



## Full Length Article

# Contributions of tailored oxygen vacancies in ZnO/Al<sub>2</sub>O<sub>3</sub> composites to the enhanced ability for H<sub>2</sub>S removal at room temperature



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## ABSTRACT

A series of Ni-doped ZnO/Al<sub>2</sub>O<sub>3</sub> adsorbents with various compositions were fabricated through the sol-gel method. They were then tested dynamically in H<sub>2</sub>S removal from a gas stream containing H<sub>2</sub>S in moist N<sub>2</sub>. The adsorbents obtained were characterized using Scanning electron microscopy (SEM), transmission electron microscopy (TEM), N<sub>2</sub> adsorption and desorption, Powder X-ray diffraction (XRD), CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD), UV-Raman spectroscopy, photoluminescence (PL) spectroscopy and X-ray photoelectron spectroscopy (XPS) techniques. The dynamic tests for H<sub>2</sub>S removal showed that the sulfur capacity tended to gradually increase at first and then decrease with the increase in Ni<sup>2+</sup> dopant content. XPS, PL and UV-Raman spectra results indicated that the concentrations of oxygen vacancies increased after doping Ni species. The increased breakthrough capacity was strongly related to the concentrations of oxygen vacancies. Oxygen vacancies played a dual role in removing H<sub>2</sub>S in the dynamic tests. They could efficiently promote H<sub>2</sub>S dissociation by providing high OH concentrations on the ZnO surface by acid-base interaction. Furthermore, oxygen vacancies could efficiently promote the counterdiffusion of HS<sup>-</sup> or S<sup>2-</sup> and O<sup>2-</sup> in the bulk of ZnO. This mechanism of anion diffusion in the ZnO lattice was supposed in this study.

## 1. Introduction

Fuel cells have significant potential as an efficient and environmentally friendly powering technology. The main electrochemical reaction involved is the reaction of hydrogen with oxygen to form water. However, the impurity H<sub>2</sub>S in hydrogenous fuels, e.g., natural gas, reforming gas, and syngas, can poison platinum catalysts, corrode electrodes, and contaminate electrolyte solutions [1–6]. H<sub>2</sub>S gas even in trace amounts is extremely toxic to the human respiratory and nerve systems [7,8]. Therefore, maintaining the H<sub>2</sub>S level in fuel gases below 0.1 ppmv is important not only to the functioning of fuel cells but also to the health of humans and to environmental protection. Cost-effective ultradeep H<sub>2</sub>S adsorbents that can be used at room temperature and mass-produced are thus urgently needed.

ZnO, a widely used metal oxide desulfurizer, has received much attention because of its good thermal stability and large equilibrium constant [9]. Previous studies [10,11], have reported that ZnO can stoichiometrically react with H<sub>2</sub>S at about 350 °C, while its reactivity can dramatically decrease with the decrease in temperature. Some efforts have been attempted to improve the performance of ZnO at room

temperature by increasing the specific surface area, for example, by supporting on inert materials [12], and by mixing with other metal oxides and doping with impurity atoms [5]. For instance, Al<sub>2</sub>O<sub>3</sub> is always mixed with ZnO to obtain a good dispersion of ZnO with small particle size [13–15]. Besides the efforts to increase the surface area, other attempts have also been done for improving the performance of ZnO by optimizing the pore structures [16–18]. A typical case is preparing zinc oxide-silica adsorbents with three-dimensionally ordered macropore (3DOM) structures for H<sub>2</sub>S removal [16]. 3DOM structures have been found to significantly reduce the mass-transfer resistance and prevent the blockage of pore channels caused by volume expansion of the adsorbent.

Besides being a desulfurizer, ZnO is also a widely known photocatalyst. It has a high redox potential, large exciton binding energy (BE), and superior physical and chemical stability [19]. Recently, point defects formed in crystal ZnO, especially oxygen vacancies (VOs) have been extensively studied because of the band-gap widening due to the generation of numerous electrons, the so-called Moss-Burstein effect [19,20]. VOs can also act as adsorption sites, preventing electron-hole recombination [21]. These characteristics imply the important role of

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VOs in improving the photocatalytic efficiency of ZnO [22]. VOs are purported to aid the design of efficient sorbents for sulfur removal. In contrast to the extensive studies in photo-catalysis, however, very few works have focused on the function of VOs in H<sub>2</sub>S removal. A report by Wang et al. [23] mentions that VOs in TiO<sub>2</sub> are potentially efficient trap centers for H<sub>2</sub>S dissociation that can promote interfacial charge transfer. A work by Cao et al. [24] indicates that the VOs can directly adsorb H<sub>2</sub>S molecules. The adsorbed H<sub>2</sub>S molecules coordinate with unsaturated Fe<sup>3+</sup>, weakening the Fe–O bond by donating electrons of H<sub>2</sub>S back into the anti-bonding orbital of the Fe–O bond. Consequently, H<sub>2</sub>S can more easily replace the O<sup>2-</sup> connected to unsaturated Fe<sup>3+</sup>, resulting in a chain reaction. To our knowledge, no studies have focused on the role of VOs yield of ZnO in the performance in H<sub>2</sub>S removal at room temperature.

Generally, VOs can either be intrinsic VOs in which no new ions are added to the structure, or extrinsic, in which the crystal is doped with a foreign ion. It is commonly accepted that intrinsic VOs are related to preparation processes or methods, while extrinsic VOs in the matrix vary with doping with metal ions [24]. Because of the similarity in ionic radii of Ni<sup>2+</sup> (0.069 nm) and Zn<sup>2+</sup> (0.074 nm), Ni<sup>2+</sup> can easily enter the ZnO lattice by substitution of Zn<sup>2+</sup>. Many studies on Ni-doped ZnO can be found in the area of materials science, specifically, optical or ferromagnetic properties [25–27]. Herein, we fabricated Ni-doped zinc oxide–aluminum composites through the sol–gel method. This was done to investigate the impact of VOs on the capacity for H<sub>2</sub>S removal by modifying the VO concentrations in the ZnO lattice. The physico-chemical properties of the composites were characterized through various techniques. The performance in H<sub>2</sub>S adsorption was evaluated using a fixed bed at room temperature. Furthermore, the role of VOs in the performance in H<sub>2</sub>S removal is discussed in detail.

## 2. Experimental

### 2.1. Chemicals

Aluminium isopropoxide (reagent grade, 99.5%) was acquired from Tianjin Guangfu Fine Chemical Industry Research Institute, methanol (AR, 99.5%), ethylene glycol (AR, 98%), zinc nitrate hexahydrate (AR, 99.0%) and nitric acid (AR, 65%) were obtained from Tianjin Kermel Chemical Reagent Co. Ltd. Ethanol absolute (AR, 99.7%) and nickel nitrate (AR, 98%) were purchased from Tianjin Zhi yuan Chemical Reagent Co. Ltd. All the chemicals were used without further purification.

### 2.2. Sorbents preparation

A series of Ni-doped ZnO/Al<sub>2</sub>O<sub>3</sub> composites with various compositions were prepared successfully through the sol-gel method. All of them with a fixed weight ratio of ZnO/Al<sub>2</sub>O<sub>3</sub>, equating to 1:1. The typical procedures are mentioned as below: 5 g aluminium isopropoxide and some distilled water were added into a three mouth flask with bathing temperature at 80 °C for 1 h, the temperature raised to 95 °C, then 0.2 ml concentrated nitric was added under stirring for 1 h to get a transparent Al sol. Next, the proper zinc nitrate hexahydrate and nickel nitrate were dissolved in a mixture of ethylene glycol (EG) and methanol to get the mixed solution (1.5 M), with atomic ratios of Ni/Zn = 0, 0.01, 0.03 0.05, respectively. The mixed solution was dripped into the transparent Al sol with continuous stirring for 1 h to get the gel. Then, the gel was transferred into a glass dish for aging 10 h at 30 °C, drying at 120 °C overnight [14]. Lastly, calcination at 300 °C in air for 5 h to achieve the final composites. The corresponding composites were also shorten for NZA-x in this paper, NZA are indexed into the doped Ni species, ZnO, Al<sub>2</sub>O<sub>3</sub>, respectively, and x denoted the percent content of Ni doping. The samples after desulfurization were labelled as NZA-xE.

### 2.3. Performance tests

The synthesized NZA-x composites were studied as sorbents for removing H<sub>2</sub>S from a gas stream containing H<sub>2</sub>S in moist N<sub>2</sub> in the dynamic tests. Briefly, samples were (40–60 mesh particle size) added into a glass reactor (inner diameter 6 mm), keeping the bed height is 2 cm, and pre-humidified with moist N<sub>2</sub> (ca. 3% moisture) achieved through a bubbler with some water by passing a flow of N<sub>2</sub> at 30 °C for 60 min. Then containing 850 mg/m<sup>3</sup> H<sub>2</sub>S in moist N<sub>2</sub> passed through the packed bed, the total flow rate was kept in 100 ml/min. H<sub>2</sub>S concentrations in the inlet and outlet were detected by gas chromatograph (Hai xin, GC-920) equipped with a flame photometric detector (FPD). The breakthrough point was defined as the concentrations of H<sub>2</sub>S in the outlet higher than 0.15 mg/m<sup>3</sup>. The adsorptive performance of sorbents was evaluated based on the breakthrough capacity (mg S/g sorbent), calculated by the equation:

$$\text{sulfur capacity (mgS/g sorbent)} = \frac{N * M_S \int_0^t (C_{in} - C_{out}) dt}{10^6 * m * M_{H_2S}}$$

where N is the total flow rate (ml/min), C<sub>in</sub> and C<sub>out</sub> are the H<sub>2</sub>S concentration in the inlet and outlet respectively (mg/m<sup>3</sup>), M<sub>S</sub> and M<sub>H<sub>2</sub>S</sub> are equal to 32 g/mol and 34 g/mol, respectively, t is the breakthrough time (min), m is the weight of the loaded adsorbents (g).

### 2.4. Characterization of materials

Powder X-ray diffraction (XRD) patterns were gained on Rigaku D/max-2500 diffractometer. N<sub>2</sub> adsorption-desorption isotherms were measured using a Micromeritics 3H-2000PS2 instrument. The BET surface areas were calculated by the standard Brunauer-Emmett-Teller method. The Barrett-Joyner-Halenda (BJH) modal was used to calculate the pore size distributions and the total pore volumes. X-ray photoelectron spectroscopy (XPS) measurements were measured on a V.G. Scientific ESCALAB250 spectrometer. UV-Raman measurements were carried out in backscattering geometry at room temperature using the UV (325 nm) line of a He–Cd laser. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were taken using Nanosem430 electron microscopy and Tecnai G2F20 electron microscopy, respectively. The effluent of CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD) was analyzed by a gas chromatograph, employing a thermal conductivity detector. Samples (0.2 g, 40–60 mesh) were added into the quartz reactor. Pretreated 1 h in He flow at 473 K of each sample, then cooled to 303 K. CO<sub>2</sub> was pulsed to the reactor till reaching saturation. Once the physically adsorbed CO<sub>2</sub> was purged off, the CO<sub>2</sub>-TPD experiments were started from 303 K with a heating rate of 10 K/min to 873 K under He flow (30 mL/min). Photoluminescence (PL) measurement was performed at room temperature using a He–Cd laser with a wavelength of 320 nm as the excitation source.

## 3. Results and discussion

### 3.1. XRD analysis

Fig. 1 shows the XRD pattern of ZnO/Al<sub>2</sub>O<sub>3</sub> composites doped with Ni at different ratios and annealed at 300 °C. As shown, all of the samples displayed the polycrystalline nature. The peaks appeared at 2θ = 31.5°, 36.1°, 56.6° and 66.3° are corresponding to (1 0 0), (1 0 1), (1 1 0) and (2 0 0) planes of the hexagonal wurtzite zinc oxide respectively [28], and the broadened characteristic peaks imply the even dispersion of the ZnO nanoparticles in the composites. No other distinguishable peaks related to Al or Ni species are present, indicating the existence of the amorphous form in the fabricated materials. Interestingly, the peak intensities of ZnO slightly increased with Ni doping; in other words, more growth of ZnO crystal occurred since the introduction of Ni species. We noticed that the peaks of ZnO appeared at

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