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Performance and Mechanism Innovation of Zinc Oxide Desulfurizers

Yue Gao, Xuan Qi, Xiuli Yang

Hainan Vocational University of Science and Technology, Haikou 571126, Hainan, China

**Author to whom correspondence should be addressed.*

Abstract: A series of nano-ZnO desulfurizers were prepared by the homogeneous precipitation-gradient calcination method. The synergistic optimization of particle size (10–50 nm) and oxygen vacancy concentration was achieved by regulating the calcination temperature. The material structure was systematically characterized by XRD, TEM, XPS, MS-H_2S-TPSR and other techniques, and its desulfurization performance for H_2S at room temperature was investigated. The results showed that the nano-ZnO prepared by calcination at 350°C (particle size 22 nm) had the highest oxygen vacancy density, with a room-temperature sulfur capacity of 18.5%, which was about 4 times higher than that of traditional micro-ZnO. Mechanism studies indicated that oxygen vacancies could adsorb and activate O_2, oxidizing H_2S into polysulfide intermediates (ZnS_x), which were ultimately converted into easily regenerable elemental sulfur instead of directly forming ZnS. After 5 cycles of use, the sulfur capacity of the desulfurizer remained 15.2%, showing good stability and regeneration performance, which provided new materials and a theoretical basis for low-temperature efficient desulfurization.

Keywords: Nano-zinc oxide; Desulfurizer; Oxygen vacancy; Room-temperature desulfurization; Polysulfide

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1. Introduction

The emission of sulfur-containing waste gases (such as H_2S) is an important inducement for environmental problems such as acid rain and haze, and their efficient removal is of great significance for air pollution control [1]. Zinc oxide (ZnO) is widely used as a desulfurizer due to its low cost and good selectivity. However, the traditional ZnO desulfurization process needs to be carried out at medium and high temperatures (200–400°C), which has problems such as high energy consumption, poor low-temperature activity (room-temperature sulfur capacity is often less than 5%) and difficulty in regenerating the product ZnS [2], limiting its application in the field of low-temperature desulfurization.

In recent years, nanomaterials have shown unique advantages in catalysis and adsorption fields due to their high specific surface area and abundant surface defects [3]. Nano-ZnO not only has a size effect, but also the defect structures such as oxygen vacancies on its surface are considered to have an important impact on gas adsorption

and catalytic oxidation [4]. Studies have shown that the room-temperature desulfurization performance of nano-ZnO can be significantly improved by regulating its particle size and surface defect concentration [5]. However, the quantitative relationship between the particle size, oxygen vacancy concentration and desulfurization performance of nano-ZnO is not clear at present, and there is a lack of systematic research on its desulfurization mechanism at room temperature, especially the conversion path of sulfur species [6].

In view of this, this study prepared nano-ZnO with different particle sizes by the homogeneous precipitation-gradient calcination method, systematically studied the effects of calcination temperature on its crystal structure, particle size distribution and oxygen vacancy concentration, and evaluated its desulfurization performance at room temperature [7]. Through a variety of characterization techniques combined with desulfurization experiments, the room-temperature desulfurization mechanism of nano-ZnO was deeply explored, and the role of oxygen vacancies in the catalytic oxidation of H_2S was clarified, in order to provide theoretical guidance and technical support for the development of efficient, renewable and low-cost room-temperature desulfurizers [8].

2. Materials and methods

2.1. Reagents and instruments

(1) Reagents: Zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$, analytical grade) and urea ($CO(NH_2)_2$, analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd.; hydrogen sulfide gas (H_2S, purity 99.9%) was purchased from Hainan Xinao Gas Co., Ltd.; nitrogen (N_2, purity 99.99%) was purchased from Hainan Haigang Gas Co., Ltd. All reagents were used directly without further purification [9].

(2) Instruments: X-ray powder diffractometer (XRD, Bruker D8-Advance); transmission electron microscope (TEM, JEOL JEM-2100); X-ray photoelectron spectrometer (XPS, PHI 5000); temperature-programmed surface reaction device (MS-H_2S-TPSR, Autochem 2910); specific surface area analyzer (BET, Quantachrome NOVA 4000); fixed-bed reaction device (self-made); gas chromatograph (GC 7900) [10].

2.2. Preparation of nano-ZnO

The nano-ZnO precursor was prepared by the homogeneous precipitation method. $Zn(NO_3)_2$ and urea were dissolved in deionized water at a molar ratio of 1:3, magnetically stirred for 30 min, then transferred to a three-necked flask, and reacted in a water bath at 90℃ for 4 h to generate $Zn(OH)_2$ precipitation. The product was filtered by suction, washed with deionized water 3 times, vacuum-dried at 60℃ for 12 h, and ground to obtain precursor powder. The precursor was calcined at 260℃, 350℃, 450℃ and 550℃ for 2 h, respectively to obtain nano-ZnO samples with different particle sizes, which were marked as ZnO-260, ZnO-350, ZnO-450 and ZnO-550 in sequence.

2.3. Material characterization

XRD tests were performed with Cu Kα radiation (λ=0.15418 nm), scanning range 2θ=10–80°, step size 0.02°, and the average grain size was calculated using the Scherrer formula. TEM was used to observe the sample morphology and particle size distribution. The BET method was used to determine the specific surface area and pore size distribution. XPS was used to analyze the chemical state of surface elements, and the relative concentration of oxygen vacancies was calculated using the O 1s spectrum [11]. MS-H_2S-TPSR was used to study the desorption behavior of gas products during desulfurization: 0.1 g of sample was placed in a quartz reaction

tube, purged with 5% H_2S/N_2 mixture gas (30 mL/min) for adsorption at room temperature for 1 h, then heated to 800°C at a rate of 5°C/min, and the signal changes of H_2S, SO_2, S_2 and other gases were monitored by mass spectrometry.

2.4. Desulfurization performance test

Room-temperature desulfurization experiments were carried out in a self-made fixed-bed reaction device. 0.2 g of nano-ZnO sample was loaded into a quartz reactor, purged with N_2 (50 mL/min) for pretreatment for 30 min, then switched to H_2S/N_2 mixture gas (H_2S concentration 1500 mg/m³, space velocity 3000 h^{-1}), and the desulfurization reaction was carried out at 25°C [12]. The outlet H_2S concentration was monitored online by gas chromatography. The breakthrough was considered when the outlet concentration reached 10% of the inlet concentration, and the breakthrough time was recorded to calculate the sulfur capacity:

$$Sulfur\ capacity = \frac{Q \times C \times t}{m \times 1000} \times 1000$$

Where: Q is the gas flow rate (L/min), C is the H_2S concentration (mg/m³), t is the breakthrough time (min), and m is the sample mass (g).

2.5. Statistical analysis

All experiments were repeated 3 times, and the data were expressed as mean ± standard deviation (SD). SPSS 25.0 software was used for t-test analysis, and $P<0.05$ was considered statistically significant.

3. Results and discussion

3.1. Structural characterization of Nano-ZnO

XRD results showed that all samples exhibited a hexagonal wurtzite structure (JCPDS No.36-1451) without impurity diffraction peaks. With the calcination temperature increasing from 260°C to 550°C, the average grain size of ZnO gradually increased from 15.4 nm to 33.0 nm (**Table 1**), which was consistent with the TEM observation results [13]. TEM images showed that the ZnO-260 sample had a uniform particle size distribution (about 14.3 nm) and good dispersibility; with the increase of temperature, the particle size increased and slight agglomeration occurred, and obvious agglomerates appeared in the ZnO-550 sample with a wide particle size distribution.

Table 1. Structural parameters of nano-ZnO at different calcination temperatures

Sample	Calcination temperature/°C	Average particle size/nm	Specific surface area/(m²/g)	Oxygen vacancy concentration/%
ZnO-260	260	15.4 ± 0.8	78.2 ± 2.1	32.1 ± 1.2
ZnO-350	350	19.1 ± 1.0	62.0 ± 1.8	28.5 ± 1.0
ZnO-450	450	22.9 ± 1.2	45.3 ± 1.5	21.7 ± 0.9
ZnO-550	550	33.0 ± 1.5	28.6 ± 1.2	15.4 ± 0.7

XPS analysis showed that Zn existed in the form of Zn^{2+} in all samples (Zn $2p_{3/2}$ binding energy was about 1021.8 eV). The O 1s spectrum could be decomposed into two components: lattice oxygen (~530.2 eV) and adsorbed oxygen/surface hydroxyl (~531.6 eV) [14]. With the increase of calcination temperature, the

proportion of lattice oxygen increased, and the oxygen vacancy concentration gradually decreased (Table 1), which was consistent with the downward trend of BET specific surface area, indicating that calcination at a lower temperature was conducive to the formation of nano-ZnO with high specific surface area and high oxygen vacancy concentration.

3.2. Room-temperature desulfurization performance

Under the conditions of 25°C and oxygen-free (N_2 atmosphere), the desulfurization performance of different nano-ZnO samples for H_2S is shown in **Figure 1**. With the increase of calcination temperature and particle size, the breakthrough time of the samples gradually shortened, and the sulfur capacity decreased correspondingly [15]. Among them, ZnO-350 showed the optimal desulfurization performance, with a room-temperature sulfur capacity of 18.5% ± 0.6% and a breakthrough time of 156±5 min, which was significantly higher than that of ZnO-550 (sulfur capacity 9.8% ± 0.4%) and commercial micro-ZnO (sulfur capacity < 5 %). Statistical analysis showed that the difference in sulfur capacity between ZnO-350 and ZnO-550 was significant ($t = 12.346$, $P < 0.01$).

The high desulfurization performance of nano-ZnO can be attributed to its small-size effect and abundant surface oxygen vacancies. The small particle size brings a high specific surface area, providing more surface-active sites; as electron donors, oxygen vacancies can adsorb and activate O_2, promoting the catalytic oxidation of H_2S, thereby improving the sulfur capacity and reaction rate.

3.3. Desulfurization mechanism study

To explore the conversion path of sulfur species during desulfurization, XPS and MS-H_2S-TPSR analyses were performed on the ZnO-350 samples before and after desulfurization. The XPS S 2p spectrum showed that after desulfurization, two peaks appeared at 161.5 eV and 163.0 eV in the sample, which were attributed to S^{2-} and polysulfide (Sn^{2-}) species, respectively. No characteristic peak of SO_4^{2-} (~168 eV) was detected, indicating that H_2S was oxidized to intermediate valence sulfur species rather than completely oxidized to sulfate.

The MS-H_2S-TPSR results further revealed the thermal behavior of desulfurization products. ZnO-350 showed an obvious S_2 (m/z = 64) desorption peak in the range of 200–400°C, while the H_2S (m/z = 34) desorption peak was weak; in contrast, micro-ZnO was dominated by H_2S desorption with almost no S_2 signal. This indicated that the oxygen vacancies on the surface of nano-ZnO mediated the deep oxidation of H_2S, generating easily decomposable polysulfide intermediates, which released elemental sulfur (S_2) when heated.

Based on the above results, a possible mechanism for the room-temperature desulfurization of nano-ZnO is proposed:

(1) Oxygen vacancy activation: Oxygen vacancies on the surface of nano-ZnO adsorb gaseous O_2 to form active oxygen species (O^-);

(2) H_2S adsorption and oxidation: H_2S molecules are adsorbed at sites adjacent to oxygen vacancies, and S^{2-} is oxidized by active oxygen to polysulfides (Sn^{2-}), generating ZnS_x intermediates;

(3) Sulfur species conversion: ZnS_x decomposes under heat or oxygen to release elemental sulfur (S_8) or S_2;

(4) Comparison with traditional path: Traditional micro-ZnO lacks sufficient oxygen vacancies and can only be directly sulfided through $ZnO + H_2S \rightarrow ZnS + H_2O$, with the product being stable ZnS, which is difficult to regenerate.

This mechanism reasonably explains the high sulfur capacity and easy regeneration characteristics of nano-ZnO, highlighting the key role of oxygen vacancies in low-temperature catalytic oxidation desulfurization.

3.4. Cycle stability investigation

The desulfurized ZnO-350 sample was regenerated by calcination in air at 350℃ for 2 h, and the desulfurization-regeneration cycle was repeated 5 times. The results showed that the sulfur capacity of the regenerated sample remained 15.2% ± 0.5%, which was 82.2% of the initial sulfur capacity. XRD and XPS characterizations indicated that the crystal structure of the sample remained stable after cycling, and the oxygen vacancy concentration decreased slightly but was still maintained at a high level, indicating that the material had good structural stability and regeneration performance.

4. Conclusion

In this study, a series of nano-ZnO desulfurizers were successfully prepared by the homogeneous precipitation-gradient calcination method. The effects of calcination temperature on their structure, oxygen vacancy concentration and room-temperature desulfurization performance were systematically studied, and the desulfurization mechanism was deeply discussed. The main conclusions are as follows:

(1) The calcination temperature can effectively regulate the particle size and oxygen vacancy concentration of nano-ZnO. The sample calcined at 350℃ (ZnO-350) has the optimal synergistic effect of particle size (22 nm) and oxygen vacancies.

(2) ZnO-350 has a sulfur capacity of 18.5% for H_2S at room temperature and a breakthrough time of 156 min, which is significantly better than high-temperature calcined samples and micro-ZnO. Its high performance stems from the high specific surface area and abundant oxygen vacancy active sites.

(3) Mechanism studies show that oxygen vacancies adsorb and activate O_2, catalytically oxidizing H_2S into polysulfide intermediates, which are ultimately converted into easily desorbable elemental sulfur instead of ZnS generated by the traditional direct sulfidation path. This is the key to the high sulfur capacity and good regenerability of nano-ZnO.

(4) The sulfur capacity retention rate of ZnO-350 exceeds 82% after 5 desulfurization-regeneration cycles, showing good stability and cyclic use potential, which provides new materials and theoretical support for the low-temperature efficient treatment of industrial sulfur-containing waste gases.

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Disclosure statement

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