

Synthesis of Composites ZnO-Al₂O₃, ZnO-Al₂O₃-CuO and Evaluation of its Activity for COS Conversion, H₂S Sorption Treatment

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Abstract

Two ZnO-Al₂O₃ and ZnO-Al₂O₃-CuO composites were synthesized by precipitation method. The obtained composites have been characterized by physico-chemical methods such as XRD, TEM, BET. Synthetic conditions were investigated as precipitation temperature, pH. The results showed that ZnO presented in all composites in wurzite, CuO in monoclinic and Al₂O₃ in amorphous phase. The optimum specific surface area attains ZnO-Al₂O₃ and ZnO-Al₂O₃-CuO was 83.9 and 89.4 m²/g, respectively. The results of COS treatment showed that ZnO-Al₂O₃ (10%) presented the highest conversion, reaching 81%. For the capacity of H₂S treatment, ZnO-Al₂O₃-CuO composite gives the best processing capacity with sulfur capacity of 31 gS/100 g of composite, up to 150% in comparison with unadded CuO composite.

Keywords: H₂S removal; COS removal; Zinc oxide; Desulfurization

Introduction

Natural gas contains certain amounts of H₂S and COS. In case of presence of these gases, the utilization of natural gas in industry can cause serious consequences due to their acidity. These gases can corrode directly metallic equipment and event can be converted to H₂SO₄ as a strong corrosive agent [1]. In addition, for living environments, H₂S has an unpleasant odor and with the exposure to high levels, can give fatal damage to human body [2]. There are a different H₂S gas treatment technologies that have been deployed in industry such as: (i) Chemical sorption method (using of sodium hydroxide, KOH), (ii) Physical sorption methods (using organic solvents: propylene carbonate, dimethyl ether), (iii) Physico-chemical method (using diisopropanolamine, methyldiethanolamine, alkyl ethers and so on) [3]. There are advantages and disadvantages for each other methods. However, these technologies only handle sulfur content down to 100 ppm. In order to ensure a deeper

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level of sulfur treatment, solid phase sorbents technology has been developed. This method allows the deep treatment of H₂S, under 1 ppm. Typical metal oxide used in this technology is ZnO oxide. ZnO oxide has high sulfur sorption capacity, but slow sorption kinetic limits its capacity [4-6]. CuO oxide is also known to have rapid kinetic sorption with H₂S [7,8]. However, its sorption capacity is low. Hence, a combination of these two phases could improve sulfur sorption capacity. For COS, the treatment is through the hydrolysis of COS to H₂S and H₂S, which will be absorbed after [9]. To catalyze the hydrolysis of the COS gas, Al₂O₃ oxide is known to be a potential catalyst. In the present study, we aim to synthesize the composite ZnO-Al₂O₃ and ZnO-Al₂O₃-CuO and evaluate its catalytic activity for COS and H₂S treatment.

Experimental

Materials and chemical compounds

Chemical compound used has analytical purity (Sigma Aldrich): Na₂CO₃ 99%, Zn(NO₃)₂·6H₂O 99%, Cu(NO₃)₂·3H₂O 99%, Al(NO₃)₃ 99%.

Catalysts Synthesis

Synthesis of ZnO-Al₂O₃

Co-precipitation method: The adequate amount of Zn(NO₃)₂ and Al(NO₃)₃ salts (99%, TQ) dissolved in distilled water and simultaneously dropped in Na₂CO₃ solution at controlled temperature and stirring constantly. The obtained solution was aged at 80°C for 2 h. The mixture was then filtered, washed and dried at 100°C and after that, calcined 350°C for 2 h. Experiments were conducted with the influence of factors such as synthesis method, temperature, pH, reactant concentration, stirring speed and heating mode.

Sequential precipitation: In this method, each salt (Zn(NO₃)₂, Al(NO₃)₃) was precipitated one after the other and the others experimental conditions was the same ones of co-precipitation method.

Synthesis of ZnO-Al₂O₃-CuO

The procedure was the same one of co-precipitation described above but with the mixture of three salts Cu(NO₃)₂, Al(NO₃)₃ and Zn(NO₃)₂.

Characterization

The crystalline structure of materials was determined by X-ray diffraction, on the D8 Advance (Bruker) apparatus. The morphological characteristics were determined by Transmission Electron Microscopy (TEM), on the model JEOL-JEM-1010. The specific surface area was measured on BET Micrometrics 2390 Gemini VII (USA).

Absorption test

The sulfur sorption capacity was determined on a device which is a type of continuous micro flow system with a U-shaped absorption tube [10]. The amount of material used in the tube was of 1.5 g, cleaned under N₂ flow for 30 minutes before introduce flow of 5% H₂S/N₂, with flow rate of 70 mL/min at 300°C for 1 h. The sulfur content of the sample sorption after test was determined on the Model CS-MAT 5500 apparatus.

Results and Discussion

Synthesis investigation of materials ZnO-Al₂O₃

Effect of synthetic methods: The FIG. 1a and 1b show the XRD patterns of ZnO-Al₂O₃ synthesized by two methods. In two patterns, it appears clearly diffraction maximum at angles of $2\theta=31.8^\circ$, 34.5° , 36.2° corresponding to the wurzite phase of ZnO and no peak characteristic of the Al₂O₃ crystalline phase was found. This one may be explained by the well dispersed of the aluminum nanocrystal on/in ZnO phase and/or amorphous structure of alumina formed.

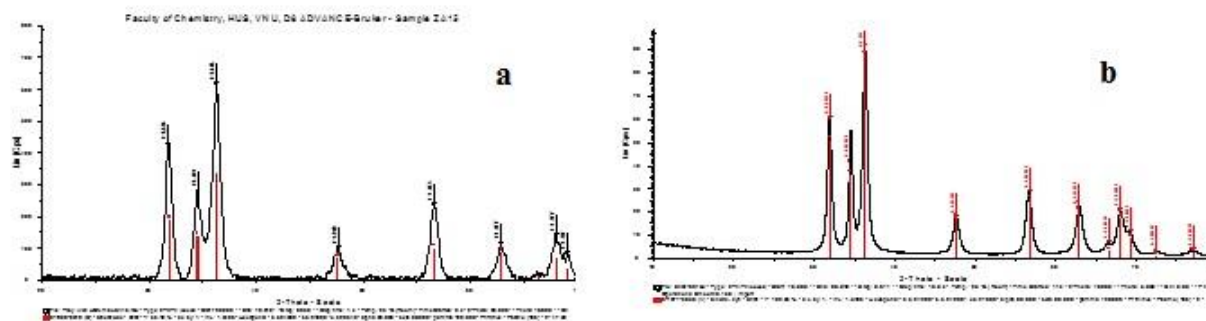


FIG. 1. XRD patterns of ZnO oxides synthesized by (a) Co-precipitation and (b) Sequential precipitation methods.

The specific surface areas determined were of 82.4 and 76.2 m²/g for ZnO prepared by co-precipitation and sequential precipitation method, respectively. The results obtained show that the specific surface area of the ZnO-Al₂O₃ composite material prepared by the first method has nearly the same surface area of the one by the second method. However, TEM images obtained showed that, with the co-precipitation method (FIG. 2a), the aluminum oxide particles were quite homogenously dispersed in the ZnO phase and the aggregation decreased significantly in comparison with the second method (FIG. 2b).

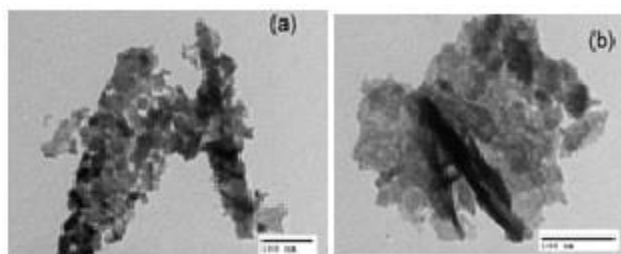


FIG. 2. TEM images of ZnO-Al₂O₃ synthesized by various methods: (a) Co-precipitation, (b) Sequential precipitation.

This can be explained by the fact that, by co-precipitation method, the $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$ [11] and $\text{Al}(\text{OH})_3$ are simultaneously formed, the Al^{3+} ions are homogenously dispersed in the mixture and facilitated substitution of Zn^{2+} ion by Al^{3+} in intermediate hydroxyl carbonates. And after the calcination the ion Al^{3+} was inserted into the octahedral and tetrahedron cavities in the lattice of ZnO due to smaller ionic radius of cation Al^{3+} . As a result, aluminum oxide was better distributed in the ZnO active phase.

On the other hand, the good dispersion of alumina in the sample prevented the agglomeration of ZnO particles. In addition, Co-precipitation method is simpler than sequential precipitation method. Thus, the method of co-precipitation was selected for further studies.

Effect of co-precipitation temperature: The role of co-precipitation temperature on the morphology of obtained composites was examined. The results are shown in TABLE 1. The composite ZnO-Al₂O₃ (7% wt) was denoted in common term CT-ZA-7.

TABLE 1. Dependence of specific surface area (SBET) of the materials versus co-precipitation temperature.

Samples denoted	Reaction temperature (°C)	S _{BET} (m ² /g)
CT-ZA-07-30	30	30.19
CT-ZA-07-50	50	68.2
CT-ZA-07-70	70	83.9
CT-ZA-07-90	90	80.4

The specific surface area of the materials tends to increase, from 30.19 m²/g to 83.9 m²/g when the co-precipitation temperature increases from 30°C to 70°C. From 70°C to 90°C, the specific surface area decreased slightly. Thus, the appropriate co-precipitation temperature is of 70°C to 90°C. At this temperature range, the material obtained has a specific surface area about 80 m²/g.

Effect of pH: To ensure co-precipitation of Zn²⁺ and Al³⁺ ions occurred simultaneously, the lowest pH selected was of 7. The change in specific surface area of the product according to the pH of the reaction medium shown in TABLE 2. During the experiments, solution of Na₂CO₃ was used to adjust the pH from 7 to 11. The results showed that as the pH of the co-precipitation increased from 7 to 11, the specific surface area of the material tended to decrease. Hence, the pH equal 7 was the appropriate value for the co-precipitation reaction.

TABLE 2. Effect of pH on specific surface area.

Samples denoted	pH in reaction medium	S _{BET} (m ² /g)
CT-ZA-07-7.0	7.0	83.9
CT-ZA-07-9	9.0	68.15
CT-ZA-07-11	11.0	55.16

Synthesis of composite ZnO-Al₂O₃-CuO

The composite ZnO-Al₂O₃ (10% wt) was chosen to be modified by CuO. The XRD pattern of ZnO-Al₂O₃-CuO (11, 3% wt) prepared by co-precipitation method is presented in FIG. 3.

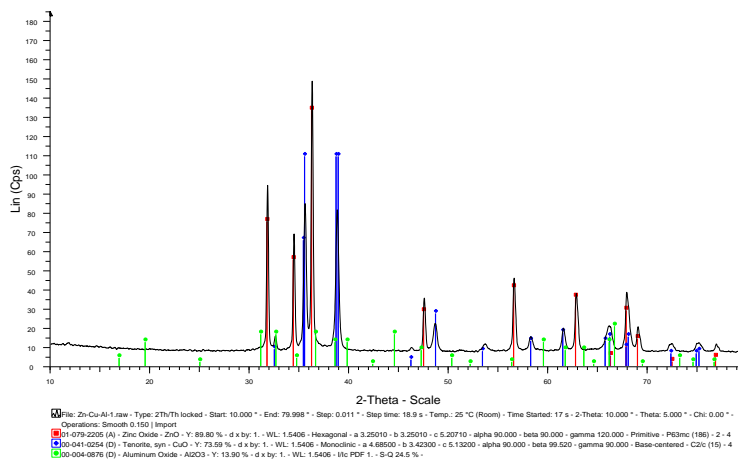


FIG. 3. XRD pattern of ZnO-Al₂O₃-CuO (11.3%).

The XRD pattern of ZnO-Al₂O₃-CuO showed very strong diffraction maximums at angles of 2θ equals 31.8°, 34.4°, 36.3°, which is characteristic of the crystal wurtzite phase of ZnO oxide. In addition, the strong diffraction maximums at angles of $2\theta=35.5^\circ$ correspond to the monoclinic structure of CuO. No diffraction maximums of Al₂O₃ crystal phase was found. This is attributed to the amorphous state of Al₂O₃ in the obtained materials [12].

FIG. 4 shows a TEM image of the 11% CuO-ZnO-Al₂O₃ material sample. The TEM image in FIG. 4 showed that the added phase seems to be well dispersed in ZnO phase. The particles were in spherical form with diameter less than 10 nm. It was obvious that the particles agglomerated in porous palettes.

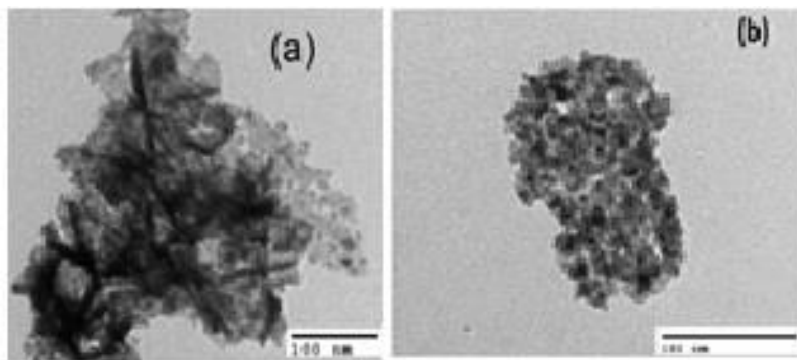


FIG. 4. TEM image of the CuO-ZnO-Al₂O₃ sample.

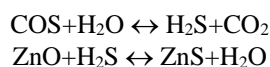
TABLE 3 shows the results of surface area measurements of ZnO-Al₂O₃ modified by CuO using co-precipitation method (denoted as CT-CZA). The results in TABLE 3 show that the specific area surface was not really influenced by added content of CuO and equal from 84.2 m²/g to 85.1 m²/g.

TABLE 3. Specific surface area CuO-ZnO-Al₂O₃ samples vs. content of CuO.

Samples denoted	CuO content (wt%)	S _{BET} , (m ² /g)
CT-CZA-01	4.3	84.2
CT-CZA-03	5.6	84.9
CT-CZA-04	8.2	85.1
CT-CZA-05	11.3	89.4
CT-CZA-06	15.0	89.3
CT-CZA-07	22.5	85.2

Catalytic activity evaluation

COS conversion on material ZnO-Al₂O₃: Incorporation of Al₂O₃ onto ZnO material promotes COS hydrolysis in the presence of H₂O to form H₂S. The resulting H₂S will then be sorbed onto ZnO. This process is described as follows:



The role of Al₂O₃ content on the COS conversion yield was shown in FIG. 3.

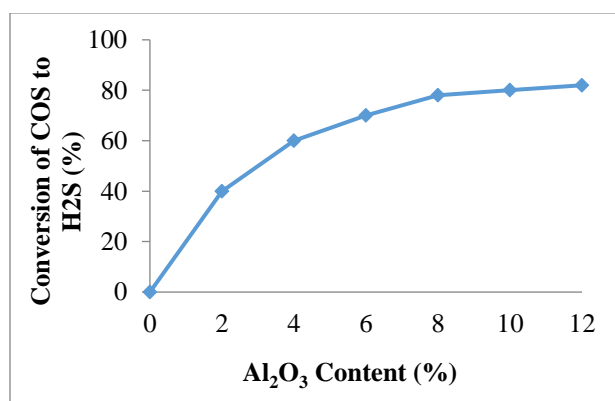


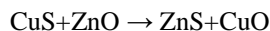
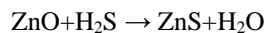
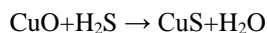
FIG. 4. Effect of Al₂O₃ content on COS conversion.

From the FIG. 5 it is observed that the COS conversion yield increased sharply when content of Al₂O₃ from 2% to 10 wt%. The COS conversion is nearly unchangeable with higher content of Al₂O₃. Hence, Al₂O₃ content of 10% was selected as the best composition.

H₂S sorption test on material ZnO-Al₂O₃-CuO: The role of CuO content on the sulfur treatment efficiency of ZnO-Al₂O₃-CuO was investigated and showed FIG. 6.

The results in FIG. 6 shown that the H₂S sorption capacity of composite ZnO-Al₂O₃-CuO was improved from 20 gS/100 g sorbent to 31% gS/100 g sorbent, corresponding the CuO content from 0% to 11.3 wt%. Higher CuO content of 11.3 wt%,

H₂S sorption capacity was likely unchangeable. According to these result, by more rapid kinetic than one of ZnO, H₂S was firstly adsorbed on CuO active site to form before transferring S to ZnO site. This phenomenon allows a better sulfur sorption of these material. On the hand, it allows a deeper H₂S treatment. This mechanism is described as following:



However, CuS is not stable and decomposed easily in H₂S and CuO, before react with ZnO to form ZnS. Thus, when CuO content increase until a certain content, there is a CuO phase amount in excess which not react with H₂S but not with ZnO.

That explained why CuO content equal 11.3% was the best value to these composites in H₂S treatment.

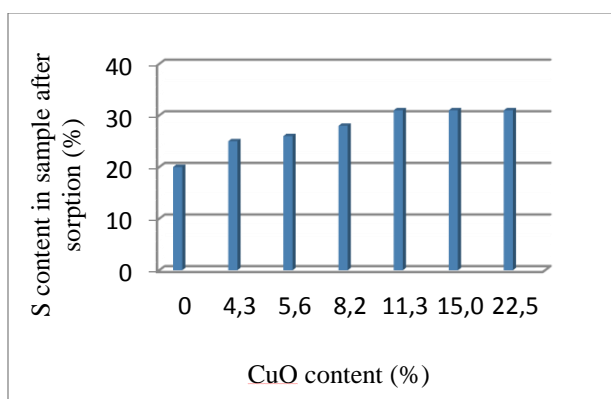


FIG. 5. Effect of CuO content on the sulfur sorption capacity of the material ZnO-Al₂O₃-CuO.

Conclusion

The composites ZnO-Al₂O₃ and ZnO-Al₂O₃-CuO were studied. For the composite ZnO-Al₂O₃, the most appropriate synthetic condition, to obtain the highest specific surface area, was determined as following: co-precipitation method, reaction co-precipitation equal 70°C and pH equal 7. At this condition ZnO-Al₂O₃ material has the highest surface area of 83.9 m²/g. The composite composed from wurzite crystal structure ZnO phase and amorphous to Al₂O₃ as indicated by XRD patterns. In the case of composite materials ZnO-Al₂O₃-CuO. The TEM images showed a good dispersion of CuO and Al₂O₃ on the ZnO phase. The XRD results indicated the presence of monoclinic phase of CuO and wurzite phase of ZnO.

For ZnO-Al₂O₃ composite, the catalytic test showed that the COS conversion was proportional with the content of Al₂O₃ and attain the maximum conversion of 81% at 10% of Al₂O₃ content. The results of the H₂S sorption study on ZnO-Al₂O₃-CuO composite showed that sulfur sorption capacity increased with CuO content and reached an optimum value of 11%, corresponding a sulfur capacity of 31 gS/100 g material. In comparison without CuO, the sulfur sorption onto ZnO-Al₂O₃-CuO 11% composite has increased approximately 150%.

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