Fabrication of hierarchical porous ZnO and its performance in Ni/ZnO reactive-adsorption desulfurization

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Abstract: To investigate the effect of texture structure on the desulfurization performance in the Ni/ZnO reactive adsorption desulfurization (RADS) system, two kinds of ZnO porous materials with rod-shaped morphology were synthesized and their structure was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and N₂ adsorption/desorption. The formation mechanisms of hierarchical porous ZnO (ZnO with meso and macro pores) were also studied. Their application performance was evaluated in the RADS process over Ni/ZnO absorbent. Due to the difference in structure between the two kinds of ZnO, the two ZnO based adsorbents showed different desulfurization activity.

Key words: Ni/ZnO, reactive adsorption, desulfurization, texture structure, hierarchical pore

1 Introduction

With increasingly stringent environmental regulations, deep desulfurization for production of gasoline oil has become an important issue, and technologies for ultra-deep desulfurization of refinery streams have become an important subject of environmental catalysis studies worldwide (Song, 2003; Song and Ma, 2003; Brunet et al, 2005). Desulfurization should also be taken into consideration in processing of fuel for fuel-cells, which has a more rigorous requirement for sulfur content (e.g., <1 µg/g sulfur) than fuel for internal combustion engines. Approaches to deep desulfurization include hydrosulfurization (HDS) and non-HDS processing. Although the development of high-performance catalysts for HDS processes can produce fuels with a sulfur content of <10–50 µg/g, this approach will result in unnecessary olefin saturation, excessive hydrogen cost and octane number reduction while removing sulfur species. Adsorption desulfurization (ADS) is achieved by using solid sorbents, which can adsorb organosulfur compounds from refinery streams, with excellent olefin control and reducing octane number loss (Babich and Moulijn, 2003; Fan et al, 2004). Recently, one novel method, reactive adsorption, has been implemented in S-Zorb desulfurization technology (Khare and Gyanesh, 2001). This technology can reduce the sulfur content of fuel to lower than 1 µg/g, meeting the requirement for sulfur content of fuel cells (Ma et al, 2005),

and has been used on industrial scale in China. The sorbent, which consists of kieselguhr, alumina, zinc oxide and nickel, was developed by Sud-Chemie AG (Germany). This Ni/ZnO reactive adsorption desulfurization catalyst has an “auto-regenerative” mechanism (Siriwardane et al, 2000). Ni acts as the hydro-desulfurization site, while ZnO plays the crucial role in taking up generated H₂S, converting the H₂S into ZnS in the process. First, NiO in the adsorbent precursor is converted into reduced state Ni in H₂ atmosphere, and then the organosulfur reacts with Ni to form transition state sulfur species (NiS_x) due to its relative electronegativity. Second, the C-S bonds of the organosulfur compounds are broken under the influence of the strong adsorption potential. Finally, ZnS forms due to the reaction of ZnO with sulfur species, and NiS_x is converted back into Ni in a H₂ atmosphere, sulfur is immobilized onto the adsorbent in the form of ZnS while Ni remains in its reduced state. That is, Ni is “auto-regenerated” in the reaction (Ryzhikov et al, 2008; Mangnus et al, 1992; Bezverkhyy et al, 2008). Based on the mechanism, the regeneration rate of the nickel surface can determine the activity of the adsorbent. ZnO plays an important role in rapid conversion of NiS_x to Ni⁰ on the nickel surface. Thus, the reaction rate of ZnO with H₂S or NiS_x is crucial as it determines the performance of the adsorbent. Conventional micron ZnO exhibits inferior reactivity with hydrogen sulfide because of its low surface area, topology and crystalline structure, so its sulfur-fixation capability and activity are limited. Recently, our research group has synthesized nano zinc oxide by a low-temperature solid-phase method, and the reactivity/performance of the corresponding Ni/ZnO

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adsorbent was greatly improved (Zhang et al, 2010). Although nano ZnO has many superior properties such as large surface area, high reactive activity and enhanced sulfur capacity, sintering becomes its limitation. In the present work, two kinds of ZnO porous materials with rod-shaped morphology were synthesized and their application performance in RADS process was evaluated.

2 Experimental

2.1 Materials

$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CH}_3\text{CH}_2\text{OH}$, NaOH , $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ (PEG-6000), pseudo-boehmite of analytical reagent grade and diatomite were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Attapulgit was purchased from Anhui Mingmei Minerals Co., Ltd. (China). All the chemicals were used without further purification.

2.2 Synthesis

Macroporous single-crystal zinc oxide was synthesized by the hydrothermal method. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution (0.5 mol/L) and NaOH solution (5 mol/L) were mixed at a ratio of 1:1 while being stirred to obtain $[\text{Zn}(\text{OH})_4]^{2-}$ solution. PEG-6000 (0.006 mol/L) was added in the transparent solution and continually stirred until the mixture became clear and homogeneous. Then the solution was transferred into a Teflon-lined autoclave and heated at 200 °C for 12 h. After the autoclave cooled, the ZnO powder was obtained by centrifugation, and then it was washed 3 times with absolute ethanol, and dried at 80 °C for 12 h. The as-prepared ZnO sample was labeled as ZnO-a.

The hierarchical poly-crystalline ZnO assembly was synthesized by a precursor thermal decomposition reaction. The precursor zinc oxalate was obtained by the solvothermal method. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.5 mol/L) was dissolved in absolute ethanol and marked solution A; $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (0.5 mol/L) and PEG-6000 (0.006 mol/L) were dissolved in absolute ethanol and marked solution B; Solution B was dropped into solution A to obtain a homogeneous and stable ZnO precursor sol. The ZnO precursor sol was transferred into a teflon-lined autoclave and heated at 100 °C for 12 h. Subsequently, the mixture was cooled, centrifuged, and washed 3 times with absolute ethanol, then dried at 80 °C for 12 h. ZnO powder was obtained from the precursor by thermal decomposition at 400 °C for 4 h. The as-prepared ZnO sample was labeled as ZnO-b.

Ni/ZnO adsorbents were prepared via the incipient impregnation method. ZnO-a or ZnO-b was first prepared by extruding a mixture of ZnO, pseudo-boehmite and diatomite at a weight ratio of 5:3:2. After drying and calcination of the shaped catalyst, Ni was introduced by impregnation of $\text{Ni}(\text{NO}_3)_2$ solution (Ni content in the adsorbent was 5wt%). Then the obtained products were calcined at 400 °C for 4 h, and the samples were named according to their composition. NiO/ZnO-x and Ni/ZnO-x indicate the nickel composite in the form of the oxide-state or reduced-state, respectively, where ZnO-x denotes the corresponding ZnO-a and ZnO-b as mentioned above.

2.3 Characterization

The crystal structure of as-prepared materials was identified by X-ray powder diffraction (XRD), with a PANalytical X'Pert PRO MPD diffractometer, equipped with a curved graphite monochromator, using Cu-K α radiation ($\lambda=1.5418$ Å) operating at 45 kV and 40 mA at a scanning speed of 5 °/min. The morphology and structure of sample powder were observed by scanning electron microscopy (SEM), with a S-4800 scanning electron microscope (Hitachi, Ltd., Japan). Transmission Electron Microscopy (TEM) images were recorded on a JEM-2100UHR analytical microscope operated at 200 kV. Samples for TEM were prepared by dispersing the sample in ethanol and putting a drop of the suspension on a carbon-coated copper grid. The solution was allowed to evaporate leaving behind the nano-crystals on the carbon grid.

The pore properties of the samples were measured from nitrogen adsorption/desorption isotherms. The N_2 adsorption and desorption isotherms were measured at -196 °C on a Micromeritics ASAP 2010 instrument. The specific surface areas and pore size distributions were calculated by the BET and BJH methods, respectively.

2.4 Performance evaluation

The experiments for activity evaluation were carried out in a fixed-bed reactor. FCC gasoline from Shenghua oil refinery (China) was used as feedstock. Prior to the reaction, the NiO/ZnO adsorbent was reduced to Ni/ZnO with a H_2 flow rate of 80 mL/min at 360 °C for 4 h. The evaluation test was performed under conditions of 400 °C, 0.5 MPa, H_2 /oil volumetric ratio = 300, and LHSV (liquid hourly space velocity) 2 h⁻¹. The reaction products were analyzed quantitatively with a Agilent 7890 Gas Chromatograph.

3 Results and discussion

3.1 Preparation and characterization of ZnO materials

XRD patterns of ZnO-a and ZnO-b are shown in Fig. 1(a and b), respectively. The as-synthesized ZnO by two different paths were both wurtzite phases (JCPDS 01-089-0510, crystal system: hexagonal) and well crystallized. For ZnO-a, the diffraction peaks were very sharp and the intensity of the diffraction peaks was very strong. However, for ZnO-b, the diffraction peaks were broadened, which indicated that the particle size of ZnO-b was smaller than that of ZnO-a. The nano-crystal size of ZnO-b calculated by the Scherrer equation was about 20 nm. XRD patterns of the precursor of ZnO-b are shown in Fig. 1(c), which suggested that the precursor is $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (JCPDS 00-014-0740, crystal system: monoclinic), and ZnO-b can be easily obtained from the low-temperature thermal decomposition reaction.

The morphology and texture of the as-prepared samples were observed by SEM and TEM. As shown in Fig. 2, they had similar structure on a mesoscopic scale and were roughly rod-shaped at different scales. The morphology of ZnO-a is shown in Fig. 2 (upper), and the average diameter and length

Fig. 1 X-ray diffraction patterns of (a) ZnO-a, (b) ZnO-b and (c) the precursor of ZnO-b

of rods were about 300 nm and 6 μm , respectively. The crystals of the precursor of ZnO-b were relatively smaller than ZnO-a (Fig. 2 (middle)). Macropores were formed by the stacking of the rods of ZnO or zinc oxalate precursor. As we know, the shape memory effect and crystal oriented attachment exist generally in low-temperature solid-phase reactions. Thus, the mesoscopic morphology of ZnO-b was maintained after thermal transformation and the size of ZnO-b crystal (Fig. 2 (below)), as mentioned above, was much smaller than that of ZnO-a, and the average diameter and length of ZnO-b rods were about 50 nm and 1 μm . Furthermore, the HRTEM images showed that the surface of the rods was very rough (see Fig. 3), which was because of the agglomeration of disordered nanocrystals, and indicated that the mesoscopic scale rod-like structure formed by a self-assembly process.

The crystal structure of the two kinds of ZnO crystals were further investigated by using TEM/HRTEM, as shown in Figs. 3 and 4. It can be seen in Fig. 3 that the end of a ZnO-a nanorod is pointed like a sword. The selected area electron diffraction (SAED) pattern indicated that the nanorod was a single crystal and could be indexed as hexagonal, which was in accordance with the XRD results (Fig. 1). In Fig. 4, it can be seen that the ZnO-b nanorod was composed of hexagonal nano-flakes whose size was 20-30 nm. A lot of mesopores

were formed between them. The SAED pattern in rod-like assembly indicated that the nanorod was poly-crystalline in structure. It can be concluded that the two kinds of ZnO had different crystal structure characteristics.

In order to give further insight into the porous structure and the pore size distribution of the as-obtained ZnO, detailed characteristics of ZnO materials were studied by the nitrogen adsorption/desorption isotherms and mercury intrusion method. The nitrogen adsorption/desorption results are presented in Table 1. From the mercury intrusion data we know both the materials possessed macro pores, and average pore diameter were about 128 nm (ZnO-a) and 117 nm (ZnO-b), respectively. Compared with ZnO-a (Fig. 5 (left)), two pronounced peaks were found on the mesopore scale from the BJH pore diameter distribution curve of ZnO-b (Fig. 5 (right)), which might be caused by tiny crystal grains with different sizes. The corresponding isotherms of mesoporous ZnO was identified as type IV with a hysteresis loop of type H3, which implied that the pore structure of ZnO-b was slit-shaped and was non-uniform in shape and size. Obviously, the pore size distribution of ZnO-b was hierarchical, and its specific surface area and pore volume were larger than ZnO-a, which may be attributed to the great difference in the texture structure and the process of ZnO crystal growth (Figs. 3 and 4).

Fig. 2 SEM images of ZnO-a (upper) and the precursor of ZnO-b (middle) and ZnO-b (below)

Fig. 3 TEM/HRTEM images and its corresponding SAED patterns of ZnO-a

Fig. 4 TEM/HRTEM images and a corresponding SAED pattern of ZnO-b

Fig. 5 N_2 adsorption-desorption isotherms and pore size distribution of ZnO-a (left) and of ZnO-b (right)

Table 1 The pore property of ZnO from different preparation methods

Sample	Specific surface area $m^2 \cdot g^{-1}$	Pore volume $cm^3 \cdot g^{-1}$	Pore diameter nm
ZnO-a	3.17	0.01	12.7
ZnO-b	31.75	0.16	17.61

3.2 Growth mechanism of ZnO materials

In general, the larger ZnO crystal is a polar crystal whose positive polar plane is rich in Zn and the negative polar plane is rich in O (Zhang et al, 2004). In the hydrothermal process, the growth unit of ZnO is the $[Zn(OH)_4]^{2-}$ tetrahedron. The mechanism of the formation may be explained with the assistance of the schematic shown in Fig. 6. At the very beginning, PEG surfactant macromolecules induced the formation of rod-like structures. Surfactant

macromolecules were selectively adsorbed on some crystal planes through hydrogen bonding, which gave rise to the growth rate diversity of $[Zn(OH)_4]^{2-}$ tetrahedra on different crystalline planes of ZnO (Cheng et al, 2008; Li et al, 2008). The growth rate on the planes decreased in the order of $V(0001) > V(\bar{1}01\bar{1}) > V(\bar{1}010) > V(\bar{1}011) > V(000\bar{1})$. The faster the growth rate, the quicker disappearance of the plane. Therefore, the (0001) plane, with the maximum growth rate, disappeared gradually in the hydrothermal process, and led to the pointed shape at one end of the c axis (Dem'yanets and Lyutin, 2008). However, the (000 $\bar{1}$) plane, with the slowest growth rate, was maintained in the hydrothermal process, and led to the plain shape at the other end of the c axis. As shown in Fig. 6, the precursor of ZnO single-crystal was $[Zn(OH)_4]^{2-}$, and the process was in-situ crystal growth.

The growth mechanism of ZnO-b was different from that of ZnO-a, as shown in Fig. 7. The first step was the formation

Fig. 6 Growth schematic diagram of ZnO-a single-crystals

Fig. 7 Formation schematic diagram of ZnO-b poly-crystals

of rod-like precursor microcrystals due to the induction of surfactants. Then ZnO crystals formed after the thermal decomposition of the precursor. Fig. 4 shows that the ZnO rods are composed of many hexagonal nanocrystals, and the rod morphology of the precursor could be maintained by nanocrystal ZnO assembling through crystal oriented attachment at relatively low temperature. Mesopores formed during the ZnO nanocrystal self-assembly process while the macropores were kept due to the aggregation of the rod-like assemblies.

3.3 Evaluation of performance of Ni/ZnO adsorbents

To investigate the effect of texture structure on the desulfurization performance in Ni/ZnO RADS system, two kinds of adsorbents were prepared using the as-obtained ZnO materials. The sulfur content of the feedstock of Ni/ZnO RADS system was 672 $\mu\text{g/g}$. The desulfurization capability of the adsorbents is shown in Fig. 8. It can be seen that the breakthrough sulfur capacity of Ni/ZnO-b was greatly higher than that of Ni/ZnO-a, and the S concentration in the products was below 10 $\mu\text{g/g}$ until 48 h. In comparison with Ni/ZnO-b, the breakthrough curve of the Ni/ZnO-a adsorbent went up rapidly at an early stage. To some extent, the results of reactive adsorption of sulfur were related to the textural structure of ZnO samples. Figs. 9 and 10 show the mechanism of reactive adsorption for the two kinds of Ni/ZnO adsorbents (Bezverkhyy et al, 2009; Sehested, 2006).

According to the reactive adsorption mechanism, organosulfur compounds in FCC gasoline oil was adsorbed

selectively at Ni active sites and generated NiS_x and H_2S , while ZnO converted into ZnS by capturing the sulfur from NiS_x or H_2S . Sulfur was fixed in the form of ZnS. Therefore, ZnO played an important role in transferring sulfur species for the process of NiS_x “self-regeneration” back to Ni^0 . The reaction rate of zinc oxide with H_2S and sulfur species on nickel surface was crucial, because it determined the performance of the reactive adsorption desulfurization adsorbent (Babich and Moulijn, 2003). Considering that sulfidation on the ZnO surface was diffusion-controlled (Ryzhikov et al, 2008), a larger surface area and smaller crystal size of ZnO would facilitate diffusion and hence enhance the desulfurization activity. So the improved capacity of reactive adsorption of sulfur can be attributed to the promoted diffusion effect and large specific surface area of hierarchical pore ZnO-based Ni/ZnO adsorbent.

Single crystal ZnO obtained by the one step hydrothermal method had a large crystal grain size and low specific surface area. As a result, the capacity of reactive adsorption of sulfur was relatively small. As shown in Fig. 9, when ZnO on the outside of the particles was converted into ZnS completely, the ZnO inside the particles was difficult for the H_2S to access because of the diffusion limitation. While for polycrystalline assembly ZnO (ZnO-b), the small crystal grains could form many effective mesopores and tiny nanocrystals. This kind of ZnO has an extremely high surface activity due to the increase in the number of active sites on the surface. The uneven atomic steps on the surface increased the chance of contact between the adsorbent and the reactant molecules. As shown in Fig. 10, mesopores in the grains and the high surface area were helpful to improve the Ni dispersion on ZnO. The efficiency of sulfur transferring was improved (Bezverkhyy et al, 2009). So, an enhanced Ni-Zn synergistic effect can contribute to the excellent sulfur-fixation capability of ZnO.

4 Conclusion

Two kinds of ZnO porous materials with rod-shaped morphology were synthesized and their application performance in RADS system was evaluated. Macroporous single-crystal zinc oxide was obtained from a hydrothermal method and a hierarchical poly-crystalline zinc oxide assembly was obtained from rod-like macroporous precursor thermal transformation. The hierarchical poly-crystal ZnO

Fig. 8 Breakthrough curves of the Ni/ZnO-a and Ni/ZnO-b adsorbents

Fig. 9 The mechanism of reactive adsorption in Ni/ZnO-a absorbent (from Bezverkhyy et al, 2009; Sehested, 2006)

Fig. 10 The mechanism of reactive adsorption in Ni/ZnO-b absorbent (from Bezverkhyy et al, 2009; Sehested, 2006)

assembly maintained the rod-like precursor morphology after phase transformation for the shape memory effect in a low temperature solid-phase reaction. The developed hierarchical pore structure is composed of meso-pores formed between the nanoclusters and the macro-pores formed between the rod-like assemblies. Compared with macroporous rod-like ZnO-based Ni/ZnO-a absorbent, hierarchical pore ZnO-based Ni/ZnO-b absorbent possesses higher desulfurization performance, which can be attributed to the enhanced diffusion effect and higher surface area in hierarchical pore ZnO-based Ni/ZnO-b absorbent.

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