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Article

Ordered mesoporous Cu-ZnO-Al₂O₃ adsorbents for reactive adsorption desulfurization with enhanced sulfur saturation capacity

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ABSTRACT

To enhance sulfur adsorption and reactive activity, ordered mesoporous Cu-ZnO-Al₂O₃ adsorbents were prepared by a novel one-pot evaporation-induced self-assembly strategy using P123 as a structure-directing agent and ethanol as the solvent for reactive adsorption desulfurization. The metal oxide precursor molecules around P123 micellized, and self-assembly simultaneously occurred during evaporation from an ethanol solution at 60 °C, leading to the formation of the p6mm hexagonal symmetry mesoporous structure. Characterization results prove that the Cu-ZnO-Al₂O₃ adsorbents possess an ordered mesoporous structure with high thermal stability, large surface area (386–226 m²/g), large pore volume (0.60–0.46 cm³/g), and good dispersion of ZnO and Cu, which is beneficial for transforming S-compounds to ZnO. The sulfur saturation capacity of the ordered-mesoporous-structure Cu-ZnO-Al₂O₃ adsorbents is larger (49.4 mg/g) than that of the unordered mesoporous structure (13.5 mg/g).

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1. Introduction

S-compounds in transportation fuels can cause acid rain and release PM 2.5. Hence, it is increasingly important to perform ultra-deep desulfurization, to alleviate environment pollution. The Environmental Protection Agency has proposed a strict regulation, in which the sulfur content should be reduced to 10 ppm [1,2]. However, by conventional hydrodesulfurization (HDS), it is difficult to remove the sulfur from fuels and satisfy the new regulation for gasoline without loss of the octane number [3]. FCC gasoline contains about 20–40 wt% olefins [4], which may provide a fairly good octane number. Olefins can easily be reacted with hydrogen in the hydrodesulfurization reaction. In order to maintain a high octane number, the tech-

nology and catalyst should exhibit good selectivity during desulfurization. Researchers are trying to achieve maximum sulfur removal with minimum olefin saturation. Therefore, a novel ultra-deep desulfurization technology for gasoline is important to prevent the loss of octane number when upgrading FCC gasoline. Over the years, researchers have developed new methods such as adsorption [5,6], oxidation [7], extraction [8], and biodesulfurization [9], for the ultra-deep desulfurization of products. The advantages of adsorption and reactive adsorption, such as high desulfurization, high selectivity, and low energy consumption, can aid in developing the technology and catalyst. A reactive adsorption desulfurization (RADS) technology, called the “S-Zorb” technology, was developed and industrialized by Conoco Phillips Petroleum Co, and Ni/ZnO adsor-

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bents were used in the fluidized bed to produce low-sulfur gasoline during the S-Zorb process [10,11]. However, frequent regeneration decreases the sulfur saturation adsorption capacity of ZnO. More importantly, the Ni-based catalyst was always used at a high space velocity to control the selectivity of the RADS, and could not reach the level required for ultra-deep desulfurization. Therefore, it is important to develop a novel RADS catalyst and technology for inhibiting olefin saturation. There have been some efforts over the years to design and develop the desulfurization technology and catalyst to avoid the loss of octane number. In our previous research [12], Cu/ZnO adsorbent exhibited good desulfurization activity, stability, and selective hydrogenation in a fixed-bed reactor for RADS. Cu-based catalysts are used in many fields, such as methanol steam reforming [13], water-gas shift reaction [14], and so on. Active metal Cu has a low melting point and Tammann temperature, and is prone to migration to the surface of metallic particles [15], which leads to good selectivity. Wang et al. [16] investigated the adsorption of thiophene on active metal (100) surfaces by using the density functional theory (DFT), and suggested that Cu-based materials could be the next generation of adsorbents for RADS.

Nowadays, Cu-based adsorbents face issues with the sulfur saturation adsorption of ZnO and stability in a fixed-bed reactor. Metallic Cu particles may be easily sintered in the reaction process; however, ZnO and Al₂O₃ can be regarded as stabilizers to prevent the Cu particles from sintering in the Cu crystallites [17,18], to thereby improve the activity and stability. The dynamic capacity of ZnO-based adsorbents and the reactive activity are always dependent on the particle size [19,20] of ZnO and Cu, respectively. ZnO not only acts as a support, but also as an S-acceptor [21]. ZnO has been used widely in the catalytic process, and the properties of ZnO, such as particle size, confinement [22,23], and morphology [24] influence the catalytic performance [25]. Therefore, many nanostructured ZnO have been synthesized [26,27]. An active component, when supported on a porous carrier such as alumina, can stabilize small particles by the commonly used methods [28]. The pore volume can increase in dynamic capacity to promote the reaction of H₂S with ZnO, at the depth of the alumina matrix. Alumina is widely used as a catalyst or catalyst support binder for a variety of applications [29]. Ordered mesoporous alumina has higher surface areas, larger pore sizes, ordered pores, and better stability than bulk alumina materials [30]. The high surface area favors the dispersion of active metals and enhances molecular interdiffusion. Tian et al. [31] reported that the matrix of ordered mesoporous alumina could improve the dispersion of Ni nanoparticles, which is promising for long-term stability tests.

To enhance the sulfur adsorption of Cu-based adsorbents for reactive adsorption desulfurization, ordered-mesoporous-structure Cu-ZnO-Al₂O₃ adsorbents were designed and synthesized by a one-pot evaporation-induced self-assembly (EISA) strategy. The ordered mesoporous structures provide a high thermal stability, and large specific surface areas and pore volumes. Therefore, the ordered-mesoporous-structure Cu-ZnO-Al₂O₃ adsorbents are beneficial for transforming S-compounds to ZnO; moreover, they exhibit larger sulfur sat-

uration capacity than unordered mesoporous structures.

2. Experimental

2.1. Chemicals

Zinc acetate dehydrate (Zn(AC)₂·2H₂O), copper nitrate trihydrate (Cu(NO₃)₂·3H₂O), aluminum isopropoxide (Al(OiPr)₃), nitric acid (HNO₃), and ethyl alcohol (C₂H₅OH) were provided by Sinopharm Chemical Reagent Company (China). The block copolymer poly (ethylene glycol)-block-poly (propylene glycol)-block-poly-(ethylene glycol) (Pluronic P123, PEG-20-PPG-70-PEG-20) was purchased from Sigma-Aldrich (Germany). All other reagents (Grade AR) were purchased and used without any further purification.

2.2. Preparation of ordered mesoporous CuO-ZnO-Al₂O₃ adsorbents

In a one-pot EISA synthesis process [32], P123 (2.1 g) was dissolved in ethyl alcohol, followed by the addition of 67 wt% HNO₃ (2.3 mL) and 4.08 g aluminum isopropoxide Al(OPri)₃. Zinc acetate dehydrate Zn(AC)₂·2H₂O and copper nitrate trihydrate Cu(NO₃)₂·3H₂O were stirred vigorously at atmospheric temperature, and left for more than 24 h. The obtained mixture was then placed in an oven at 60 °C to evaporate ethanol. The precursors were calcined at 500 °C for 4 h at a heating rate of 1 °C/min. The ZnO content was varied as 0, 5, 15, 20, and 25 wt%. The CuO content was fixed at 10 wt% in all adsorbents in this work. The series of adsorbents are denoted as Cu-xZnO-Al₂O₃, where x represents the percentage ZnO content.

2.3. Characterization of catalysts

The samples were characterized by X-ray powder diffraction (XRD) to obtain information on the structural properties of the adsorbents, using a PANalytical instrument with Cu K_α radiation at a scan step of 0.02° and 2°.

N₂ adsorption-desorption experiments were performed on a ChemBET 2000 instrument (Quantachrome, USA). Nitrogen was used as the adsorption agent at -196 °C. Brunauer-Emmett-Teller (BET) surface areas were calculated from the isotherms, and the total pore volumes were calculated by the Barrett-Joyner-Halenda (BJH) method. The BJH pore sizes were calculated using the desorption branch of the isotherms.

Temperature-programmed reduction by H₂ (TPR) was carried out to assess the reducibility of the Cu-ZnO-Al₂O₃ adsorbents. Approximately 100 mg of each catalyst loaded into a U-shaped quartz reactor and heated up to 650 °C in a flow of 10% H₂/Ar gas mixture at a heating rate of 10 °C/min. The consumption of H₂ was monitored with a TCD. The average volume-surface diameter and dispersion of Cu were calculated according to previously reported equations [33,34]. The dispersion and area of surface Cu were calculated according to the following equations:

$$D = (2 \times Y/X) \times 100\% \quad (1)$$

$$S = 2 \times Y \times N_{av} / (X \times M_{cu} \times 1.4 \times 10^{19}) =$$

$$1353 \times Y/X \text{ (m}^2 \text{ - Cu/g - Cu)} \quad (2)$$

In these equations, N_{av} is Avogadro's constant, M_{Cu} is the relative atomic mass of copper (63.46 g/mol), and 1.4×10^{19} is the number of copper atoms per square meter, because the average surface area of a copper atom is $7.11 \times 10^{-2} \text{ nm}^2$.

The average volume-surface diameter can be expressed as:

$$D_{v,s} = 6/(S \times \rho_{Cu}) \approx 0.5 \times X/Y \text{ (nm)} \quad (3)$$

where ρ_{Cu} is the density of copper (8.92 g/cm^3).

Transmission electron microscopy (TEM) images of the samples were acquired using a JEOL JEM-2100 UHR microscope. The sample particles were first ground and then suspended in alcohol in an ultrasonic bath, following which they were placed in a Cu cellulose-coated grille.

Thermogravimetry (TG) was used to investigate the thermal behaviors of the Cu-ZnO-Al₂O₃ precursors. The TG experiments were carried out in air at a heating rate of $20 \text{ }^\circ\text{C/min}$.

The composition of the hydrocarbon groups in gasoline was determined with an Agilent 7890N gas chromatograph with a PONA capillary column. Quantitative analysis of the total sulfur concentration in model gasoline was performed by a Multi EA 3100 S/N trace analyzer. The detection range was $0.1\text{--}1000 \text{ mg/L}$.

2.4. Adsorbent activity tests

The desulfurization performances of the adsorbents for model gasoline upgradation were evaluated in a fixed-bed reactor. The oxidized states of the adsorbents (approximately 1 g) were reduced in the constant-temperature zone of the reactor, which was embedded between the quartz sand beds. First, in situ activation was performed in hydrogen flow at 1 MPa for 6 h. After cooling to $400 \text{ }^\circ\text{C}$ at 1 MPa, the model gasoline was fed into the reactor with a syringe pump at a predetermined flow rate, a H_2 /feed volumetric rate of 200/1, and LHSV of 1 h^{-1} .

The activity of the adsorbent was estimated using RADS (amount of reacted thiophene):

$$x_T = \frac{C_s^0 - C_s}{C_s^0} \times 100\% \quad (4)$$

where C_s^0 is the thiophene content in the feedstock (wt%) and

C_s is the thiophene content in the products (wt%).

$$\text{Effluent} = vt/m_{\text{adsorbent}} \quad (5)$$

The breakthrough sulfur capacity was determined as follows:

$$q_{\text{breakthrough}} = \frac{v}{1000m} \int_0^t (C_s^0 - C_s) dt \quad (6)$$

where $q_{\text{breakthrough}}$ is the breakthrough sulfur capacity of the adsorbent (mg/g), v is the feed volumetric flow rate (mL/min) at any time t (min), and m is the weight of the adsorbents (g). The breakthrough time was defined as the RADS time when the sulfur concentration of the effluent-desulfurized feed exceeded 10 mg/L .

The ZnO conversion to ZnS (X) at the sulfur breakthrough point (10 mg/L) is expressed as [20]:

$$X = \frac{q_{\text{breakthrough}} \times \frac{81.38}{32.07}}{\text{ZnO amount}} \times 100\% \quad (7)$$

3. Results and discussion

3.1. Characterization

N_2 adsorption-desorption isotherms of the samples synthesized by the one-pot EISA method are shown in Fig. 1. The Al₂O₃ sample shows typical type-IV curves with the H1 hysteresis loop, attributed to ordered cylindrical mesoporous channels [35]. The hysteresis loops at a higher relative pressure (p/p_0) from 0.5 to 0.9 indicate the uniform mesoporosity of the Al₂O₃ sample. The shapes of the isotherms and loop hysteresis with the proper addition of Cu and Zn species are similar to those of the Al₂O₃ sample, whereas the capillary condensation of N_2 of the adsorbents are diminished. These results indicate that the ordered mesoporous structure was not destroyed by the addition of an appropriate amount of Cu and Zn species. However, for a ZnO content of 25 wt%, the isotherm exhibited typical type-IV curves with the H4 hysteresis loop. This indicates that the ordered mesoporous structure was blocked and destroyed with the addition of ZnO particles. The pore distribution of the Cu-ZnO-Al₂O₃ adsorbents is presented in Fig. 1. (2), and their detailed characteristics are presented in Table 1. The results suggest that the one-pot EISA method can form

Fig. 1. N_2 adsorption-desorption isotherms (a) and pore distribution (b) for the samples. (1) Al₂O₃, (2) Cu-Al₂O₃, (3) Cu-5ZnO-Al₂O₃, (4) Cu-10ZnO-Al₂O₃, (5) Cu-15ZnO-Al₂O₃, (6) Cu-20ZnO-Al₂O₃, (7) Cu-25ZnO-Al₂O₃.

Table 1

BET surface area, pore volume, and BJH pore diameter of samples.

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Cu dispersion	
				Cu particle size ^b (nm)	Dispersion ^a (%)
Al ₂ O ₃	426	0.60	5.75	—	—
Cu-Al ₂ O ₃	386	0.59	5.42	2.3	44
Cu-5ZnO-Al ₂ O ₃	360	0.51	5.49	2.7	38
Cu-10ZnO-Al ₂ O ₃	345	0.50	4.65	3.8	26
Cu-15ZnO-Al ₂ O ₃	257	0.48	4.04	4.2	24
Cu-20ZnO-Al ₂ O ₃	226	0.46	3.53	4.8	20
Cu-25ZnO-Al ₂ O ₃	183	0.36	3.13	6.7	15

^a calculated by Eq. (1).^b calculated by Eq. (3).

Cu-ZnO-Al₂O₃ with ordered mesoporous structures, high surface areas, and large pores.

The small-angle XRD (SAXRD) and WAXRD patterns of the samples are shown in Fig. 2. The Al₂O₃ sample displays two peaks at $2\theta = 1.27^\circ$ and 2.18° , which are attributed to the (100) and (110) planes, respectively. The results indicate that the hexagonally ordered mesoporous structure Al₂O₃ with a space group of *p6mm* symmetry was successfully synthesized [32,35,36]. The samples with Zn and Cu species also exhibit obvious (100) diffraction, suggesting that the samples retain their ordered mesoporous structures, which implies that these structures were not destroyed by the impregnation of appropriate amounts of Zn and Cu. However, when 25 wt% Zn was added, the obvious (100) diffraction disappeared, implying that the ordered mesoporous structure was destroyed. Thus, ordered mesoporous CuO-ZnO-Al₂O₃ adsorbents were successfully synthesized by the one-pot EISA method; this agrees with the N₂ adsorption-desorption results. To further investigate the structure of the samples, WAXRD patterns for the calcined and reduced samples are shown in Fig. 2(b) and Fig. S1, respectively. All the samples were calcined at 500 °C and reduced at 400 °C. The WAXRD pattern of Al₂O₃ exhibits no obvious peaks, suggesting that the sample has amorphous walls. Besides, no peaks of the ZnO and CuO phases with alumina are detected in Fig. 2(b). This implies that the ZnO and CuO particles are small in size or are well dispersed. However, for Cu-25ZnO-Al₂O₃, there are some diffraction peaks. The diffraction peaks due to the

ZnAl₂O₄ phase (JCPDS Card 01-071-09681) appear at $2\theta = 31.3^\circ$, 36.8° , 55.6° , 59.3° , and 65.2° . The peaks at $2\theta = 31.4^\circ$, 37.0° , 45.1° , 59.6° , and 65.7° are attributed to CuAl₂O₄ (JCPDS Card 00-001-1153). During calcination, strong metal-support interaction (SMSI) is favored, to form the CuAl₂O₄ and ZnAl₂O₄ phases, which destroys the ordered mesoporous structures; this agrees with the results of N₂ adsorption-desorption. There are no obvious peaks in Fig. S1(1). In Fig. S1(2)–(6), the peaks at $2\theta = 43.3^\circ$ and 50.4° are due to the (111) and (200) planes of Cu (JCPDS Card 00-085-1326). The WAXRD patterns of the reduced samples did not exhibit the ZnO phase, indicating that the ZnO species were incorporated into the Al₂O₃ matrix. There are no diffraction peaks for the Cu phase in Fig. S1(7), indicating that CuAl₂O₄ could not be reduced to the Cu phase at 400 °C.

TEM images of the ordered mesoporous samples are shown in Fig. 3. The typical ordered mesoporous Al₂O₃ is obvious, with the regular alignment of cylindrical pores (Fig. 3(a)), which is in accordance with the results of N₂ adsorption and SAXRD. Furthermore, the ordered mesoporous structure is maintained even with an increase in the Cu and Zn contents, as shown in Fig. 3(b) and (c). However, the mesoporous structure was blocked by 25 wt% ZnO (Fig. 3(d)). These results may fit with the characteristics observed in the N₂ adsorption-desorption and XRD. Fig. 3(e) shows a fine and good dispersion of copper particles on the surface of the supports. The reduction process did not destroy the ordered mesoporous structure. In the HRTEM image, the reduced Cu-20ZnO-Al₂O₃ catalyst shows a

Fig. 2. Small-angle XRD (a) and WAXRD (b) patterns of as-synthesized samples. (1) Al₂O₃, (2) Cu-Al₂O₃, (3) Cu-5ZnO-Al₂O₃, (4) Cu-10ZnO-Al₂O₃, (5) Cu-15ZnO-Al₂O₃, (6) Cu-20ZnO-Al₂O₃, (7) Cu-25ZnO-Al₂O₃.

Fig. 3. TEM images of the ordered mesoporous samples: (a) Al_2O_3 , (b) $\text{Cu-Al}_2\text{O}_3$, (c) $\text{Cu-20ZnO-Al}_2\text{O}_3$, (d) $\text{Cu-25ZnO-Al}_2\text{O}_3$, (e, f) reduced $\text{Cu-20ZnO-Al}_2\text{O}_3$, HAADF-STEM and corresponding EDX elemental mapping of $\text{Cu-20ZnO-Al}_2\text{O}_3$.

spacing of 0.21 nm, corresponding to the Cu (111) plane in Fig. 3(f). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) elemental mapping of the ordered mesoporous $\text{Cu-20ZnO-Al}_2\text{O}_3$ adsorbent reveals that Cu, Zn, Al, and O elements are homogeneously distributed over the adsorbent (Fig. 3).

TG curves (Fig. 4) show the weight loss of the as-made samples in air atmosphere, which were obtained to investigate the decomposition behavior. The weight loss at around 110–125 °C is attributed to the desorption of physically adsorbed water and organic molecules [37]. Two significant weight loss steps at around 130 °C are due to the decomposition of P123. The third weight loss step at approximately 280 °C is due to the decomposition of carbonaceous and nitrogenous species. The pro-

nounced weight loss at around 336 °C is attributed to the dihydroxylation during transformation into alumina [38]. There was no pronounced weight loss above 400 °C. These results demonstrate that P123 and other groups are readily removed by calcination at 500 °C. Moreover, the ordered mesoporous $\text{Cu-ZnO-Al}_2\text{O}_3$ adsorbents exhibit no weight-loss peaks for a temperature as high as 550 °C, indicating their high thermal stability.

The differences in the TPR profiles could be interpreted as the change in the ZnO contents, for which the results are shown in Fig. 5. According to previous H_2 -TPR studies of copper oxide, the reduction peak is generally at around 250 °C [39]. The reduction peaks of highly dispersed CuO species interacting with the support occur at a low temperature of approximately 330

Fig. 4. TG curves of the as-synthesized precursors: (a) Al_2O_3 , (b) $\text{Cu-Al}_2\text{O}_3$, (c) $\text{Cu-20ZnO-Al}_2\text{O}_3$, (d) $\text{Cu-25ZnO-Al}_2\text{O}_3$.

Fig. 5. TPR profiles of $\text{CuO-ZnO-Al}_2\text{O}_3$ samples: (1) $\text{Cu-Al}_2\text{O}_3$, (2) $\text{Cu-5ZnO-Al}_2\text{O}_3$, (3) $\text{Cu-10ZnO-Al}_2\text{O}_3$, (4) $\text{Cu-15ZnO-Al}_2\text{O}_3$, (5) $\text{Cu-20ZnO-Al}_2\text{O}_3$, (6) $\text{Cu-25ZnO-Al}_2\text{O}_3$.

°C for low ZnO content. The reduction peaks of CuO species with a stronger interaction with the support are due to the second peak at 355 °C. However, broad reduction profiles at around 250–550 °C were observed in the Cu-25ZnO-Al₂O₃ catalyst. Gaussian fitting was used for further investigation of the Cu species. The low-temperature reduction at 345 °C is attributed to the reduction of CuO species. The high-temperature reduction at 472 °C is attributed to the reduction of the CuAl₂O₄ phase [40]. Notably, the CuAl₂O₄ and ZnAl₂O₄ phases appear in the unordered mesoporous sample at the same calcination temperature, indicating that it is more easy to form CuAl₂O₄ and ZnAl₂O₄ in the unordered mesoporous sample than in the ordered mesoporous sample [41], because of the weak support-metal interactions of the ordered mesoporous samples, due to fewer -OH groups and vacancies over the surface of amorphous Al₂O₃ [42].

The results of copper dispersion and the average diameter during N₂O oxidation and the following H₂ titration are shown in Table 1. The dispersion of copper during the reduction of Cu-ZnO-Al₂O₃ adsorbents decreased from 44% to 15% with increasing ZnO content. The average diameter of copper particles in the ordered mesoporous structure was 2.3, 2.7, 3.8, 4.2, and 4.8 nm, with increasing ZnO content; however, that of the unordered-mesoporous-structure Cu-25ZnO-Al₂O₃ adsorbent was 6.7 nm. The results show that the ordered mesoporous sample possessed larger pores to disperse the copper particles, as compared to the unordered mesoporous sample. These results agreed with the N₂ adsorption-desorption, XRD, and TEM results.

Combining all results for the characterization of the adsorbent, the possible formation mechanism of the ordered mesoporous Cu-ZnO-Al₂O₃ catalyst is illustrated in Fig. 6. The EISA method is assigned to the liquid-crystal template pathway [43] for non-siliceous mesoporous materials [44,45]. In our synthesis system, the precursor molecules of alumina, zinc oxide precursor, and copper oxide around the P123 micellized, and self-assembly simultaneously occurred, during evaporation from an ethanol solution at 60 °C, resulting in the formation of the *p6mm* hexagonal symmetry mesoporous structure. The ordered mesoporous structure with concentric mesopores was caused by the directing agent P123 [46]. The stable ordered mesoporous was successfully synthesized after calcination in air to remove the templates, following which an ordered mesoporous skeleton was formed, with the alumina, zinc oxide, and copper oxide nanoparticles dispersed well across the surface of the mesoporous skeleton.

Fig. 6. Mechanism pathways for the formation of the ordered mesoporous structure of Cu-ZnO-Al₂O₃ catalyst.

3.2. RADS performance

Before evaluating the desulfurization performance of the ordered-mesoporous-structure Cu-ZnO-Al₂O₃ adsorbents, that of the traditional Cu-20ZnO-Al₂O₃-C adsorbent was evaluated for FCC gasoline in a fixed-bed reactor, to compare the characteristics. The properties of the Cu-ZnO-Al₂O₃-C adsorbent are shown in Fig. S2. The properties of FCC gasoline and products are listed in Table S1. Both, the Cu-20ZnO-Al₂O₃-C and Cu-20ZnO-Al₂O₃ adsorbent, have less olefin saturation to avoid the loss of the octane number.

In order to investigate the role of the ordered mesoporous structure in enhancing the sulfur capacity, the experiments for desulfurization performance were performed in a fixed-bed micro reactor, and the results are shown in Fig. 7. The Cu-ZnO-Al₂O₃ adsorbents had very high activities, and the sulfur content could be reduced from 100 to below 10 µg/g, thus achieving the level required for ultra-deep desulfurization. The ordered mesoporous Cu-ZnO-Al₂O₃ adsorbents exhibited better desulfurization activities than the unordered mesoporous structure. The ordered-mesoporous-structure Cu-20ZnO-Al₂O₃ adsorbents exhibited a large sulfur capacity (49.4 mg/g) with increasing ZnO content. However, the sulfur capacity of the Cu-25ZnO-Al₂O₃ adsorbent sharply decreased at 36.1 mg/g. The adsorbent Cu-20ZnO-Al₂O₃-C prepared with the common method presents a low sulfur capacity of 13.5 mg/g. These results imply that the ordered mesoporous Cu-ZnO-Al₂O₃ adsorbents have larger sulfur capacity. A series of characterization results showed that ZnAl₂O₄ existed in the Cu-25ZnO-Al₂O₃ catalyst, indicating that there is an inactive component in the RADS process. The ordered mesoporous skeleton of ZnO and Al₂O₃ was destroyed by ZnAl₂O₄, leading to the low dispersion of ZnO and preventing sulfur diffusion. The ZnAl₂O₄ phase in the spinel structure enabled strong interaction between Al₂O₃ and ZnO [47]. As shown by the XRD, H₂-TPR, and TEM results, the Cu particles and ZnO in the matrix of the ordered mesoporous structure are small in size and show good dispersion, thereby increasing the desulfurization activities and enhancing sulfur capacity.

Fig. 7. RADS performance of Cu-ZnO-Al₂O₃ adsorbents, obtained for a hydrogen pressure of 1 MPa, gas to liquid ratio of 200, LHSV of 1 h⁻¹, and temperature of 400 °C.

Table 2

ZnO conversion of different adsorbents at the sulfur breakthrough.

Adsorbent	Cu-5ZnO-Al ₂ O ₃	Cu-10ZnO-Al ₂ O ₃	Cu-15ZnO-Al ₂ O ₃	Cu-20ZnO-Al ₂ O ₃	Cu-25ZnO-Al ₂ O ₃	Cu-20ZnO-Al ₂ O ₃ -C
Conversion (%)	65.4	63.2	63.1	62.7	36.7	17.2

The calculated ZnO conversions of the different adsorbents at breakthrough points are presented in Table 2. The ordered-mesoporous-structure Cu-ZnO-Al₂O₃ adsorbents have higher ZnO conversions than the unordered mesoporous structure. In the RADS system, the S-compounds decomposed on the active metal surface, thereby sulfurizing it, followed by the transfer of sulfur to ZnO in the hydrogen condition [48]. ZnO acts not only as a support on the active metal, but also as an S-compound acceptor. The well-dispersed ZnO in the ordered mesoporous sample could facilitate the sulfidation of ZnO by H₂S with weak metal-support interaction [49]. This process is beneficial for maintaining the initial state of the active metal of Cu and improving ZnO conversion, thus sustaining good activity over long periods of the RADS process. Moreover, the ordered mesoporous structure could inhibit the string of Cu particles to improve the desulfurization activities and stability. Hence, compared with the unordered mesoporous structure, ordered mesoporous Cu-ZnO-Al₂O₃ adsorbents show good re-active activity, larger sulfur capacity, and stability.

4. Conclusions

In summary, a series of Cu-ZnO-Al₂O₃ adsorbents with ordered mesoporous structure were synthesized by the EISA strategy and were successfully applied for RADS. The ordered mesoporous structure is maintained even after the addition of 10 wt% CuO, for various ZnO contents between 0 and 20 wt%.

The characterization results confirmed that for an appropriate amount of ZnO, the ordered mesoporous structure is maintained, resulting in thermal stability, and large specific surface areas and pore volumes in the Cu-ZnO-Al₂O₃ adsorbents. The ordered mesoporous Cu-ZnO-Al₂O₃ adsorbents exhibit larger sulfur saturation capacity than the unordered mesoporous adsorbent. The ordered mesoporous structure could provide a larger pore structure, thus enabling the high dispersion of ZnO; it is therefore useful for transforming S-compounds to ZnO to enhance the desulfurization activity. Thus, the ordered mesoporous structure of Cu-ZnO-Al₂O₃ adsorbents could enhance the desulfurization activity and prevent frequent regeneration during RADS.

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Graphical Abstract

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Ordered mesoporous Cu-ZnO-Al₂O₃ adsorbents for reactive adsorption desulfurization with enhanced sulfur saturation capacity

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The ordered mesoporous Cu-ZnO-Al₂O₃ adsorbents were synthesized by one-pot evaporation-induced self-assembly strategy, which showed improvement in desulfurization activity and sulfur saturation capacity in reactive adsorption desulfurization (RADS).

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反应吸附脱硫中有序介孔 Cu-ZnO-I₂O₃ 吸附剂提高其饱和硫容

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摘要: 目前汽柴油中的含硫化合物是造成酸雨和 PM_{2.5} 的重要原因之一。随着污染的日益严重, 对汽柴油的深度脱硫受到越来越多的关注。环境保护组织颁布了较为严格的法律措施, 规定硫含量低于 10 ppm。然而, 传统的加氢脱硫工艺 (HDS) 很难满足在深度 HDS 的同时辛烷值损失较少。为了减少辛烷值损失, 脱硫技术和催化剂应具有较好的选择性。因此, 在 FCC 汽油升级的过程中, 减少辛烷值损失的超深度脱硫工艺是重要研究课题之一。目前, 一些新型的深度脱硫技术包括吸附脱硫、氧化脱硫和生物脱硫。其中吸附脱硫具有高选择性、低能耗等优点, 而反应吸附脱硫则被广泛研究和工业化生产。常见 Ni/ZnO 吸附剂利用高空速控制辛烷值损失, 但频繁的再生过程影响催化剂的稳定性。目前, 一种新型的 Cu/ZnO 吸附脱硫剂用于固定床中, 具有较高的脱硫活性、稳定性和高选择性。

目前, 铜基吸附剂面临着 ZnO 的饱和硫容、稳定性及活性组分 Cu 结焦问题。Al₂O₃ 作为稳定剂可以提高反应活性和

稳定性, 其中有序介孔能够提供较大的比表面积、孔径、规整的孔结构和较好的分散活性组分的能力, 从而有利于分子之间的扩散. 本文利用一步溶剂蒸发自组装法合成了具有有序介孔的 $\text{Cu-ZnO-Al}_2\text{O}_3$ 吸附剂. SXRDXRD/WXRDXRD 结果, 证实合成了具有有序介孔结构的 Al_2O_3 , 且添加 Cu 和 Zn 物种后, 其结构并未发生改变, 但当 Zn 的添加量达到 25 wt% 时, 其有序介孔结构发生改变. 有序介孔的 $\text{Cu-ZnO-Al}_2\text{O}_3$ 吸附剂具有较高的比表面积、孔容及孔径, 添加过量的 ZnO 后, 其比表面积明显降低. TEM 和 AADF-STEM 结果发现, 所制 $\text{Cu-ZnO-Al}_2\text{O}_3$ 吸附剂具有规则的介孔结构, 并且 Cu, Zn, Al 和 O 分散均匀, 与 XRD 和 BET 结果一致. 热重结果表明, 有序介孔 $\text{Cu-ZnO-Al}_2\text{O}_3$ 吸附剂具有较好的热稳定性. 通过与商业 $\text{Cu-ZnO-Al}_2\text{O}_3$ 吸附剂进行对比, 有序介孔 $\text{Cu-ZnO-Al}_2\text{O}_3$ 吸附剂具有较高脱硫活性、饱和硫容及稳定性.

关键词: $\text{Cu-ZnO-Al}_2\text{O}_3$; 有序介孔结构; 一步溶剂蒸发自组装法 (EISA); 反应吸附脱硫; 饱和硫容

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