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Acidic sites and deep desulfurization performance of nickel supported mesoporous AlMCM-41 sorbents

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ABSTRACT

Nickel particles supported on mesoporous MCM-41 or AlMCM-41 (SiO_2/Al_2O_3 = 30, 50) sorbents were prepared by an incipient wetness impregnation (IWI) of nickel nitrate and the ultra-deep desulfurization properties for model fuels or diesel were evaluated under ambient conditions. Among the tested sorbents, 15%Ni-AlMCM-41 (30) presented the highest sulfur adsorption capacity toward thiophene, benzothiophene and commercial diesel. The pore structure, acidic sites and surface features of the sorbents were characterized by means of BET, XRD, NH_3-TPD, Py-FT-IR and XPS techniques, it revealed that Lewis acidic sites played important role in the removal of organic sulfur compounds over reduced 15%Ni-AlMCM-41 (30). After regeneration of used sorbent, approximately 100% of organic sulfur adsorption capacity was recovered.

1. Introduction

The combustion of commercial fuels (diesel, gasoline, and jet fuels) in internal combustion engines emits SO_x, a major air pollutant. Therefore, the removal of organosulfur compounds has become an important issue in recent years. Many countries have implemented more stringent regulations for refineries to produce diesel or gasoline with low sulfur content. For instance, U.S., Europe and other countries have already reduced the upper limit of sulfur concentration in gasoline to 10 ppm [1]. Deep desulfurization of transportation fuels is of an important significance not only for clean air but also for use in fuel cell [2,3]. The current hydrodesulfurization (HDS) process is not feasible to produce ultra-clean transportation fuels for fuel cell applications [3,4]. Despite being highly efficient in removing aliphatic organosulfur compounds, HDS catalysts are less effective for the removal of thiophene (T), benzothiophene (BT), dibenzothiophene (DBT), and their alkylated derivatives, such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) [5–7].

Recently, adsorptive desulfurization and biodesulfurization [8] technologies were studied in desulfurization of fuels in order to avoid the shortcomings of HDS. Among alternative methods, adsorptive desulfurization is a widely used technology because it can operate at ambient conditions [9,10]. Adsorptive desulfurization on the nickel-based sorbents is promising among all new approaches for ultra-deep desulfurization due to high sulfur-adsorption capacity and selectivity [11,12]. Mesoporous-molecular sieve, such as SBA-15 and MCM-48 supported nickel for adsorptive desulfurization have been reported [13,14]. Song et al. reported MCM-48 supported nickel sorbents, i.e. Ni20/MCM-48 can treat 170 L of commercial ultra low sulfur diesel (ULSD) with sulfur content from 15 to 1 ppmw, higher than 30%Ni/SBA-15 for 50 mL/kg reported by Park et al. [13].

However, the performance of sorbents studied cannot meet the requirement in industry; the interaction mechanism between organosulfur molecules and nickel based mesoporous material has not been reported yet to the best of our knowledge. The objective of the present work is to improve the adsorptive desulfurization performance of nickel-based sorbents by nickel loaded AlMCM-41 and to investigate the interaction of organosulfur molecules with Ni particles on high surface area MCM-41 or AlMCM-41. The used sorbents were characterized by XPS and FT-IR spectra.

2. Experimental

2.1. Preparation of sorbents

Mesoporous material, MCM-41 was prepared at room temperature (RT) according to procedure reported in the literature [15]. First, 2.0 g of $C_{16}H_{33}(CH_3)_3N^+Br^-$(CTAB) was dissolved in 205 mL of NH_4OH (25 wt%) and 270 mL deionized (DI) water at 40 °C under the stirring in order to form homogeneous rod-style micelle. Then, 10 mL of tetraethyl orthosilicate (TEOS) was added. After continuous stirring for 2 h, the obtained white slurry was filtered and washed with 2 L of DI water, dried at RT and followed by

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calcination at 550 °C in air for 6 h. Finally, the synthesized support was referred to as “M41” hereinafter.

AlMCM-41 materials with different SiO_2/Al_2O_3 molar ratios (30,50) were synthesized using aluminum isopropoxide as an Al source. First, 26.4 g of CTAB was dissolved in 150 mL of DI water at 40 °C with stirring to make a homogenous solution. The aforementioned solution was then added to alumina sol formed from the hydrolysis of aluminum isopropoxide [16]. 150 mL Na_2SiO_3 (14.3 wt%) was added drop wise to the aforementioned solution by adjusting pH = 11 using H_2SO_4 (2 mol/L). The sol formed was transferred into a stainless steel autoclave with Teflon-lined for hydrothermal synthesis at 120 °C for 96 h. The obtained solid product was filtered and washed with DI water, dried in vacuum at 80 °C for 24 h and calcined at 550 °C in air (300 mL/min) for 6 h. Finally, the synthesized material was referred to as “AlM41 (30,50)” hereinafter.

Ni-M41 and Ni-AlM41 (30,50) with different Ni loadings (5, 15 and 30 wt%) were prepared *via* IWI method using M41 and AlM41 (30,50) as a support. An appropriate amount of $Ni(NO_3)_2{\cdot}6H_2O$ was dissolved in DI water and mixed with solid M41 or AlM41 (30,50) under stirring. The obtained slurry was dried at 100 °C overnight and calcined in air at 450 °C for 4 h.

2.2. Characterization of fresh and used sorbents

Nitrogen adsorption isotherms of sorbents were studied at 77 K on a domestic assembly system [17], which was used to calculate BET surface areas. The pore size distribution was calculated by BJH method as reported in the literature [18]. The X-ray diffraction (XRD) patterns were collected using a PANalytical X’Pert PRO Diffractometer with a Cu K_α monochromatic radiation source, operated at 40 kV and 30 mA. Temperature- programmed desorption of ammonia (NH_3-TPD) were conducted on Auto Chem 2910 (Micromeritics, USA). Approximately 100 mg of sorbent was taken in a U-shaped quartz tube and pretreated at 200 °C in argon (20 mL/min) for 30 min. When sorbent was cooled to 30 °C, the ammonia was injected in pulse to the sample until saturation. After physiosorbed ammonia was purged with argon, TPD was carried out from 30 to 600 °C at heating rate of 10 °C/min. FT-IR spectra of sorbents with and without pyridine (Py) adsorption were collected on BIO-RAD FTS 3000 spectrophotometer. Each Py-FT-IR was conducted by adsorption of pyridine over sample (pretreated at 350 °C) in a flow of helium (30 mL/min) at 100 °C for 30 min. Then, physiosorbed pyridine was purged in helium (30 mL/min) for 20 min. Finally, the obtained sample (10 mg) was ground with 200 mg of KBr to record IR spectrum. XPS analyses were conducted on a PHI-1600 ESCA spectrometer equipped with Mg Kα X-ray source (1253.6 eV). The samples were pressed onto a piece of double-sided sticking tape and mounted on the sample probe, then, outgassed in a pre-evacuation chamber and subjected into the analyzer chamber. Binding energy (BE) of the sample was calibrated to the C 1s line (284.4 eV).

2.3. Preparation of model fuels

Three model fuels were used in this study. Thiophene, BT, and thiophene+ naphthalene (N) dissolved in n-octane, respectively. The obtained model fuels were referred as TO (243 ppm-S), BTO (238 ppm-S) and TNO (243 ppm-S) hereinafter. In addition, the commercial diesel (gas station of Tianjin, China) with a sulfur containing 235 ppm was used for the investigation in adsorption capacity of sorbents.

2.4. Procedure of adsorptive desulfurization

Adsorptive desulfurization performance of different sorbents was investigated at RT and atmospheric pressure. The whole desulfurization assembly consisted of fuel feed tank (or DG-2, BT01-micropump, Tianjin Xieda Electronic Ltd., China), the column with temperature controller and fuel flow control device. The 1–1.5 g of sorbent was charged into glass column with 7.2 mm inner diameter and reduced *in situ* at 450 °C for 6 h in hydrogen (50 mL/min) prior to adsorption. After the temperature of the column decreased to RT in hydrogen, the model or commercial diesel fuels were introduced into the column with a flow rate of 3 mL/h. The effluent from the sorption column was collected periodically and analyzed by WK-2000 sulfur analyzer (Jiangyan Kedi instrument Ltd., China). The sulfur breakthrough curves were obtained by plotting the transient sulfur concentration vs. the cumulative volume of treated model or commercial fuels. The sorption amounts (breakthrough sulfur capacity) of sorbents were calculated by Eq. (1):

$$Q\,(\text{breakthrough or saturation}) = \left(\frac{v}{m_{sorbent}}\right)\left(\frac{\rho_{fuel}X_i}{MW_{sulfur}}\right)\int_0^t\left[1-\frac{C(t)}{C_i}\right]dt \qquad (1)$$

where Q is the breakthrough or saturation sulfur capacity of unit mass of sorbent (mmol/g), v is the flow rate of fuel (cm^3/min), $m_{sorbent}$ is the mass of the sorbent charged in column, ρ_{fuel} is fuel density (~0.832 g/cm^3), X_i is the total sulfur fraction (by weight) in the feed, MW_{sulfur} is molecular weight of sulfur, C_i is the total sulfur concentration in fuel (ppmw-S) and $C(t)$ is the effluent total sulfur concentration (ppmw-S) at any time t (min). The integral part on the right-hand side of Eq. (1) is the area above breakthrough curves at any time t.

2.5. Sorbent regeneration

The regeneration of used 15%Ni-AlM41 (30) sorbent was conducted by means of alcohol extraction to remove sulfur species, the sorbent was then dried at 100 °C for 12 h. Finally, the obtained sample was calcined at 530 °C in air (300 mL/min) for 5 h.

3. Results and discussion

3.1. Characterization of the sorbents

Fig. 1 shows the N_2 adsorption isotherms and pore size distribution of M41 and AlM41 (30,50) as well as those of fresh and used 15%Ni-M41 and 15%Ni-AlM41 (30,50) sorbents. The nitrogen adsorption isotherms of M41 and AlM41 (50) revealed that the amount of nitrogen adsorption suddenly increased in the range of 0.23–0.4 (Fig. 1A(a) and (b)) due to the capillary condensation of N_2 molecules in uniform mesopores, indicative of typical of mesoporous material. The content of N_2 adsorption declined with increasing Al contents and the loadings of Ni particles, similar to the observation of Liu et al. [19]. The specific surface area (S_{BET}), pore volume (V_T) and average pore diameter (D_a) of M41 and AlM41 (30,50) are listed in Table 1. The M41 has large S_{BET} (925 m^2/g) and lower D_a (2.62 nm) due to synthesis at RT [20] whereas Al-M41 (30,50) exhibits relatively large D_a (3.58 and 3.68 nm). As reported earlier by Wang et al. [20], the tails of surfactant molecules moved or vibrated more flexibly during synthesis at high temperature, resulting in the formation of a large pore structure.

The loading of 15 wt% Ni particles resulted in the decline of S_{BET}, V_T and D_a of M41, AlM41 (30,50) (Table 1) because a large amount of Ni particles occupied or blocked the channels of M41 and AlM41 (30,50). After regeneration of used 15%Ni-AlM41 (30), no significant variation in N_2 adsorption isotherm (Fig. 1A(g)) and pore size distribution were observed (Fig. 1B(g)). This indicated the stability and regenerated ability of 15%Ni-AlM41 (30) sorbent.

The small angle XRD pattern of M41 (Fig. 2A(a)) consists of an intensive diffraction peak at $2\theta = 2.5°$ and two weak peaks at