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# Synthesis of Composites $ZnO-Al_2O_3$, $ZnO-Al_2O_3-CuO$ and Evaluation of its Activity for COS Conversion, $H_2S$ Sorption Treatment

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## Abstract

**Two $ZnO-Al_2O_3$ and $ZnO-Al_2O_3-CuO$ 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 $Al_2O_3$ in amorphous phase. The optimum specific surface area attains $ZnO-Al_2O_3$ and $ZnO-Al_2O_3-CuO$ was 83.9 and 89.4 $m^2/g$, respectively. The results of COS treatment showed that $ZnO-Al_2O_3$ (10%) presented the highest conversion, reaching 81%. For the capacity of $H_2S$ treatment, $ZnO-Al_2O_3-CuO$ 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:** $H_2S$ removal; COS removal; Zinc oxide; Desulfurization*

## Introduction

Natural gas contains certain amounts of $H_2S$ 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 $H_2SO_4$ as a strong corrosive agent [1]. In addition, for living environments, $H_2S$ has an unpleasant odor and with the exposure to high levels, can give fatal damage to human body [2].

There are a different $H_2S$ 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].

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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 level of sulfur treatment, solid phase sorbents technology has been developed. This method allows the deep treatment of $H_2S$, 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 $H_2S$ [7,8]. However, the 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 $H_2S$ and $H_2S$, which will be absorbed after [9]. To catalyze the hydrolysis of the COS gas, $Al_2O_3$ oxide is known to be a potential catalyst. In the present study, we aim to synthesize the composite ZnO-$Al_2O_3$ and ZnO-$Al_2O_3$-CuO and evaluate its catalytic activity for COS and $H_2S$ treatment.

## Experimental

### Materials and chemical compounds

Chemical compound used has analytical purity (Sigma Aldrich): $Na_2CO_3$ 99%, $Zn(NO_3)_2$. $6H_2O$ 99%, $Cu(NO_3)_2.3H_2O$ 99%, $Al(NO_3)_3$ 99%.

## Catalysts Synthesis

### Synthesis of ZnO-$Al_2O_3$

**Co-precitation method:** The adequate amount of $Zn(NO_3)_2$ and $Al(NO_3)_3$ salts (99%, TQ) dissolved in distilled water and simultaneously dropped in $Na_2CO_3$ 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 ($Zn(NO_3)_2$, $Al(NO_3)_2$) was precipitated one after the other and the others experimental conditions was the same ones of co-precipitation method.

### Synthesis of ZnO-$Al_2O_3$-CuO

The procedure was the same one of co-precipitation descibed above but with the mixture of three salts $Cu(NO_3)_2$, $Al(NO_3)_3$ and Zn $(NO_3)_2$.

### 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 $N_2$ flow for 30 minutes before introduce flow of 5% $H_2S/N_2$, 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 $ZnO-Al_2O_3$

**Effect of synthetic methods:** The FIG. 1a and 1b show the XRD patterns of $ZnO-Al_2O_3$ synthesized by two methods. In two patterns, it appears clearly diffraction maximum at angles of 2θ=31.8°, 34.5°, 36.2° corresponding to the wurzite phase of ZnO and no peak characteristic of the $Al_2O_3$ 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.

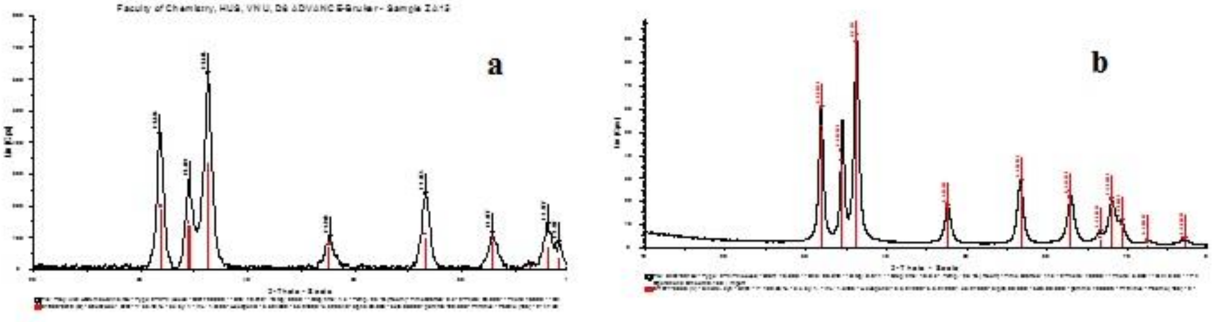

FIG. 1. **XRD patterns of ZnO oxides synthesized by (a) Co-precipitation and (b) Sequential precipitation methods.**

The specific surface areas determined were of 82.4 and 76.2 $m^2/g$ for ZnO prepared by co-precipitation and sequencial precipitation method, respectively. The results obtained show that the specific surface area of the $ZnO-Al_2O_3$ 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).

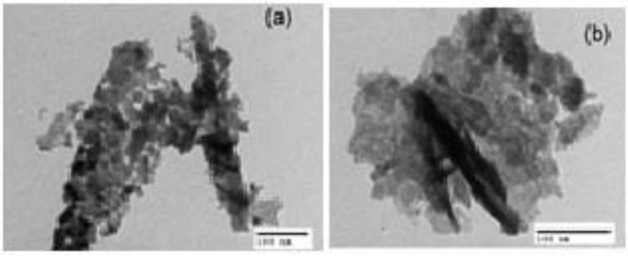

FIG. 2. **TEM images of $ZnO-Al_2O_3$ synthesized by various methods: (a) Co-precipitation, (b) Sequential precipitation.**

This can be explained by the fact that, by co-precipitation method, the $2ZnCO_3.3Zn(OH)_2$ [11] and $Al(OH)_3$ are simultaneously formed, the $Al^{3+}$ ions are homogenously dispersed in the mixture and facilitated substitution of $Zn^{2+}$ ion by $Al^{3+}$ n 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 $ZnO-Al_2O_3$ (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 $m^2/g$ to 83.9 $m^2/g$ 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 $m^2/g$.

**Effect of pH:** To ensure co-precipitation of $Zn^{2+}$ and $Al^{3+}$ 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 $Na_2CO_3$ 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 $ZnO-Al_2O_3-CuO$

The composite $ZnO-Al_2O_3$ (10% wt) was chosen to be modified by CuO. The XRD pattern of $ZnO-Al_2O_3-CuO$ (11, 3% wt) prepared by co-precipitation method is presented in FIG. 3.

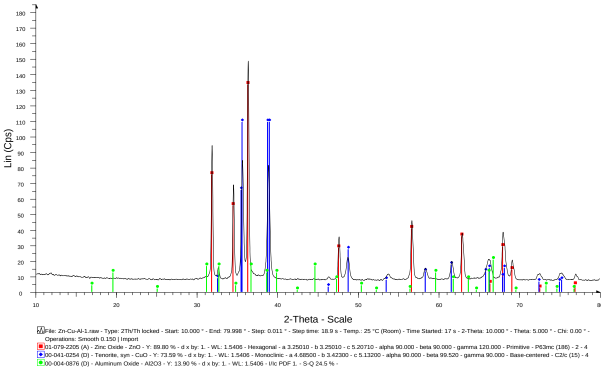

FIG. 3. **XRD pattern of $ZnO-Al_2O_3-CuO$ (11,3%).**

The XRD pattern of $ZnO-Al_2O_3-CuO$ 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 2θ=35.5°C correspond to the monoclinic structure of CuO. No diffraction maximums of $Al_2O_3$ crystal phase was found. This is attributed to the amorphous state of $Al_2O_3$ in the obtained materials [12].

FIG. 4 shows a TEM image of the 11% $CuO-ZnO-Al_2O_3$ 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.

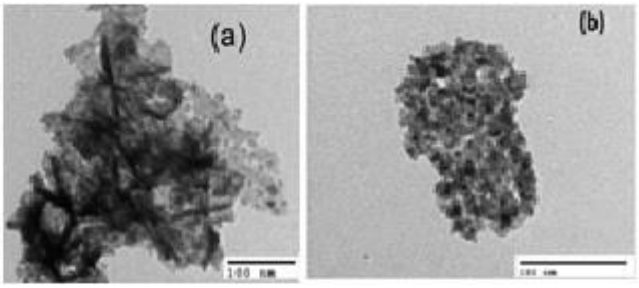

FIG. 4. **TEM image of the $CuO-ZnO-Al_2O_3$ sample.**

TABLE 3 shows the results of surface area measurements of $ZnO-Al_2O_3$ 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 $m^2/g$ to 85.1 $m^2/g$.

TABLE 3. **Specific surface area CuO-ZnO-$Al_2O_3$ 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-$Al_2O_3$:** Incorporation of $Al_2O_3$ onto ZnO material promotes COS hydrolysis in the presence of $H_2O$ to form $H_2S$. The resulting $H_2S$ will then be sorbed onto ZnO. This process is described as follows:

$$COS+H_2O \leftrightarrow H_2S+CO_2$$
$$ZnO+H_2S \leftrightarrow ZnS+H_2O$$

The role of $Al_2O_3$ content on the COS conversion yield was shown in FIG. 3.

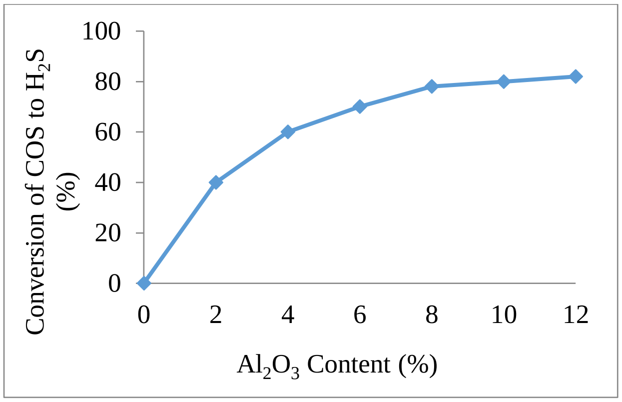

FIG. 5. **Effect of $Al_2O_3$ content on COS conversion.**

From the FIG. 5 it is observed that the COS conversion yield increased sharply when content of $Al_2O_3$ from 2% to 10 wt%. The COS conversion is nearly unchangeable with higher content of $Al_2O_3$. Hence, $Al_2O_3$ content of 10% was selected as the best composition.

**$H_2S$ sorption test on material ZnO-$Al_2O_3$-CuO:** The role of CuO content on the sulfur treatment efficiency of ZnO-$Al_2O_3$-CuO was investigated and showed FIG. 6.

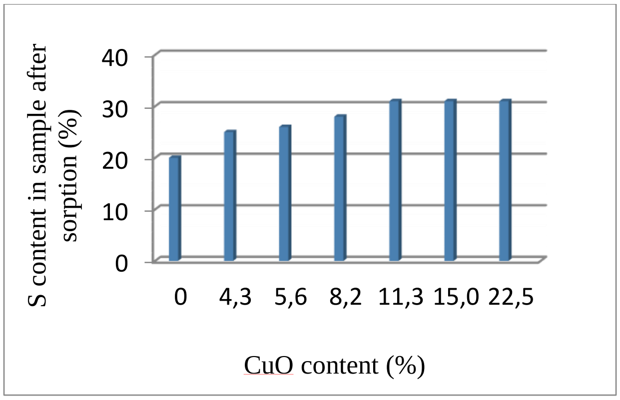

FIG. 6. **Effect of CuO content on the sulfur sorption capacity of the material ZnO-$Al_2O_3$-CuO.**

The results in FIG. 6 shown that the $H_2S$ sorption capacity of composite ZnO-$Al_2O_3$-CuO was improved form 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%, $H_2S$ sorption capacity was likely unchangeable. According to these result, by more rapid kinetic than one of ZnO, $H_2S$ 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 $H_2S$ treatment. This mechanism is described as following:

$$CuO+H_2S \rightarrow CuS+H_2O$$

$$ZnO+H_2S \rightarrow ZnS+H_2O$$

$$CuS+ZnO \rightarrow ZnS+CuO$$

Howerver, CuS is not stable and decomposed easly in $H_2S$ and CuO, before react with ZnO to form ZnS. Thus, when CuO content increase until a certain content, there is a CuO phase amout in excess which not react with $H_2S$ but not with ZnO. That explained why CuO content equal 11.3% was the best value to these composites in $H_2S$ treatment.

## Conclusion

The composites ZnO-$Al_2O_3$ and ZnO-$Al_2O_3$-CuO were studied. For the composite ZnO-$Al_2O_3$, 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-$Al_2O_3$ material has the highest surface area of 83.9 $m^2/g$. The composite composed from wurzite crystal structure ZnO phase and amorphous to $Al_2O_3$ as indicated by XRD patterns. In the case of composite materials ZnO-$Al_2O_3$-CuO. The TEM images showed a good dispersion of CuO and $Al_2O_3$ on the ZnO phase. The XRD results indicated the presence of monoclinic phase of CuO and wurzite phase of ZnO.

For ZnO-$Al_2O_3$ composite, the catalytic test showed that the COS conversion was proportional with the content of $Al_2O_3$ and attain the maximum conversion of 81% at 10% of $Al_2O_3$ content. The results of the $H_2S$ sorption study on ZnO-$Al_2O_3$-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-$Al_2O_3$-CuO 11% composite has increased approximately 150%.

## Acknowledgement

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