



# Article Synthesis of ZnO-CuO and ZnO-Co<sub>3</sub>O<sub>4</sub> Materials with Three-Dimensionally Ordered Macroporous Structure and Its H<sub>2</sub>S Removal Performance at Low-Temperature

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Abstract:  $H_2S$  is a common but hazardous impurity in syngas, biogas, or natural gas. For some advanced power generation technologies, such as integrated gasification combined cycle (IGCC), solid oxide fuel cells,  $H_2S$  content needs to be reduced to an acceptable level. In this work, a series of highly porous Zn-Cu and Zn-Co composites with three-dimensionally ordered macropores (3DOM) structure were synthesized via the colloidal crystal template method and used to remove  $H_2S$  at 150 °C and one atm. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption studies, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were carried out to analyze the fresh and spent adsorbents. The results show that all the adsorbents possess well-ordered macropores, a large surface area, and a highly dispersed active phase. The relative content of Zn and (Cu or Co) has a significant influence on the desulfurization performance of adsorbents. The addition of CuO significantly increases the sulfur capacity and 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub> shows the largest sulfur capacity of all the adsorbents, reaching up to 102.5 mg/g. The multiple adsorption/regeneration cycles of 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub> and 3DOM-Zn<sub>0.5</sub>Co<sub>0.5</sub> indicate that the as-prepared adsorbents are stable, and the sulfur capacity can still exceed 65% of the fresh adsorbents after six cycles.

Keywords: porous materials; H<sub>2</sub>S removal; low-temperature desulfurization; metal oxide; regeneration ability

## 1. Introduction

Hydrogen sulfide ( $H_2S$ ) is a major impurity that originates from varieties of processes such as coke ovens, coal or natural gas manufacturing, and oil refining [1,2].  $H_2S$  impurity must be removed since it is highly hazardous to both the environment and industrial processes. For example,  $H_2S$  can corrode industrial equipment and pipelines, and sulfur dioxide generated by  $H_2S$  combustion is a cause of acid rain. The olfactory threshold of  $H_2S$  is 0.005 ppm and the acceptable environment limit for  $H_2S$  is 0.02–0.1 ppm [3].

Many methods, including alcohol amine absorption, adsorption, ionic liquid absorption, etc., have been developed to remove H<sub>2</sub>S from gas streams [4–6]. Among these methods, adsorption has attracted more and more attention from scholars because of its low cost and high desulfurization activity. In 1976, various metal oxides were thermodynamically screened to remove H<sub>2</sub>S, and 11 metal oxides were found to have high-temperature desulfurization potential by Westmoreland et al. [7], including Zn, Fe, Mn, Co, V, W, Mo, Ca, Sr, Ba, and Cu. The adsorption reaction mechanism is based on the formation of metal sulfides from metal oxides and hydrogen sulfide [8,9]. Compared with high-temperature (>500 °C) desulfurization, mid-(200–500 °C) and low-temperature (<200 °C) desulfurization can simplify operations and reduce costs. Because of its thermal stability and desulfurization activity, ZnO has attracted much attention in low and mid-temperature desulfurization [10–12].

Bulk ZnO has a large particle size, insufficient porosity, and low surface area, which results in low sulfurization kinetics and grains agglomeration. To solve this problem,



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). porous ZnO and ZnO nanoparticles supported on meso-/microporous materials have been extensively studied. Tran et al. [13] prepared a porous ZnO with high porosity using agarose gels as templates. The result showed that porous ZnO exhibited a much higher sulfur capacity ( $457 \text{ mg} \cdot \text{g}^{-1}$ ) than that of the commercial ZnO ( $245 \text{ mg} \cdot \text{g}^{-1}$ ). Yang et al. [14] synthesized a series of mesoporous  $ZnO/SiO_2$  sorbents with the aid of activated carbon. The presence of activated carbon made ZnO highly dispersed and produced more oxygen vacancies in ZnO. The highest H<sub>2</sub>S adsorption capacity of this material could reach up to 160.95 mg $\cdot$ g<sup>-1</sup> and corresponding ZnO utilization was 69%. Moreover, with the increase of ZnO loading, the adsorption capacity decreased due to ZnO agglomeration. Furthermore, researchers investigated the desulfurization performance of ZnO/mesoporous silica prepared in various ways. Wang et al. [15,16] prepared mesoporous SBA-15 with different loading of ZnO nanoparticles via incipient wetness impregnation and investigated H<sub>2</sub>S removal ability. The prepared materials could remove  $H_2S$  from 1000 ppm to less than 0.1 ppm at a zinc loading of 3.04 wt% and a sulfur capacity of 436.6 mg  $g^{-1}$ . They also found that as the reaction proceeded, the formation of zinc sulfide would condense in the pores and limit the gas diffusion, thereby reducing adsorption ability. Geng et al. [17] adopted a melt infiltration method to prepare ZnO supported on SBA-15, MCM-41, and MCM-48 and conducted desulfurization experiments at room temperature. Compared with the impregnation method, melt infiltration could make ZnO nanoparticles more uniform in the pores. The optimal ZnO loading on SBA-15 and MCM-41 was 20 wt%, and on MCM-48 was 30 wt%, and the sulfur capacities were 41.0, 54.9, 53.2 mg $\cdot$ g<sup>-1</sup>, respectively.

However, pure ZnO has some drawbacks, such as grain agglomeration and zinc evaporation. The addition of another metal oxide as an active additive was investigated [18–23]. For instance, a series of ZnO/TiO<sub>2</sub> composites with different Zn/Ti ratios were prepared from amorphous citrate precursors by Lew et al. [19]. The desulfurization result indicated that the addition of TiO<sub>2</sub> could stabilize ZnO adsorbents but raise operation temperature. Tran et al. [13] found that Ni-doped ZnO adsorbent showed a much higher desulfurization capacity compared with pure ZnO as Ni provided additional active sites. Moreover, The Ni-doped ZnO adsorbent was easily and completely regenerated by heat treatment in air. Furthermore, Shangguan et al. [20] combined Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> additives with ZnO adsorbents. The prepared materials showed an improved performance and a high resistance to generating COS. Balsamo et al. [21] loaded mixed oxides of Zn and Cu on activated carbon. The utilization ratio of the active phase increased along with CuO content and CuO could obviously promote the reactivity of ZnO. Generally, incorporating zinc oxide with another metal oxide produces a synergistic effect during desulfurization processes and the surface reactions are more complex.

Recently, 3DOM materials with interconnected pores have been extensively studied and have attracted widespread attention in the fields of photonics, batteries, and catalyst support [24–26]. 3DOM materials have an ordered skeleton structure that consists of uniform close-packed macropores, ranging from several nanometers to several hundred nanometers. The materials have some advantages including high surface area, excellent internal diffusion, large porosity, and large pore volume due to their unique structure, making them attractive as catalysts, especially for diffusion-controlling processes. In earlier studies, ZnO- [27], Fe<sub>2</sub>O<sub>3</sub>- [28], CuO- [29], Co<sub>3</sub>O<sub>4</sub>- [30] based 3DOM have been prepared and their desulfurization abilities were investigated. The results showed that the structure provided open and interconnected pores and improved metal oxides dispersion, resulting in better reaction kinetics and higher H<sub>2</sub>S breakthrough capacity. However, few reports of the materials with mixed metal oxides used as H<sub>2</sub>S removal adsorbents have been found.

According to the above findings, 3DOM structure can promote gas diffusion inside the adsorbent and improve adsorption-reaction kinetics. Copper oxide or cobalt oxide, as additives, have a synergic effect with ZnO-based adsorbent in the desulfurization processes. In this work, a series of 3DOM ZnO-CuO and 3DOM ZnO-Co<sub>3</sub>O<sub>4</sub> adsorbents were synthesized for the first time. The total metal oxide's loading was 30 wt.% but with different Zn/Cu or Zn/Co atomic ratios. The H<sub>2</sub>S removal performance of the adsorbents was evaluated under dry conditions. The initial and spent adsorbents were characterized by XRD, SEM, TEM, N<sub>2</sub> sorption, and thermogravimetry-mass spectrometry (TG-MS). The regeneration ability was also studied. This study intends to provide a new insight for a rational design of efficient ZnO-based adsorbents.

## 2. Materials and Methods

# 2.1. Chemicals

Zinc nitrate hexahydrate (AR, 99%), Copper dinitrate (AR, 99%), and Cobalt nitrate hexahydrate (AR, 99%) were obtained from Shanghai Macklin Biochemical Co. Ltd (Shanghai, China). Styrene (AR, 99.5%), tetraethyl orthosilicate (AR, 99%) and citric acid (AR, 99%) were provided by Energy Chemical (Anhui, China). Potassium persulfate (AR, 99.5%) was purchased from Modern Oriental Technology development Co. Ltd (Beijing, China). Methanol (AR, 99.5%), ethylene glycol (AR, 99.5%), ethanol (AR, 99.7%) were obtained from Shanghai Titan Scientific Co. Ltd (Shanghai, China). Hydrochloric acid (36–38 wt%) was purchased from Beijing lanyi chemical products Co. Ltd. (Beijing, China).

## 2.2. Preparation of Adsorbents

3DOM adsorbents were prepared by the colloidal crystal template method as described elsewhere [31,32]. Before preparation, the monodispersed polystyrene (PS) microspheres and well-arrayed assembly template are required. The typical preparation process of 3DOM adsorbents is as follows. First, tetraethyl orthosilicate (TEOS), anhydrous ethanol, hydrochloric acid, and distilled water at a molar ratio of 1:3.9:0.3:1.8 were mixed to obtain silicon sol. Then a certain amount of zinc nitrate hexahydrate and copper dinitrate (or a certain amount of zinc nitrate hexahydrate and cobalt nitrate hexahydrate) were dissolved in a mixture of methanol and ethylene glycol (2:3, V/V) to achieve a metal nitrate solution with a concentration of 1 M. Then the silicon sol and metal nitrate solution were mixed to get a final precursor solution with different metal contents. The well-arrayed PS hard templates were thoroughly immersed in the precursor solution for 6h and the excessive solution was removed by vacuum filtration. After that, the wet template was air-dried at room temperature overnight. Finally, the obtained material was calcined under flowing air in tube finance. The temperature was raised from room temperature to 300 °C at a heating rate of 1 °C/min and held for 2 h, then raised to 500 °C at 1 °C/min and held for 3 h. In this work, the nominal metal oxides content (Zn + Cu, Zn + Co) was set to 30 wt%, whereas the atomic ratio of Zn:Cu or Zn:Co was varied. The adsorbents were denoted as 3DOM- $Zn_xM_{1-x}$ , where M stands for Cu or Co; x indicates the atom fraction of Zn with respect to Zn + M. Letters S and R, represent the spent and regenerated adsorbents, respectively.

## 2.3. Adsorbents Characterization

Nitrogen adsorption-desorption isotherms were determined by the auto surface area and pore size analyzer (Quadrasorb SI) at liquid nitrogen boiling temperature (77 K). The specific area of adsorbents was evaluated by the Brunauer–Emmett–Teller (BET) method and the pore characteristics were evaluated by the Barrett–Joyner–Halenda (BJH) method. The phase structure of the adsorbents was determined by X-ray diffraction (XRD, D8 Advance, Bruker, Germany). X-ray photoelectron spectroscopy (XPS) measurements were performed using ESCALAB 250Xi spectrometer equipped with a monochromated Al K $\alpha$  source. The morphology of adsorbents was observed by scanning electron microscope (SEM, SU8010, Hitachi, Japan) and high-resolution transmission electron microscope (HRTEM, JEM2100F, JEOL, Akishima-shi, Japan).

# 2.4. H<sub>2</sub>S Adsorption Experiments

 $\rm H_2S$  dynamic adsorption tests were carried out at 150 °C to determine the breakthrough capacities of adsorbents under a dry atmosphere on a quartz tubular fixed bed (6 mm inner diameter  $\times$  380 mm long). The apparatus is shown in Figure 1. For desulfurization experiments, ~0.04 g as-prepared adsorbent was ground to 40–80 mesh and placed in the middle of a quartz tube, supported by quartz wool. The required gas composition was supplied by separated gas cylinders using mass flow controllers. Prior to the desulfurization test, the air inside the apparatus was removed by N<sub>2</sub> for 20 min at the flow rate of 50 mL/min. Then the fixed bed was heated to 150 °C. When the temperature was reached, the sulfur breakthrough capacity was measured using an H<sub>2</sub>S/N<sub>2</sub> mixture with 1000 ppm H<sub>2</sub>S as a sulfur source. The initial concentration of H<sub>2</sub>S was 200 ppm and the breakthrough point was set when the tail gas contained 20 ppm H<sub>2</sub>S, which was determined by a gas chromatograph (huaai, GC-9560) equipped with a flame photometric detector (FPD). The detection limitation of GC was 0.5 ppm. After desulfurization, the spent adsorbents were regenerated under flow air in a tube furnace at 650 °C for 3 h and the desulfurization performance of regenerated adsorbents was evaluated under the same conditions as fresh adsorbents.



Figure 1. Apparatus for desulfurization test.

The breakthrough capacity (BC) was calculated by the following equation:

$$BC = \frac{\mathbf{v} \times \int_0^t (C_0 - C_t) dt \times \mathbf{M}_s \times 10^{-3}}{\mathbf{V}_{mol} \times \mathbf{m}_{ads}}$$
(1)

where BC is the breakthrough sulfur capacity (mg S/g adsorbent), v is the gas flow rate (L/min), t is the breakthrough time (min),  $C_0$  and  $C_t$  are initial and outlet concentration of H<sub>2</sub>S (ppm), respectively, M<sub>s</sub> is the molar weight of S (32 g/mol), V<sub>mol</sub> is the molar volume (24.45 L/mol at room temperature, 1 atm), m<sub>ads</sub> is the weight of adsorbent (g).

## 3. Results and Discussion

#### 3.1. Characterization of Adsorbents

3.1.1. Morphology and Porous Structure of Adsorbents

Figure 2 shows the SEM images of PS templates and as-prepared materials. From Figure 2a,b, it can be seen that the as-synthesized PS microspheres are approximately spherical with a diameter of about 320 nm, and they are monodispersed. After assembly, the template with a close-packed and well-arrayed structure was obtained. Figure 2c-i shows the prepared adsorbents with different metal oxides content. Obviously, all the materials had uniform, interconnected pore structures, resembling a honeycomb. The pore size of 3DOM materials was about 210 nm, indicating a shrinkage of about 35% relative to the initial size of PS microspheres. The shrinkage was due to the melting of the PS template and sintering of metal oxides. Similar phenomena have been observed in other literature [26,28,33]. Furthermore, the macropores were connected by "windows" (the diameter is ~40 nm), which was caused by the removal of tightly packed PS spheres during calcination. These windows were important for the diffusion of gas molecules inside the adsorbents. Among the above materials, silica acted as a solidification agent and carrier for metal oxides, which stabilized 3DOM structures. From Figure 2d-i, it can be concluded that when the total metal oxides content was fixed, 3DOM structures can basically remain unchanged when adjusting the ratio of Zn/M.



**Figure 2.** SEM images of PS template (**a**,**b**); 3DOM-Zn (**c**); 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub> (**d**); 3DOM-Zn<sub>0.33</sub>Cu<sub>0.66</sub> (**e**); 3DOM-Zn<sub>0.66</sub>Cu<sub>0.33</sub> (**f**); 3DOM-Zn<sub>0.5</sub>Co<sub>0.5</sub> (**g**); 3DOM-Zn<sub>0.33</sub>Co<sub>0.66</sub> (**h**); 3DOM-Zn<sub>0.66</sub>Co<sub>0.33</sub> (**i**).

Figure 3 shows the high-resolution transmission electron microscopy (HRTEM) images of typical as-prepared adsorbents and the metal elements mapping of  $3DOM-Zn_{0.5}Cu_{0.5}$  and  $3DOM-Zn_{0.5}Co_{0.5}$ . As shown in Figure 3, the 3DOM materials contained highly periodically arrayed uniform macropores, which was consistent with SEM results. The walls of the adsorbents were formed by SiO<sub>2</sub> and nanocrystallized particles, and the shrinkage during calcination led to significant mesoporous within the wall [28]. In Figure 3b,c, EDX elemental mappings demonstrated a uniform distribution of Zn, Cu, or Zn, Co, indicating metal oxides were successfully loaded on the skeleton and the 3DOM structure could prevent the agglomeration of metal oxide nanoparticles.



Figure 3. HRTEM images and EDX mapping of 3DOM-Zn (a); 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub> (b); 3DOM-Zn<sub>0.5</sub>Co<sub>0.5</sub> (c).

 $N_2$  adsorption-desorption analysis was carried out to study the physical properties of prepared adsorbents. The nitrogen adsorption-desorption isotherms and pore size distribution are presented in Figure 4. It can be seen that all the 3DOM materials displayed similar curves, conforming to the type II isotherm according to the IUPAC classification [34,35]. Owing to the unrestricted monolayer or multilayer adsorption, the middle section of isotherms was approximately linear. The nitrogen adsorption increased significantly when  $P/P_0$  was close to one, which indicated the materials possessed a macroporous structure [36]. Moreover, in the  $P/P_0$  range of 0.8–1.0, H<sub>3</sub> hysteresis hoops could be observed in all materials, indicating the presence of mesoporous in the wall of macropores [36,37], which could be seen in the SEM and TEM images. Moreover, the inflection points of all 3DOM materials appeared at relative pressure below 0.1. This demonstrated the existence of a certain number of micropores [38].



**Figure 4.** Nitrogen adsorption – desorption isotherms of 3DOM-Zn and 3DOM-Zn<sub>x</sub>Cu<sub>1-x</sub> (**a**), 3DOM-Zn and 3DOM-Zn<sub>x</sub>Co<sub>1-x</sub> (**b**) (insert is pore size distribution calculated by BJH method).

The textural parameters are summarized in Table 1. Compared with 3DOM-Zn, the addition of copper oxide or cobalt oxide could increase the BET specific surface area. Since the formation and growth of CuO/Co<sub>3</sub>O<sub>4</sub> grains are different from those of ZnO under the same condition, inconsistent shrinkage occurred during the calcination process [39,40]. The shrinkage led to the formation of micropores, which was consistent with the results of insert images in Figure 4 [27], and the increase in the number of micropores increased the specific surface area. As the Zn/Cu ratio decreases, the BET specific area increased. 3DOM-Zn<sub>0.33</sub>Co<sub>0.66</sub> also possessed the largest specific area among the three adsorbents containing cobalt oxide, while the specific area of 3DOM-Zn<sub>0.5</sub>Co<sub>0.5</sub> was slightly less than that of 3DOM-Zn<sub>0.66</sub>Co<sub>0.33</sub>. This may be caused by the sintering of different grains during the calcination process. Furthermore, the proportion of micropores increased with the addition of copper/cobalt oxide, while the average pore sizes calculated by the Barret–Joyner–Halenda (BJH) method almost remained unchanged.

Fable 1. Textural	parameters of 3DOM materials <sup>1</sup>	
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Name	$S_{BET}$ (m <sup>3</sup> /g)	$V_t$ (cm <sup>3</sup> /g)	d <sub>BJH</sub> (nm)	
3DOM-Zn	187.1	0.467	3.361	
3DOM-Zn <sub>0.33</sub> Cu <sub>0.66</sub>	213.2	0.335	3.387	
3DOM-Zn <sub>0.5</sub> Cu <sub>0.5</sub>	209.1	0.379	3.423	
3DOM-Zn <sub>0.66</sub> Cu <sub>0.33</sub>	198.4	0.337	3.437	
3DOM-Zn <sub>0.33</sub> Co <sub>0.66</sub>	237.1	0.288	3.405	
3DOM-Zn <sub>0.5</sub> Co <sub>0.5</sub>	217.5	0.264	3.347	
3DOM-Zn <sub>0.66</sub> Co <sub>0.33</sub>	221.7	0.442	3.389	

<sup>1</sup> S<sub>BET</sub>, BET specific area; V<sub>t</sub>, total pore volume; d<sub>BIH</sub>, pore size determined from BJH data.

In summary, the prepared adsorbents possess a well-arrayed and interconnected porous framework which contains hierarchically pores composed of macro-, meso-, and micropores. The adsorbents have a high surface area, which can be affected by the Zn/Cu or Zn/Co ratio.

#### 3.1.2. XRD Analysis

Figure 5 shows the XRD patterns of as-prepared adsorbents and SiO<sub>2</sub> with a 3DOM structure. It can be seen that both the 3DOM-Zn and SiO<sub>2</sub> exhibited a typical amorphous structure. However, as shown in Figure 5a, the peaks of 3DOM-Zn at ~24° shifted slightly towards the larger angles compared to those of SiO<sub>2</sub> but with no obvious peaks [41]. This might be attributed to the following reasons, the ZnO nanoparticles were too small to be detected by the XRD method and the ZnO was well dispersed in the SiO<sub>2</sub> matrix [42,43]. Compared with the standard card of CuO (JCPDS PDF no. 48-1548), all the adsorbents

containing CuO showed CuO diffraction peaks, which could be indexed to (1,1,-1), (1,1,1), (2,0,-2), (0,2,0), (1,1,-3), (3,1,-1), (2,2,0) crystal faces, and the peak intensity decreased with the increase of ZnO content. 3DOM-Zn<sub>0.66</sub>Cu<sub>0.33</sub>, which possessed the lowest content of copper, had very weak diffraction peaks. Figure 5b shows the XRD patterns of 3DOM-Zn and adsorbents with different Zn/Co ratios. The relatively weak but clear reflections at  $31.3^{\circ}$ ,  $36.9^{\circ}$ ,  $38.5^{\circ}$ ,  $59.4^{\circ}$ , and  $65.2^{\circ}$  appeared in the XRD pattern, assigning to the cobalt oxide phase (JCPDS PDF no. 42-1467). Furthermore, adsorbents with different Zn/Cu or Zn/Co ratios can be regarded as Zn-doped, Cu-doped, or Co-doped adsorbents, and doping will affect lattice parameters to some extent [8], and this is also the reason why some samples have weak diffraction peaks. However, the very weak diffraction peaks of ZnO appeared in both the 3DOM-Zn<sub>x</sub>Cu<sub>1-x</sub> and 3DOM-Zn<sub>x</sub>Co<sub>1-x</sub> XRD patterns rather than 3DOM-Zn. The results indicated that zinc oxide and copper oxide (or cobalt oxide) combined together partially through intra-grain and inter-granular coupling, and the latter made the faint diffraction peak of zinc oxide appear [44,45].



Figure 5. XRD patterns of 3DOM- $Zn_xCu_{1-x}$  (a) and 3DOM- $Zn_xCo_{1-x}$  (b).

# 3.1.3. XPS Analysis

Combining the XRD analysis and previous studies, the phase composition of asprepared adsorbents could be roughly determined. XPS was further performed to analyze amorphous species. Figure 6a shows the Zn 2p spectra of all the prepared adsorbents, two characteristic peaks in the pattern at binding energy (BE) values of 1022.5 eV and 1045.7 eV were observed, corresponding to the Zn 2p3/2 and Zn 2p1/2, respectively [18]. The two characteristic peaks shifted slightly towards higher binding energy with the addition of copper oxide or cobalt oxide but still maintained the original shape of the peaks. A part of copper oxide or cobalt oxide would interact with zinc oxide to form CuO/ZnO or  $Co_3O_4/ZnO$  heterogeneous composite [46]. Moreover, the electronegativity of Cu or Co was higher than Zn, and ZnO acted as an electron donor. Thus, the characteristic peaks shifted slightly. The results indicated that all the adsorbents contained ZnO species. Cu 2p scan spectra are shown in Figure 6b. The appearance of two peaks (933.2 eV and 953.5 eV), as well as two satellite peaks between 940-945 eV and 960-965 eV illustrated the presence of CuO (Cu<sup>2+</sup>) [47]. In the XPS spectra of Co, as shown in Figure 6c, the peaks at 781.3 eV and 797.6 eV illustrated the presence of Co<sup>3+</sup> and Co<sup>2+</sup>, and no metallic Co could be identified by XPS spectra. Similarly, with the increase of Cu or Co content, the peak intensity increased, which was consistent with XRD results.



Figure 6. XPS spectra of Zn 2p (a), Cu 2p (b) and Co 2p (c) of the adsorbents.

# 3.2. H<sub>2</sub>S Removal of Synthesized Adsorbents

The H<sub>2</sub>S removal performance of all the prepared adsorbents was carried out via a fixed bed at 150 °C, 1atm. Figure 7a shows the breakthrough curves and the corresponding breakthrough sulfur capacities are displayed in Figure 7b. Clearly, adsorbents with different active phase contents possess remarkable differences in desulfurization ability. Under the same test condition, 3DOM-Zn had the shortest breakthrough time (about 170 min), and it also had the lowest sulfur capacity (45.9 mg/g) and active phase utilization (32.5%). The addition of Cu/Co into the adsorbents could improve desulfurization performance at different levels. Among the three adsorbents containing Co, both the sulfur capacity and active phase utilization increased with the increase of Co content, and the sulfur capacity of 3DOM- $Zn_{0.33}Co_{0.66}$  reached up to 72.7 mg/g. The addition of copper had a greater impact on the adsorption performance and the breakthrough times were much longer than others. The sulfur capacity and active phase utilization of 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub> reached up to 102.5 mg/g and 72.7%, respectively. As demonstrated in the characteristic results of XRD, HRTEM and nitrogen adsorption, the inter-connected macropores, large specific area, and well-dispersed nanoparticles were beneficial to improve desulfurization performance due to excellent mass transfer inside the adsorbents and easy access to the active phase. Pore structure plays an important role in gas-solid non-catalytic reactions, especially reactions which produce large amounts of products, such as the reaction of metal oxide and  $H_2S$  [27]. However, the difference of specific area between 3DOM-Zn<sub>x</sub>Co<sub>1-x</sub> and 3DOM-Zn<sub>x</sub>Cu<sub>1-x</sub> (such as 3DOM-Zn<sub>0.33</sub>Co<sub>0.66</sub> and 3DOM-Zn<sub>0.33</sub>Cu<sub>0.66</sub>, 237.1 vs 213.2 m<sup>2</sup>/g) might illustrate that the specific area was not the major cause of the improvement of adsorption ability (72.7 vs. 102.5 mg/g). The copper oxide/cobalt oxide activity and size of nanoparticles might also be the reason for the difference in desulfurization performance. Further studies of fresh and spent adsorbents are needed.





The  $H_2S$  removal performance of as-prepared adsorbents was also compared to the reported results of metal oxide-based adsorbents, and the results are shown in Table 2. Clearly, the prepared adsorbents, especially 3DOM- $Zn_{0.5}Cu_{0.5}$  and 3DOM- $Zn_{0.33}Co_{066}$ , showed much better sulfur capacities even at low metal oxide proportion, indicating the bi-metal oxide had a synergistic effect on desulfurization. In conclusion, the bi-metal oxide materials demonstrate promising potential in  $H_2S$  removal.

## 3.3. Analysis of Spent Adsorbents

The spent 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub> and 3DOM-Zn<sub>0.5</sub>Co<sub>0.5</sub> were selected to analyze physical properties and the desulfurization process. As mentioned above, the inter-connected macropores can enhance the diffusion kinetics and increase the specific area, thereby improving the dispersion of the active phase and desulfurization ability of adsorbents. It is necessary to figure out the structure change of adsorbents during the desulfurization process. Figure 8 shows the SEM images of spent 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub> and 3DOM-Zn<sub>0.5</sub>Co<sub>0.5</sub>. Compared to Figure 2d,g, the spent adsorbents still maintained a relatively complete three-dimensional and well-ordered structure but the surface of adsorbents changed from smooth to rough, with granules appearing. Moreover, it can be seen that some mesopores between macropores were blocked by the products, even local collapse occurred. The reason for the phenomenon is that the desulfurization of hydrogen sulfide is a process of volume expansion. The adsorbents become denser and denser, and pore block even occurs in some serious cases during the process [28]. Figure 9 shows the HRTEM images of the

Adsorbents	Proportion of Metal Oxide (%)	Feed Gas Composition	Synthesis Temperature (°C)	Desulfurizaion Temperature (°C)	Breakthrough Capacity (mg/g Sorbent)	Ref.
3DOM- CuO/SiO <sub>2</sub>	50	500 mg/m <sup>3</sup> H <sub>2</sub> S, N <sub>2</sub> balance	500	Room temperature	97	[29]
3DOM- Co <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub>	57	$3\%  { m H_2O}, 500  { m mg/m^3} \ { m H_2S}, { m N_2}  { m balance}$	500	30	75	[30]
3DOM- Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	71.8–72.3	300 mg/m <sup>3</sup> H <sub>2</sub> S, 5 % H <sub>2</sub> , N <sub>2</sub> balance	500	350	38.92	[28]
Z30/K6	30	800 ppm H <sub>2</sub> S, N <sub>2</sub> balance	300	Room temperature	37.6	[48]
ZnO/SBA-15-F	15	200 ppm H <sub>2</sub> S, N <sub>2</sub> balance	550	Room temperature	21.8	[49]
20Cu/MSU-1	20	5% H <sub>2</sub> S, 95% CH <sub>4</sub>	450	Room temperature	18.3	[50]
SZ-30-400	30	100 ppm H <sub>2</sub> S, N <sub>2</sub> balance	400	Room temperature	90.7	[43]
3DOM-Zn	30	200 ppm H <sub>2</sub> S, N <sub>2</sub> balance	500	150	45.9	This work
3DOM- Zn <sub>0.5</sub> Cu <sub>0.5</sub>	30	200 ppm H <sub>2</sub> S, N <sub>2</sub> balance	500	150	102.5	This work
3DOM- Zn <sub>0.33</sub> Co <sub>066</sub>	30	200 ppm, H <sub>2</sub> S, N <sub>2</sub> balance	500	150	72.7	This work

Table 2. Summary of the performance of metal oxide-based adsorbents for H<sub>2</sub>S removal.

species of adsorption products need to be further determined.



Figure 8. SEM images of spent 3DOM- $Zn_{0.5}Cu_{0.5}$  (a) and 3DOM- $Zn_{0.5}Co_{0.5}$  (b).



Figure 9. HRTEM images and EDX mapping of spent 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub> (a); 3DOM-Zn<sub>0.5</sub>Co<sub>0.5</sub> (b).

XRD and XPS analysis was performed to study sulfur species after the adsorption test. The XRD patterns of spent and regenerated 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub> and 3DOM-Zn<sub>0.5</sub>Co<sub>0.5</sub> are shown in Figure 10. As shown in Figure 10a, there was almost no copper oxide and zinc oxide in  $3DOM-Zn_{0.5}Cu_{0.5}$ -R after adsorption and the XRD pattern was in good agreement with the characteristic of copper sulfide (JCPDS PDF no. 06-0464), indicating copper sulfide was the main product during the adsorption process. However, in the pattern of  $3DOM-Zn_{0.5}Co_{0.5}-R$ , after the adsorption of  $H_2S$ , the peaks of  $Co_3O_4$  became weak and only a few peaks corresponded to cobalt sulfide in the pattern of  $3DOM-Zn_{0.5}Co_{0.5}-R$ . The relatively high kinetics and low limitation of thermodynamics of cobalt oxide and H<sub>2</sub>S made the reaction occur almost exclusively on the solid surface, and a quantity of cobalt oxide remained unreacted [30]. The XPS spectra of spent adsorbents are shown in Figure 11. Similar to the fresh adsorbents, two distinguished peaks could be noticed in Zn 2p spectra, which was consistent with characteristic Zn 2p3/2 and Zn 2p1/2. This indicated that the oxidation state of Zn in both fresh and spent adsorbents were  $Zn^{2+}$  and no metallic Zn was produced in the adsorption process. Figure 11b shows Cu 2p spectra of 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub>-R. Compared to Figure 6b, the Cu 2p main peaks were shifted to lower binding energies (933.2 to 932.5 eV, 953.5 to 952.3 eV), which could be attributed to the appearance of CuS [47,51]. Besides, the weak peaks at 933.2 eV and 953.5 eV, together with a satellite peak indicated few CuO still existed. As shown in Figure 11c, S 2p spectrum curve could be fitted by three characteristic peaks, with the binding energies at 161.8 eV, 162.7 eV, and 169.5 eV, respectively, which suggested the formation of ZnS, CuS, and metal sulfate [52,53]. In the XPS spectrum of Co, multiple peaks could be observed, and the two peaks around 782.5 eV and 798.0 eV were ascribed to Co 2p1/2 and Co 2p3/2, respectively. The curve was fitted with four peaks with a binding energy of 778.8 eV, 782.5 eV, 786.1 eV, and 798.0 eV, respectively. The peaks at 778.8 eV and the satellite peak at 804.3 eV were characteristic of CoO [54]. In addition, two peaks at 782.5 eV and 798.0 eV were regarded to be CoS. Also, no metallic Co could be found from the spectrum. For sulfur species of 3DOM-Zn<sub>0.5</sub>Co<sub>0.5</sub>-R, as shown in Figure 11e, the spectrum had a great difference from that in Figure 11c. The curve could be fitted into three peaks with the binding energy of 162.7 eV, 164.8 eV, and 169.0 eV, corresponding to CoS, element S, and sulfate, respectively [55].



Figure 10. XRD patterns of spent (a) and regenerated (b) 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub> and 3DOM-Zn<sub>0.5</sub>Co<sub>0.5</sub>.



**Figure 11.** XPS spectra of different element: Zn 2p of  $3DOM-Zn_{0.5}Cu_{0.5}$  and  $3DOM-Zn_{0.5}Co_{0.5}$  (**a**), Cu 2p (**b**) and S 2p (**c**) of  $3DOM-Zn_{0.5}Cu_{0.5}$ ; Co 2p (**d**) and S 2p (**e**) of  $3DOM-Zn_{0.5}Co_{0.5}$ .

Based on the XPS analysis of 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub>-R and 3DOM-Zn<sub>0.5</sub>Co<sub>0.5</sub>-R and previous literature, both the copper oxide and cobalt oxide have good desulfurization kinetics [7]. 3DOM structures could avoid pore blockage caused by rapid grain growth. In the desulfurization of 3DOM-Zn<sub>x</sub>Co<sub>1-x</sub>, a quantity of elemental S was produced, and S would attach to the surface of the adsorbents, which will slow down the reaction and prevent H<sub>2</sub>S from reacting with the active phase inside. This resulted in a smaller sulfur capacity than that of 3DOM-Zn<sub>x</sub>Cu<sub>1-x</sub>.

## 3.4. Successive Sulfidation-Regeneration Performance

Taking into account the economy and convenience of the adsorbents, the regeneration ability of 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub> and 3DOM-Zn<sub>0.5</sub>Co<sub>0.5</sub> was investigated. The spent adsorbents were regenerated in a tube furnace at 650 °C with the flow air at the rate of 100 mL/min for 3 h. Figure 12 shows the sulfur capacities of the above two adsorbents within six adsorption/regeneration cycles. It can be clearly seen that the sulfur capacities of 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub> significantly decreased by more than 30% after the 1ST cycle. From the 2nd to 6th cycles, sulfur capacities almost remained unchanged. A similar phenomenon occurred on  $3DOM-Zn_{0.5}Co_{0.5}$ , but the decline rate was about 25%, less than that of  $3DOM-Zn_{0.5}Cu_{0.5}$ . Based on the SEM, XRD, and XPS analysis above, the reason for the sulfur capacity decline might be the formation of metal sulfate during the adsorption, which occupied the active phase site, destroyed well-ordered structure and it was hard to be reduced. However, a quantity of elemental S was produced during the adsorption process of 3DOM-Zn<sub>0.5</sub>Co<sub>0.5</sub>, which will attach to the surface of the adsorbent. In the regeneration process, the attached S was removed by reducing to sulfur oxide and the active phase was exposed again. Sulfur capacity was restored to a certain extent. However, the degree of regeneration is related to the regeneration conditions, such as temperature, moisture, and so on. To find a proper regeneration condition, further work needs to be done.



Figure 12. Sulfur capacity of 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub> and 3DOM-Zn<sub>0.5</sub>Co<sub>0.5</sub> during cycles.

# 4. Conclusions

In summary, a series of 3DOM adsorbents containing two active phases (ZnO, CuO or ZnO, Co<sub>3</sub>O<sub>4</sub>) were synthesized via a colloidal crystal template method. These adsorbents possessed uniform and inter-connected macropores, large surface area, and highly dispersed active phase. The results of the adsorption test showed that the relative content of Zn and (Cu or Co) had a significant influence on desulfurization performance. Among the three adsorbents containing Cu, the 3DOM-Zn<sub>0.5</sub>Cu<sub>0.5</sub> showed the highest sulfur capacity (102.5 mg/g), while 3DOM-Zn<sub>0.33</sub>Co<sub>0.66</sub> performed the largest sulfur capacity (72.7 mg/g) among adsorbents containing Co. In addition, the results of successive adsorp-

tion/regeneration indicated that the 3DOM- $Zn_{0.5}Cu_{0.5}$  and 3DOM- $Zn_{0.5}Co_{0.5}$  could retain most of the desulfurization ability after regeneration. The sulfur capacity still remained more than 65% of the original value after six times regeneration. This work will provide some reference for the preparation of novel and efficient adsorbents in the future.

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