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Research article

Superior performance of freeze-dried Ni/ZnO-Al_2O_3 adsorbent in the ultra-deep desulfurization of high sulfur model gasoline

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ABSTRACT

Reactive adsorption desulfurization (RADS) is an effective approach to the ultra-deep desulfurization under mild conditions. The sulfur adsorption capacity of the adsorbents strongly depends on the pore structure, the chemical states and the dispersion of active species. In this work, ZnO-Al_2O_3 mixed oxides with an improved structure were synthesized via a freeze-drying modified cation-anion double hydrolysis (CADH) technique and used as the support. The fresh and spent catalysts were characterized through N_2 adsorption-desorption, H_2-temperature programmed reduction, X-ray diffraction, UV–vis diffuse reflection spectroscopy, Fourier transformed infrared spectroscopy and transmission electron microscopy (TEM). Freeze drying technique provided the adsorbent with a smaller sized ZnO and an improved pore structure compared with the normal oven drying method. Evaluation results in the RADS of a high sulfur model gasoline reveals that the freeze-dried Ni/ZnO-Al_2O_3 (40 °C) with a crystallization temperature of 40 °C exhibits a superior RADS performance with an accumulative sulfur adsorption capacity of 90 mg S/g, which is 5.3% and 118% higher than those of adsorbents prepared by the normal oven drying and the conventional kneading methods. A high amount of small ZnO particles, improved textural properties and the absence of inactive $NiAl_2O_4$ phase are among the factors accounting for the superior RADS performance of Ni/ZnO-Al_2O_3 adsorbent prepared by the freeze-drying method. Upon four RADS-regeneration cycles, sample Ni/ZnO-Al_2O_3 (40°C) exhibited a high stability without evident activity loss.

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1. Introduction

The demand and use of transportation energy will continuously increase around the world in the foreseeable future [1]. The distillate of crude oil will still act as the main source for energy production and transportation fuels for rather long time. However, the presence of sulfur (0–5 wt%), nitrogen (0–0.2 wt%) and other trace constituents (e.g., oxygen, vanadium, iron and nickel) in 0–0.1 wt% in crude oils, depending on the origin, necessitates the downstream purification processes to meet relevant regulations [2]. Particularly, after combustion, sulfur compounds in fuels emit SO_x pollutants, not only deactivating catalysts in catalytic converters [3–5], but also increasing the particulate emissions due to the enhanced formation of PM2.5 and PM10 by SO_2 [6,7]. Thus, a worldwide consensus has been made among the government authorities/researchers to develop a promising technology of reducing the sulfur content to be less than 10 ppm in transportation fuels [8].

Among established technologies, the reactive adsorption desulfurization (RADS), represented by a S-Zorb process [9,10] industrialized by ConocoPhillips, has gained increasing attention due to the advantageous features of lower hydrogen consumption and negligible loss of octane number compared with the conventional hydrodesulfurization approach [11–13]. Using Ni/ZnO based adsorbents, the RADS combines both adsorptive [5,14,15] and catalytic hydrogenation capabilities [16–18] by capturing sulfur species to Ni sites followed by the storage of released H_2S in ZnO as ZnS [11]. Considering the RADS mechanism, it is obvious that the performance of adsorbents is vital to the efficiency of the whole process.

As a matter of fact, researchers from academia and industries have attempted to improve the RADS performance of Ni/ZnO based adsorbents by tailoring the physicochemical properties of adsorbents, such as pore structure, the dispersion and chemical states of active components. In our previous work [19], we synthesized a mesoporous Ni/

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$ZnO\text{-}Al_2O_3$ adsorbent for RADS using a cation-anion double hydrolysis (CADH) approach. The adsorbents thus prepared exhibited a superior RADS performance over that with the conventional kneading method due to the high dispersion of active components, absence of inactive $NiAl_2O_4$ phase and high concentration of surface Lewis acid sites [20–22]. It was shown that the adsorbent of a larger pore volume prepared via the CADH approach exhibited a better RADS performance due to the faster mass transfer rate of reactant/product molecules in the more open pore network. Therefore, to preserve the original porous network of the wet gel and increase the pore volume, drying step plays an important role. Apart from various drying techniques such as supercritical drying [23,24], contact sorption drying [25], sorption drying of particulates [26], convective drying [27,28], and oven drying [29,30], freeze drying [26,31,32] is considered to be more efficient when dealing with dense gels or solids abundant in porosity. Since water molecules exist in the form of solid during freeze drying, water is eliminated by sublimation from the pores without damaging the porous structure. By contrast, during the conventional oven drying, water within pores are removed as water vapor at high temperatures, causing the collapses of the original pore structure due to the surface tension exerted on the pore walls [32].

In this work, CADH derived $ZnO\text{-}Al_2O_3$ mixed oxides (MOs) with a large pore volume and small ZnO particle size were prepared by a freeze drying method and used as support for the preparation of Ni-based adsorbents. The physicochemical properties of materials were examined with various characterization techniques. And the adsorbents were evaluated in the RADS process and compared with previous counterparts.

2. Experimental section

2.1. Materials synthesis

2.1.1. Synthesis of $ZnO\text{-}Al_2O_3$ MOs

$Zn(NO_3)_2\cdot 6H_2O$ (98%), Pluronic P123 and sodium aluminate (98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. $ZnO\text{-}Al_2O_3$ MOs were synthesized via a CADH procedure followed by the freeze drying of the wet precipitate [33,34]. In a typical synthesis, 2.32 g of Pluronic P123 was dissolved in 30 mL of distilled water, followed by the addition of 2.97 g of $Zn(NO_3)_2\cdot 6H_2O$ with continuous stirring. To this solution, a $NaAlO_2$ solution (3.28 g/20 mL distilled water) was added under stirring [20]. Afterwards, the mixture was transferred to an autoclave and crystallized in an oven at temperatures of 40, 60 and 80 °C for 24 h. The resulting white precipitate was filtered off and washed with deionized water for several times. Subsequently, the solid product was transferred to petri-dishes covered with filter paper and frozen at 0 °C for 24 h. The obtained material was dried as in a vacuum freeze drier at −80 °C for 24 h, followed by calcination at 550 °C. The final product was denoted as $ZnO\text{-}Al_2O_3$ (X°C), where X represents the crystallization temperature.

2.1.2. Synthesis of Ni/MO adsorbents

Ni/$ZnO\text{-}Al_2O_3$ (X) materials were synthesized via an ultra sound-assisted wet impregnation method. In a typical procedure, 0.49 g of $Ni(NO_3)_2\cdot 6H_2O$ (analytical grade 98% from Shanghai Chemical Reagent, Hanson) was dissolved in 5 mL of tetrahydrofuran (Aldrich, 99%) as Ni precursor, followed by impregnation into 1 g of $ZnO\text{-}Al_2O_3$ (X) in a KQ5200E ultrasonic bath at 30 °C for 2 h [35]. The resultant solid was dried in an oven at 80 °C overnight and calcined at 400 °C for 1 h.

For comparison purpose, Ni/$ZnO\text{-}Al_2O_3$ adsorbents were also prepared through the conventional oven drying [19] and a kneading method [36], denoted as NiZA-OD and NiZA-K respectively, with a similar molar composition of that prepared using the freeze drying method. The $ZnO\text{-}Al_2O_3$ MO in sample NiZA-OD was prepared at crystallization temperature of 40 °C.

2.2. RADS experiment

A model gasoline, which consisted of thiophene (Aldrich, 99%) and n-octane (Aldrich, 99%) with a sulfur content of 3000 ppm (mg sulfur/L of model gasoline), was used in this study. RADS experiments were carried out in a fixed bed stainless steel micro-reactor (Fig. 1) with an internal column diameter of 8 mm and a length of 250 mm. Prior to desulfurization experiments, the whole system was soaked in pure ethanol for 24 h and then purged with nitrogen gas for 30 min. 1 g of sample was loaded into the middle of the reactor and reduced at 400 °C for 4 h by hydrogen (99.999%) under 0.45 MPa. After reduction, system conditions were set to 1.5 MPa of hydrogen pressure and 350 °C as the reaction temperature. Then, the pre-heated (120 °C) model gasoline was mixed with H_2 to achieve a H_2/model gasoline volume ratio of 400 and injected into the reactor at a liquid hourly space velocity (LHSV) of 4 h^{-1} at 25 °C. After desulfurization, the effluent gas was cooled in a cryogenic separator at 0 °C temperature and analyzed periodically with a BRUKER 450-GC gas chromatograph equipped with a pulsed-flame photometric detector (PFPD). The sulfur adsorption capacity of adsorbent was calculated using the Eq. (1):

$$S = \frac{v}{1000 * m_{adsorbent}} * \left(C(0) - C(t)_{av}\right) \tag{1}$$

where S is the amount of sulfur per gram adsorbent (mg S/g), the original sulfur concentration is C(0) (mg/L), and $C(t)_{av}$ (mg/L) is the average sulfur concentration in outlet during the time interval t (min), which was calculated by fitting the C(t) vs. volume of fuel curve. *v* denotes for the model gasoline flow rate (mL/min) at time t and $m_{adsorbent}$ is referred to as the weight of adsorbent.

The thiophene conversion or sulfur removal efficiency of adsorbents was measured using Eq. (2):

$$X\,(\%) = \frac{C(0) - C(t)}{C(0)} \times 100 \tag{2}$$

where X is the thiophene conversion (%), the original sulfur concentration is C(0) (mg/L), and the effluent sulfur concentration in outlet is C(t)(mg/L) at time t (min). The breakthrough curves were measured by setting the breakthrough sulfur concentration as 10 ppm (mg/L).

2.3. Characterization of adsorbents

Surface areas of adsorbents were analyzed by N_2 sorption measured on a Micromeritics TriStar 3000 analyzer and calculated using the Brunauer-Emmett-Teller (BET) method. Before analysis, adsorbents were degassed at 300 °C for 3 h. The pore size distribution (PSD) of adsorbents was derived from the adsorption branch of isotherms based on the Barrett-Joyner-Halenda (BJH) method. The phase analysis of adsorbents was examined by X-ray diffraction (XRD) with a Pan Analytical X'Pert PRO MPD X-ray diffractometer with a Cu *Kα* radiation generated at 40 kV and 40 mA. Joint Committee on Powder Diffraction Standards (JCPDS) catalogs were used for phase identification of adsorbents. The H_2 temperature programmed reduction (H_2-TPR) study of samples was performed on a Quantachrome ChemBET-3000 (USA) analyzer equipped with a thermal conductivity detector (TCD). 0.1 g of sample was transferred into a U-shaped quartz tube and treated at 400 °C in argon for 1 h and then reduced in 10% H_2/Ar mixed gas (30 mL/min) at a ramp rate of 10 °C/min from room temperature to 700 °C. The consumption of H_2 was monitored with the TCD. FT-IR spectra of sorbents for pyridine (Py) adsorption were measured on a Nicolet 6700 spectrometer coupled with a MCT liquid nitrogen cooling detector. The amount of Lewis acid was quantified according to the method described elsewhere [37]. UV–vis diffuse reflection spectroscopy (UV–vis DRS) spectra were obtained using Barium sulphate as a reference on a Hitachi U-4100 two-beam spectrophotometer. Transmission electron

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