AS50-1, respectively. Where 20, 30, 40 and 50 are the exchanging temperatures and 1 is the exchanging number of times. Using Ni(NO₃)₂ and Ce(NO₃)₃ as the Nickel and Cerium ions source, the preparation of Ni- and Ce-based sorbents was similar with the preparation of Ag-based sorbents but using distilled water as the solvent. The symbol for Ni- and Ce-based sorbents is similar to that for the Ag-based sorbents. Another series of sorbents were prepared by increasing the

ion-exchanging number of times under the same conditions mentioned above. For example, Ag/AS40-2 was prepared by exchanging Ag ion with 2 of times at 40 °C. Similarly, Ni/AS60-2, Ni/AS60-3 and Ni/AS60-4 as well as Ce/AS60-2, Ce/AS60-3, Ce/AS60-4, Ce/AS60-5 sorbents were prepared by exchanging Ni or Ce ions with various number of times at 60 °C. In addition, SBA-15 with large pore size was also used as the supports. The large pore SBA-15 (~11.55 nm) was prepared according to the literatures [20] and was labeled as SL. The aluminizing and the exchanging process of metal ion onto large pore SBA-15 were under the same methods and conditions mentioned above. For example, Ni/ASL60-4 sorbent was prepared by exchanging Ni ion onto the large pore Al-SBA-15 at 60 °C with 4 of times.

2.2. Sorbent characterization

The XRD measurements were carried out using a Germany Bruelckner D8 Advance instrument. The N₂ adsorption was carried out at –196 °C using Quantachrome NOVA. The loadings of Ag, Ni and Ce ions on sorbents were tested by ICP-AES on an IRIS Intrepid II instrument.

2.3. Reagent

A model diesel with 300 ppmw total sulfur concentration was prepared according to literature [13]. The preparation procedure was as follows: 0.0146 g of benzothiophene (BT), 0.0604 g of dibenzothiophene (DBT) and 0.0465 g of dimethyldibenzothiophene (DMDBT) were dissolved in 100 ml of *n*-octane and stirred. The sulfur concentrations were 50 ppmw S for benzothiophene, 150 ppmw S for dibenzothiophene and 100 ppmw S for dimethyldibenzothiophene. The commercial diesel was purchased in Aug. 25, 2013 from Sanhe Gas Station, Harbin, Heilongjiang Province of China. The sulfur content was approximately 187.2 ppmw. 600718.

2.4. Fixed-bed adsorption experiment

All dynamic breakthrough adsorption experiments were performed at room temperature in a vertical custom-made quartz adsorber as described elsewhere [16]. In a fixed bed system, the particle diameter of sorbents may play a role on the breakthrough time. When the diameter of particles was more than 1 mm, the diffusion in the pores may have an influence on the adsorption rate and the shape of the curve. Thus, the sorbents used in present work were in its incipient powder form (80–100 mesh). Initially, 1.0 g sorbent was loaded inside the adsorber and was activated in flowing Ar at 350 °C for 5 h to remove physically adsorbed water. The feed of fuel was at flow rate of 1.0 ml/40 min. The effluent was sampled periodically and once every 1.0 ml was collected until saturation was achieved. Breakthrough adsorption curves were generated by plotting the transient total sulfur concentration normalized by the feed total sulfur concentration versus cumulative fuel volume normalized by total bed weight (ml/g). The adsorption amounts (normalized per sorbent weight) were obtained by integral calculation [13].

2.5. Gas chromatographic analysis

All of the fuels collected during the breakthrough experiments were analyzed using a Shimadzu GC-2014 (C) gas chromatograph equipped with an Agilent DB-5 GC column and a flame photometric detector (FPD). The sulfur detection limit was 0.1 ppmw.

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