INTRODUCTION

1. The necessery of the reseach subject.

Natural gas and petroleum gas, in addition to fuel, are important raw materials for the synthesis of high economic value products (such as methanol, acetylene, etc.). However, natural gas consist of a certain amount of sulfur compounds (H_2S , COS, CS_2 , ...). The sulfur impurities, especially H_2S , are present in the exhaust gases from biodegradable waste streams of the ethanol plant. These are unwanted impurities that cause catalytic poisoning with petrochemical processes, corrosion in technological equipment, etc., and lead serious economic consequences, damage living environment.

There have been many sour gas treatment technologies to meet to the practical needs of sulfur impurities treatment: (i) chemical absorption, (ii) physical absorption, (iii) physical and chemical absorption. These methods have their strengths and weaknesses. However, these technologies only decrease sulfur content up to 100ppm. In order to ensure a deeper level of sulfur treatment, the solid phase chemical absorption technique, with its mainly absorbent ZnO, allow to lower the sulfur content to about 1 ppm, even lower. This is also the research direction of the thesis.

2. Purpuse and contents of the thesis

From the above analysis, the thesis will study to produce absorbent materials based on ZnO oxide, which is capable of deep treatement of H₂S and COS gas at low temperature (\leq 350°C). Therfore, the synthetic adsorbents have to be show a large, high porous surface area, which is nano-structured to enhance their sulfur sorption capacity. In addition, in order to be able to treat H₂S to extremely low concentration, the metal oxides catalysts capable of catalyzing the zinc oxide sulphide reaction, such as CuO, Fe₂O₃, Al₂O₃, will be added in ZnO oxide. For a purpuse of industrial applications, ZnO-based adsorbents will be impregnated on monolithic ceramics and will be evaluated the absorption capacity as well as the stability of materials.

3. The scientific and practical significance of the thesis

The thesis has systematically studied the synthesis of different morphologies of ZnO nanomaterials such as: nanoparticles, nanoflower, nanotube. Based on that, the ZnO oxide was modified by two ways to enhance the sorption capacity: to create a more porous surface of ZnO oxide with nanoflower ZnO impregneted on surface of the micro ZnO oxide, to modifie micro ZnO with CuO, Fe_2O_3 and Al_2O_3 . The results show the successful synthesis of nanostructure micro ZnO as

wel as new compossites $ZnO-\gamma-Al_2O_3$ and $CuO-Fe_2O_3-ZnO$. The sulfur sorption capacity of these materials was significantly improved.

In addition, the thesis has carried out the impregnation of new active phase above on monolithic ceramic wall coated by aluminum oxide, using bohemite suspension. The active composite layer obtained has quite regular thikness and good mechanical strength. In particular, the such active monolith system enable to treat the H_2S gas flow to very low H_2S content, about 0.1-0.2 ppm. This result opens up the possibility of using activated monoliths to treat H_2S gas streams in practice.

4. Summary of new thesis results

- Have systematically studied the synthesis of nanoflower and nanotubes ZnO. From this results, the synthesis of hierarchical morphology of nano/micro ZnO has been studied from micro ZnO. The results showed that the surface porosity of the ZnO was improved and that the sulfur sorption capacity increased to 28.8%.

- Has been studied the modification of ZnO by Al_2O_3 , CuO and Fe_2O_3 . The results showed that the sulfur sorption capacity increased to 31% at 300°C (for material 11.51% CuO-9.79% Al_2O_3 -78.65% ZnO) and reached 17.36% in weight at normal temperature (for material 3.9% CuO-4% Fe_2O_3 -7% ZnOnano/ZnOmicro).

- Have systematically studied the impregnation of active phases ZNO/ γ -Al₂O₃ and CuO-Fe₂O₃-ZnO/ γ -Al₂O₃ on monolithic honeycomb structure was. The results indicated that the impregnation method used aluminum suspension produced an active phase which coated well on the monolithic honeycomb wall. The obtained phase showed a good mechanical strength, good adhesion and high stability. The monolithic composite obtained enable to reduces the H₂S content in the treatment flow gas to the range 0.1 - 0.2 ppm.

5. Structure of the thesis

The thesis consists of 140 pages and is structured as following: Introduction in 03 pages; Chapter 1-Review in 41 pages; Chapter 2 - Experiment in 18 pages; Chapter 3 - Results and discussion in 63 pages; Conclusion in 02 pages; Reference in 12 pages; List of published articles related to thesis content in 01 page; There are 25 tables and 46 figures, graphs.

CHAPTER 1: LITERATURE REVIEW

1.1. H₂S, COS gas treatment technology in natural gas, petroleum gas and ethanol plant gas emissions

In natural gas and in petroleum gas or in alcohol plant gas there is always presence of H_2S and COS. These compounds, especially acidic H_2S gas, can form corrosion of equipment that causes cracks, poisoning of catalyst, and pollution of the environment. There are many technologies that have been developed such as Sulfurex, Ecarsol, etc. These technologies are essentially to use physical and chemical adsorption substances that allow to treat H_2S content in gas flow to about 100ppm. In order to ensure a deeper level of sulfur treatment, the solid phase chemical-based absorption technology has been developed using ZnO oxide, which has been being studied for its ability to treat H_2S to a level of 1 ppm.

1.2. H₂S, COS treatment researches based on solid ZnO absorbent

Solid sorbent researches focus primarily on the modification of ZnO phase or optimal dispersion of these phases on supports. On the first way, the ZnO is modified by different oxides such as CuO, Fe_2O_3 , MnO_x ... to enhance sulfur sorption capacity. These oxides play an important role in enhancing sorption kinetic or stability of the materials. On the second way, ZnO or ZnO modified was supported on large surface area materials such as SiO₂, SBA-15, zeolite, or monolith honeycomb ceramics in practical applications purpose ... Due to the large surface area, these supports allow maximum dispersion of the active phase, enhancing the number of active sites and thus sorption capacity.

1.3. Orientation of research content of thesis

Based on the review above, the thesis aims to study the "modification" of ZnO: morphological modification and ZnO phase modification by other metal oxides (CuO, Fe₂O₃, Al₂O₃). Then, on the orientation of application research, modified materials will be impregnated onto the monolith honeycomb ceramic. Obtained materials will be evaluated for H_2S processing treatment.

CHAPTER 2: EXPRIMENTS

2.1. Synthesis investigation of sorbents based on ZnO for removal of H_2S and COS.

2.1.1. Synthesis of nano ZnO

Nanostructured ZnO oxide (nanoparticle, nanoflower, nanotube) were synthesized by precipitation and hydrothermal precipitation. Influence of

differents parameters on the synthesis such as zinc salt precursor, concentration, temperature, pH, reaction time and temperature were examined systematically.

2.1.2. Synthesis of modified ZnO materials

 ZnO/Al_2O_3 materials were synthesized by impregnation and coprecipitation. Differents parameter such as concentration, pH and calcination conditions were investigated. The materials ZnO/Al_2O_3 modified by CuO, Fe₂O₃ was synthesized by precipitation of metal ions from salt or by Fe²⁺, Cu²⁺ ions in nano-micro ZnO suspension and calcined futher.

2.1.3. Coating active phase on monolithe

The active phases are coated onto a monolithic support by impregnation method using aluminium hydroxyde sol and/or aluminum bohemite suspension. The monolith used in the studies was the commercial honeycomb monolith.

2.2. Physico-chemical characterization methods

The materials have been characterized to structural properties by D8 Advance-Brucker (D8 Advance-Brucker), Differential Thermal (Diamond TG/DTA Perkin Elmer) and to morphological properties by Scaning Electron Microscopy (Microscope S-4800) and Transmission electron microscope (Philips Tecnai 10 microscope).

2.3. Evaluation of sorption capacity of materials

Sorbtion experimences were carried out in micro-pilot systems.

CHAPTER 3: RESULTS AND DISCUSSION

3.1. Investigation of synthesis of nanosized ZnO

3.1.1. Investigation of synthesis of nanosized ZnO from zinc salts as precursor

3.1.1.1. Effect of synthesis methods



Figure 3.1: XRD parttens of ZnO prepared by precipitation (a) and hydrothermal method (b)

Figure 3.1 shows the XRD parttens of ZnO oxides were synthesized by precipitation and hydrothermal method. Results showed the wurtzite phase of ZnO. The low intensity of background showed that the product has a high crystallinity. The specific surface area of ZnO obtained was $S_{BET} = 25.6 \text{ m}^2/\text{g}$ with precipitation and $S_{BET} = 71.9 \text{ m}^2/\text{g}$ with hydrothermal method. Thus hydrothermal methods have been selected in futher studies for the synthesis of materials with higher surface area.

3.1.1.2. Examination of the role of raw materials

The XRD parttens of the ZnO samples synthesized from two salts sources, $Zn (NO_3)_2$ and $ZnCl_2$, are respectively shown in Figure 3.2.



Figure 3.2. The XRD parttens of ZnO synthesized from $ZnNO_3$ (a) and $ZnCl_2$ (b).

The results in Figure 3.2 show that two samples of ZnO synthesized from two different salts have the same XRD patterns, with only of presence of ZnO wurzite phase, the low spectral background indicates that the product obtained is highly crystalline. The S_{BET} of the two samples was 71.9m²/g and 72.4 m²/g, respectively.

3.1.1.3. Effect of temperature

The effect of reaction temperature on the specific surface area of the ZnO samples is given in Table 3.1.

Table 3.1. Effect	of temperature on th	e
specific surface	area of the materials	

Samples name	Reaction temperature (°C)	S _{BET} (m²/g)
PNB-50	50	44,67
PNB-60	60	53,8

The results showed that when the temperature increased from 50 - 80° C, the specific surface area increased with increasing temperature and reached the value of approximately 70 m²/g at hydrothermal temperature of 80° C.

PNB-70	70	60,01
PNB-80	80	69,87
PNB-90	90	60,92

When the temperature rised to 90°C, the specific surface area tend to decrease. Thus, the appropriate temperature of the reaction is 80°C.

3.1.1.4. Effects of pH

The change in specific surface area of ZnO by the pH of the reaction medium is shown in Table 3.2. Na_2CO_3 was used to adjust pH.

Table 3.2. Effect of pH on specific				
	surface area			
Samples pH S _{BET,}				
name	P	(m ² / g)		
PNB - 7	7,0	71,9		
PNB - 7.5	7,5	69,7		
PNB - 8.5	8,5	61,0		
PNB - 11	11,0	42,8		

The results showed that in the pH range from 7 to 11, the higher the pH, the lower the specific surface area. This can be explained by the formation of the intermediate products $ZnCO_3$, $Zn(OH)_2$ (at reaction pH = 7). So pH = 7 is the appropriate value for the reaction

3.1.1.5. Effect of reagents concentration

The results of investigating the effect of $Zn(NO_3)_2$ precursor concentration on the specific surface area are presented in Table 3.3.

 Table 3.3. Effect of reagent concentration on

 specific surface area

specific surface area				
Samples $[Na_2CO_3]$ (mol/L) $[Zn(NO_3)_2]$ (mol/L) S_{BET} (m²/g				
PNB-M0.1	0,1	0,1	72,9	
PNB-	0,25	0,25	71,9	
M0.25	,	,	1	
PNB-M0.5	0,5	0,5	56,0	
PNB-M1.0	1,0	1,0	47,3	

It can be seen that when the precursor concentration increases, the surface area of the sample decreases. This may be due to an increase in the concentration of the solution, which increases the growth of the germ leading to the formation of large crystals, which, in turn, leads to a lowring the specific surface area of the materials.

3.1.1.6. Effect of stirring speed

Table 3.4. Influences the stirringspeed to specific surface area of the

products		
	Stirring	S
Samples	speed	S_{BET}
	(round/min)	(m /g)

The results in Table 3.4 show that, as the rate of agitation increases, the surface area decreases. This is explained by the fact that increasing the agitating speed can increase the crystal growth that causes the reduced surface area of the

NTH-100	100	71,9
NTH-200	200	50,3
NTH-300	300	48,5

product. Therefore, the appropriate stirring speed of ZnO synthesis under the conditions described is 100 rpm.

3.1.1.7. Effects of calcination condition

Intermediate precipitated samples, $2ZnCO_3.3Zn(OH)_2$, was analyzed by thermal analysis (TG/DTA). The results (not presented here) show that $2ZnCO_3.3Zn(OH)_2$ decomposition occured about $150^{\circ}C-250^{\circ}C$ and there is no significant mass change after $250^{\circ}C$.

From the above results, the following conditions were selected for the synthesis of nanoparticles ZnO: hydrothermal method, solution $Zn(NO_3)_2 0,25M$; Thermal temperature 80°C; stirring speed 100 rpm; calcination temperature at 300°C for 1.5 hours.

The SEM and TEM images of the synthetic ZnO samples are shown in Figure 3.3



Figure 3.3. Photo SEM (a, b) and TEM (c) of the ZnO samples

The above SEM and TEM image results show that the ZnO crystals obtained are shaped like flowers (nanoflowers) with sheets of petals formed by the aggregation of 10-20 nm nanoparticles. The thickness of each petal is about 10 - 20 nm. Each flower is 1 - 2μ m in size.

3.1.2. Research on synthesis of nanosized ZnO material from ZnO oxide 3.1.2.1. Investigate of the effect of the source material

Two sources of zinc oxide used for the synthesis of ZnO of Sigma – were Aldrich and China origin. The shape and size characteristics of ZnO synthesized from two sources are evaluated by SEM and TEM images (not shown here). Results showed that the ZnO nanoparticles produced from two sources of material were not different in size and were very small, approximately 10 nm in diameter. These particles combine to form large aggromerat of several hundred nm.

3.1.2.2. Effect of temperature

TEMs of samples were synthesized at hydrothermal temperatures of 25°C, 50-60°C and 80-90°C, respectively, as shown in Figure 3.4 (a, b, c).



Figure 3.4. TEM images of synthetic nano ZnO at temperatures of 25°C, (b) 50-60°C, (c) 80-90°C

Observation of TEM images of samples showed that when the hydrothermal temperature increased from 25° C to $80-90^{\circ}$ C, the particle size tended to drop sharply from 100 nm to 10 nm and there was no grain of material. Thus, $80-90^{\circ}$ C is the suitable hydrothermal temperature for the synthesis of nanoparticle ZnO. **3.1.2.3. Effcet of pH**

Figure 3.5 shows the TEM image of ZnO synthesized at pH = 6 and pH = 8. These TEM images shows that as the pH increases, the size of the ZnO

tends

Therefore, the appropriate nano-ZnO

synthesis medium is a weak acid

environment with pH = 6.

to

increase.



Figure 3.5. TEM images of ZnO nano at different pH values: (a, b) pH = 6, (c, d) pH = 8

3.1.2.4. Investigate the effect of rate of reactants

The shape and size of the ZnO samples at the differents ratio of ZnO/volume of H_2O_2 30% (0.5/50, 1/50 and 5/50) are shown in Figure 3.6.

nanoparticle



Figure 3.6. TEM images of ZnO with differents ZnO/H_2O_2 ratio: (b) 0.5g ZnO /50ml H_2O_2 , (d) 1.0g ZnO/50ml H_2O_2 , (f) 1.0g ZnO/50ml H_2O_2 .

The results show that the smaller the ZnO/H_2O_2 ratio, the smaller the ZnO grain size. However, if this ratio is reduced too small, the aggregate efficiency decreases. Therefore, the appropriate ratio to ZnO nanoparticle synthesis is 1 g ZnO/50 ml of solution H_2O_2 20%.

3.1.2.5. Investigate the effect of stirring speed

Figures. 3.7 (a, b, c, d, e, g) prensented TEM images of ZnO samples obtained by synthesis at different agitation speeds (100, 400 and 700 rpm).



Figure 3.7. TEM images of ZnO nanoparticles at different agitation speeds: (b) 100, (d) 400, (g) 700 rpm

TEM images Figure 3.7 shows that at low stirring speeds the ZnO nanoparticles produce small (<10 nm) and tend to accumulate. As the speed increases from 400 rpm to 700 rpm the particle size increases not so much, but the agglomeration of the formed particles was greatly reduced. Thus, the agitation speed suitable for the synthesis is ~ 400 rpm.

3.1.2.6. Effect of synthesis methods



Figure 3.8. TEM images of ZnO nanotubes in acidic (a) and alkaline solution (b).

Figure 3.8 shows the TEM images synthesized of ZnO bv hydrothermal method (180°C for 24 the hours): in acidic environment, ZnO nanotube was observed (h.3.8a), whereas ZnO nanoparticle in the basic medium (h.3.8 B). These preliminary results are fundamentally meaningful of the thesis.

3.1.2.7. Examination of calcination condition

Suitable calcination conditions for the sample were determined by thermal analysis gravimetric methods and XRD. The results are shown in Figure 3.9.



Figure 3.9. TG-DTA cuvre of ZnO nanoparticles before calcination (a) and XRD partten of ZnO after calcination (b)

The TG-DTA cuvre showed that (Fig.3.9a): The first weight decreases correspond to physical dehydration (200°C), followed by chemical dehydration (18% reduction of weight) at 200-250°C and the from 300°C, the sample weight was almost unchanged. Thus, the following conditions can be selected: calcination at 300°C for 2 hours at 1°C/min. Figure 3.9b shows the XRD partten of the ZnO sample after calcination at 300°C. The result indicated a wurtzite-phase crystalline of ZnO, with sharp peaks that showed the relatively high crystallinity of the sample.

3.2. Studying on synthesis of ZnOnanoflower/ZnOmicro (denoted ZnO nano/ZnOmicro)

ZnOnano/ZnOmicro materials were synthesized by impregnation of ZnOnano on a commercially available ZnOmicro surface to combine the nanostructures (high sulfur sorption capacity) and micro (low cost, durable) of tow materials. The sulfur sorbtion capacity of obtained materials was shown in table 3.5:

Table	3.5.	Ef	ffects	of	ZnO
nanopa	rticles	on	maxii	num	sulfur
sorption	ı capac	ity			

ZnO nano content (% wt)	Maximum Sulfur sorption capacity (% S)
ZnO micro	28,8
(commercial)	
Industrial sample	38,2
1 (in-situ)	29,7
5 (in-situ)	39,8
10 (in-situ)	45,1

The results in Table 3.5 show an interesting synergistic effect between the two ZnO phase with different nano-microstructure for the sorption of H₂S: when the ZnO nanoflower content increase (corresponding to the number times "in-situ"), sorption capacity of the material increased from 28.8% to 45.1% wt (\approx 1.5 times higher) and higher than the commercial sample of approximately 7%. The sample of 5% ZnO nanoflower in the nano/ZnO micro sample gives the

100	51,5
(ZnO nanoflower	
synthesized)	
5 (mechanical	35,0
mixture)	

same sorption capacity as the refree sample, which should be selected for larger scale of material synthesis.

3.3. Study on synthesis of ZnO/Al₂O₃ material 3.3.1. Effects of synthesis methods

The ZnO/Al_2O_3 material was synthesized by two methods: co-precipitation of metal ions (denoted CT-ZA-05) and precipitation of two precursors separately and folling by mixture, agitation them together (denoted CT-ZA-06). Figure 3.10 shows the XRD parttens of the two composite samples prepared by two methods.



Figure 3.10. XRD parttens of ZnO synthesized by co-precipitation (a) and individual precipitation (b).

The results in Figure 3.10 show that ZnO/Al_2O_3 synthesized by both methods has a similar XRD pattern: only the presence of wurzite phase ZnO and no peak characteristic for crystalline phase Al_2O_3 . It is possibly that aluminum oxide exists in amorphous form.

The surface area of the samples of CT-ZA-05, CT-ZA-06 are 82.4 m^2/g and 76.2 m^2/g , respectively. Thus, There is only feu difference in material surface area prepared by two methods.

Figure 3.11 shows the TEM image of the composite material prepared by two methods.



(b) The results show that, with the coprecipitation method (3.11a), Al_2O_3 nanoparticle were equally dispersed in the ZnO active phase, and the aggregation was significantly reduced in comparison with the

Figure 3.11. TEM images of ZnO / second method (h. 3.11b). Thus, the Al₂O₃ synthesized by different simpler precipitation method of

methods: (a) co-precipitation, (b) ion metal ions was selected for further separated precipitation. studies.

3.3.2. Effect of temperature

To investigate the effects of temperature on the product, the precipitation of metal ions was performed at different temperatures: 30°C, 50°C, 70°C and 90°C. Results are sho wn in Table 3.6.

Table 3.6. Dependence of specific surface area (S_{BET}) of the materials on the reaction temperature.

Samples	Reaction temperature (°C)	S _{BET} (m ² /g)
CT-ZA-04-30	30	30,19
CT-ZA-04-50	50	68,2
CT-ZA-04-70	70	83,9
CT-ZA-04-90	90	80,4

3.3.3. Effect of pH

Table 3.7. Influence of pH onspecific surface area

Samples	pH values	S _{BET,} m²/g
CT-ZA-	7,0	83,9
07-7.0		
CT-ZA-	9,0	68,15
07-9		
CT-ZA-	11,0	55,16
07-11		

3.3.4. Effect of Al₂O₃ content

The addition of Al_2O_3 on ZnO material promotes COS hydrolysis to form H_2S following the reaction: $COS + H_2O \leftrightarrow H_2S + CO_2$. H_2S formed then reacted with ZnO. Figure 3.12 shows the results of COS conversion of the material versus Al_2O_3 content. It can be seen that the appropriate content of Al_2O_3 to make a high COS conversion is about 10% (kl). Results of the sorption of H_2S of the

The specific surface area of the material tends to increase, from 30.19 to 83.9 m²/g when the temperature increases reaction from 30°C to 70°C. Above 90°C, specific the surface of area samples does not increase but tends to decrease slightly. Thus, the appropriate temperature of the reaction is about 70-90°C. At this temperature range, the material obtained has a specific surface area higher than 80 m^2/g .

To ensure co-precipitation of Zn^{2+} and Al^{3+} ions simultaneously, the lowest pH selected for the studies was 7 (Table 3.7). The results show that when the pH of the co-precipitation increases from 7 to 11, the specific surface area of the material tends to decrease. This can be explained in the same way as the ZnO synthesis described above. Thus, pH = 7 is suitable value for the precipitation reaction.

material showed that the maximum sorption capacity of the material reached 45.2% S.



3.3.5. Effects of calcination conditions

The thermal analysis cuvre of the sample before calcination is shown in Figure 3.13. The results showed that when the temperature was raised above 350° C, the sample mass is nearly unchangable. So the suitable calcination temperature is 350° C.

3.4. Studies of synthesis of ZnO/Al₂O₃ modified by CuO and Fe₂O₃ **3.4.1.** Investigation of synthesis of ZnO-CuO/Al₂O₃ materials **3.4.1.1.** Effect of CuO content

The structural characteristic of the ZnO/Al_2O_3 added CuO, by coprecipitation method, is given in Figure 3.14.



Figure 3.14. The XRD partten of ZnO/Al₂O₃ modified by CuO (11.3%)

The XRD partten of the ZnO/Al₂O₃ material modified by CuO show only the ZnO crystalline wurtzite phase. In addition, the peak with strong intensitie at angles of $2\theta = 35.5^{\circ}$ correspond to the monoclinic structure of CuO. No peak was found that characterizes the presence of the Al₂O₃ crystal phase. This is attributed to the amorphous state of Al₂O₃ in the material obtained

The results in Table 3.8 show that $CuO-ZnO/Al_2O_3$ modified have a large surface area and its specific surface area are not significantly changed with CuO content added.

Table 3.8.	Specific	surface	area	of
ZnO/Al ₂ O	samples	CuO mo	odifie	d.

Samples	CuO	S _{BET}
	(% wt)	(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



Figure 3.15. Effect of CuO/ZnO ratio on the sulfur sorption capacity of the material ZnO/Al_2O .

The role of CuO content on sulfur treatment efficiency are shown in Figure 3.15. The above results showed that when CuO was added, the H_2S sorption capacity of the sample increased significantly, from 20% to 24%, and reached the maximum level when the CuO content was about 10-12% (11.3 %, as calculated).



Figure 3.16. TEM image of the CuO-ZnO/Al₂O₃ sample.

Figure 3.16 shows a TEM image of the sample CuO-ZnO/Al₂O₃ with 11.3% CuO content as calculated. The TEM image in Figure 3.16 shows that the added phase CuO are dispersed evently in the main active phase ZnO and not clustered together. The sample consists of spherical nanoparticles ZnO, which are less than 10 nm in size, bundled together into thin, porous plates.

The elemental analysis by AAS (table 3.9) showed that the sample had 11.51% CuO, 9.79% Al₂O₃, 78.65% ZnO in weight. This result is consistent with theoretical calculations.

Table 5.7. Composition of ZhO/Al ₂ O ₃ mounicu			
Composition	CuO	ZnO	Al_2O_3
Content calculated, %	11,3	78,7	10
Real content, %	11,51	78,65	9,79

 Table 3.9. Composition of ZnO/Al₂O₃ modified

Thus, it can be seen that co-precipitation of metal ions takes place quite completly without loss of elemental components.

3.4.1.2. Investigation of effect of synthesis method for material modified

Two synthesis methods were carried out: co-precipitation of metal ions and multi-precipitation (co-precipitation of Cu^{2+} , Zn^{2+} ions and separeted precipitation of Al^{3+} ion, and following an aging). The specific surface area of the precipitation samples were given in Table 3.10.

Samples		Synthesis methods	S _{BET} (m ² /g)
No prensence of CuO	ZnO/Al ₂ O ₃	Precipitation - aging 3h - filtration- drying- calcination	83,9
	CT- CZA-05	Precipitation - aging 3h - filtration- drying- calcination	89,4
	CT- CZA-08	Precipitation - aging 0h - filtration- drying- calcination	54,7
	CT- CZA-09	Precipitation - aging 1h - filtration- drying- calcination	62,5
	CT- CZA-10	Precipitation - aging 2h - filtration- drying- calcination	71,4
Modified by	CT- CZA-11	Precipitation - aging 4h - filtration- drying- calcination	92,1
CuO	CT- CZA-12	Precipitation - mixture of cacbonat - aging 1h – filtration - drying- calcination.	68,1
	CT- CZA-13	Precipitation - mixture of cacbonat - aging 2h - filtration- drying- calcination.	83,8
	CT- CZA-14	Precipitation - mixture of cacbonat - aging 3h - filtration- drying- calcination.	99,4

Table 3.10. Effect of synthesis method on S_{BET}

The results presented in Table 3.10. It is obvious that, by modification using precipitation method, the aging time increased from 0h - 2h, the specific surface area increased from 54.7 to 71.4 m²/g, and reaches over 89 m²/g with aging time of 3h. After 3 hours, the specific surface area raised not significantly. Hence, the appropriate aging time is 3h.

Samples prepared by the second method also had their own surface area improved as the aging time increased. However, in terms of how the material is synthesized, the precipitation method is simpler than the multi-step deposition method.

3.4.2. Studies of synthesis of ZnO-Fe₂O₃/Al₂O₃ material 3.4.2.1. Synthesis of Fe₂O₃-ZnO nano/ZnOmicro



Figure 3.17. XRD partten of material micro-nano ZnO modified by Fe₂O₃

The crystalline structure of Fe₂O₃ nanoparticles ZnO (FZnano/ZnOTM) is shown in Figure 3.17. (ZnOTM is ZnO micro comercial). Figure 3.17 shows the microstructure of the composite adsorbent material on Fe₂O₃-ZnO nanoparticles.



Figure 3.18. SEM image of materials based on Fe_2O_3 and ZnO nanoparticles with different Fe_2O_3 nano/ZnO nano/ZnO ratio (%): (a) 1/14/85; (B) 4/11/85; (C) 8/7/85.

The SEM image (fig.18) showed that for ZnOnano/ZnOTM samples, ZnOnano were not dispersed on ZnOTM surface but formed into thin, isolated porous panels; for the sample 1% $Fe_2O_3nano/ZnOnano/ZnOTM$, apart from isolated clumps, a small amount of nanoparticles were dispersed on the surface of the ZnOTM, indicating the adhesion improvement of the ZnO nanoparticles in the presence of Fe_2O_3nano . In case of iron content of 4% and 8%, the nanoparticles tend to shrink into sheets or into flower form.

Table 3.11. Specific surface area (S_{BET}) and maximum absorbed capacity of the material

Materials	Ratio F/Z/ZnOTM (%)	S _{BET} (m²/g)
ZnO commercial	-	9,8

The specific surface area and the maximum sulfur sorbetion capacity of the samples are presented in Table 3.11. The results in Table 3.11 show that the incorporation of iron and zinc oxide nanocomposites with

(ZnOTM)		
Micro-nano ZnO	0/15/85	13,2
	1/14/85	16,0
FZ-nano/ZnOTM	4/11/85	15,4
	8/7/85	15,3

different mass ratios on the ZnO commercial surface did not significantly improve the specific surface area of the ZnO commercial material.

3.4.2.2. Research of synthesis of Fe $_2O_3/ZnO$ nano-micro material modified by Al_2O_3 and CuO.

A) Research of the choice of suitable modifiers

The results in Fig. 3.19 (SEM image) show that, when modified by CuO and γ -Al₂O₃, the nanoparticles oxides disperse relatively evenly on commercial ZnO surface particles. In addition, the sample modified by Al₂O₃ indicated the presence of small amounts of thin, porous, stand-alone plates, which is attributed to the aggregation of Al, Zn and Fe nanooxides.



Figure 3.19. SEM images of the sorbents based on Fe_2O_3 and ZnO micronano modified by (a, b) CuO; (C, d) γ -Al₂O₃.

The analysis of the specific surface area of modified samples (Table 3.16) shows that specific surface area of samples modified by γ -Al₂O₃ raised, while the ones by CuO was unchangable.

Table 3.12. Effect of added oxides on specific area of materials based on Fe₂O₃-ZnO micro-nano composite.

Nº	Samples	S_{BET} (m^2/g)
1	Origin sample	15
2	Sample modified	18
	by 4% CuO	
3	Sample modified	46
	by 4% γ-Al ₂ O ₃	



Figure 3.20. Effect of the added oxides on H_2S sorption capacity of the material, with sorption time of 2h.

Results of H₂S sorption (sorption time 2h) capacity of thesse samples are shown in Figure 3.20. The results showed that the addition of CuO made increase the sorption capacity by 2%, while the one of γ -Al₂O₃ reduced slightly the sorption capacity. Thus, the nature of the added oxide rather than the specific surface area of sample determined the H₂S sorption capacity. Therefore, the CuO oxide was chosen as the added compound for Fe₂O₃/ZnO nano-micro material for further studies.

b. Effect of the added oxides content



Figure 3.21. Influence of CuO content on H_2S sorption capacity of Fe_2O_3 -ZnOnano-micro material.

c. Effect of the synthesis method for samples modified by CuO



Figure 3.22. Comparison of the maximum absorbed capacity of the two denaturation methods by impregnation and coprecipitation

The effect of CuO content on the maximum sulfur sorption capacity of ZnOnano/micro material modified by Fe₂O₃ and CuO (CFZnano/micro) was shown in Figure 3.21. The results showed that when the CuO content increase from 1% to 4% wt, the sulfur maximum sorption capacity of material tended to increase and reach maximum (17.5g S/ 100g of material) at 4% CuO. Thus, the appropriate added CuO content was chosen as 4% wt.

two The different synthesis methods have been investigated: co-precipitation of metal hydroxy ZnOmicro on and salt impregnation on ZnO micro. The effect of added oxides on the sulfur sorption capacity is shown in Figure 3.22. The graph shows that, with different CuO content, prepared the material by impregnation method has a lower sorption capacity than that one by co-precipitation.

Thus, the co-precipitation method is still more effective than on of impregnation for modification of Fe_2O_3 ZnO/nano-micro material in the purposes

of low-temperature H₂S sorption.

3.4.2.3. Characterization and H_2S treatment capacity of CuO-Fe₂O₃-ZnOnano/ZnO micro



Figure 3.23: XRD patterns of differents materials:

a- ZnO micro; b- 15%ZnOnano/85% ZnO micro; c- (4% Fe₂O₃+11% ZnO)nano/85% ZnO micro; d- (4%CuO+4%Fe₂O₃+7%ZnO)nano/85%ZnO micro

The crystalline structure of the sorption materials based on the metal oxide composite is shown in Figure 3.23. The results showed that the samples of micro ZnO and nano-micro composite samples had the same XRD pattern with the wurzit phase structure (JCPDS Card No. 36-1451). In addition, low spectral background high purity showed obtained.

The microstructure characteristic of the materials evidenced by TEM images is shown in Figure 3.24.



Figure 3.24. SEM images of differents materials: a- ZnO micro; b- 15% ZnO nano/85% ZnO micro; c- (4% Fe₂O₃+11% ZnO)nano/85% ZnO micro; d- (4%CuO+4%Fe₂O₃+7%ZnO) nano/85%ZnO micro

The SEM image shows a good dispersion of nanoparticles oxides of the sample based on the composite of CuO, Fe_2O_3 and ZnO nanostructured oxides supported on ZnO micro. The iron oxide and copper supported for the dispersion of zinc oxide nanoparticles on the ZnO surface microscope

Table 3.13. Composition of samples (4%CuO+4%Fe₂O₃+7%ZnO)nano/85%ZnO micro phân tích bằng phương pháp AAS. The composition of the metal oxides in Table 3.13 show that the XT3 material has a high purity, reaching

Nº	Samples	Theorical composition (%wt)	Real composition (%wt)
1	ZnO	92,0%	92,0%
2	Fe ₂ O ₃	4,0%	4,0%
3	CuO	4,0%	3,9%

99.9%, of which, ZnO occupies 92.0% wt, Fe_2O_3 4.0% wt and CuO 3.9% wt.

The specific surface area and maximum sorption capacity of the samples are shown in Table 3.14.

Table 3.14. Specific surface area (S_{BET}) and of the materials

Stt	Samples	S _{BET} , m ² /g	maximum sulfur sorption capacity (Sg/100g material)
1	ZnO micro	9,8	0,59
2	15%ZnOnano/85%ZnOmicro (XT1)	13,2	1,53
3	(4%Fe ₂ O ₃ +11%ZnO)nano/85% ZnO micro (XT2)	15,4	3,1
4	(4%CuO+4%Fe ₂ O ₃ +7%ZnO)n ano/85%ZnO micro (XT3)	19,0	17,36
5	(4%CuO+11%ZnO)nano/85% ZnO micro	16,7	3,08
6	ZnO nano (XT4)	71,0	7,91

The results in Table 3.14 show that the addition of metal nanooxide on ZnO surface did not significantly improve the specific surface area of the orriginal ZnO material, but greatly enhanced the maximum sulfur sorption capacity. Specifically, the maximum sulfur sorption capacity increased from 0.59 to 17.36 g/ 00 g of material.

3.5. Study coating material on support

3.5.1. Study of monolith ceramic composition

Monolith ceramic was used as a support for impregnating active phases. The EDX spectrum showed that the main constituents of monolith were SiO_2 (51.58%), Al_2O_3 (34.57%), MgO (13.67%), ZnO (0.02%).

3.5.2. Effect of coating method

The active phase covered on monolithe by using three methods of impregnation: the frist using aluminium sol, the second using and the third using the the mixture aluminium sol with the bohemit suspension with organic additives. Figure 3.25 shows the results of the SEM of uncoated monolith and three alumina coated samples with the above three methods.



Figure 3.25. The SEM image of the monolith before (a) and after alumina by impregnation method in sol (b, c).

The SEM image shows the blistering phenomenon with the coating using the aluminum sol method (fig.3.25b). The peeling phenomenon is still observed with the aluminum sol-suspension (fig.3.25c) and no longer with suspension method (Fig.3.25d). In this method, a thin layer of aluminum oxide (150 μ m), spread evenly, reaches 21.4% wt after 3 dipping times. The adhesion strength cheked by ultrasonic vibration showed that the cover layer only lost about 8% wt in comparision with the previous one.



Figure 3.26. The SEM images of the monolith surface before (a) and after (b) covering alumina layer by dipping in suspension method

Figure 3.26 shows the SEM images of the monolith surface before and after coating with the suspension method The result showed that a layer of aluminum oxide was deposited on the monolith surface (h.3.26b). Thus the alumina suspension method giva the best results and was selected for coating the γ -Al₂O₃ carrier on a monolithic surface.

3.5.3. Investigation of coating process on based- ZnO material supported on γ -Al₂O₃/Monolith.

3.5.3.1. Process of coating ZnO oxide "monolayer"

Monolith material deposited by the γ -Al₂O₃ layer continue to be dispersed ZnO active layer on dry and wet impregnation methods of zinc salt and following heat treatment. The results showed that wet impregnation gave better impregnation effect (higher ZnO content).

The effects of wet impregnation toward ZnO content after each impregnation are shown in Table 3.15.

Bång 3.15. ZnO content versus impregnation times

Stt Samples Impregnation	ZnO
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The results in Table 3.15 show that, after the second impregnation, the ZnO content

		times	content
			(%wt)
1	M7	1	0,025
2	M8	2	0,075
3	M9	3	0,112
4	M10	4	0,150

in the sample increased significantly compared to the first impregnation (0.075% vs. 0.025%) and was significantly higher than in the first method.

Thus wet impregnation method was suitable to disperse the ZnO active phase on the γ -Al₂O₃ support. After four times the ZnO content was of 0.15%.

3.5.3.2. Investigation of process of coating single-layer ZnO oxide modified by Fe_2O_3 , CuO

ZnO, CuO, Fe₂O₃ oxide nanoparticles were dispersed on γ -Al₂O₃/Monolith, by wet impregnation method using a mixture of metal salts. The results are presented in Table 3.16.

Nº	Impregantion times	Active phase content dispersed, %wt		
		ZnO nano + micro	Fe ₂ O ₃	CuO
1	1	0,152	0,002	0,003
2	2	0,163	0,008	0,007
3	3	0,178	0,009	0,008

Table 3.16: Active ph	hase content toward	impregnation times
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The results in Table 3.16 show that, after 3 impregnation times, the amount of Fe_2O_3 , CuO on the monolith reaches the desired ratio (92% ZnO: 4% CuO: 4% Fe 2 O 3).

3.5.4. Evaluation of activity and stability of materials during H₂S treatment 3.5.4.1. ZnOnano/γ-Al₂O₃/Monlith material

Evaluation experiments of activity and stability of material was carried out in a continuous flow system with a gas mixture containing 25 ppm H_2S in N_2 , at temperature of 300°C and velocity of 4.8 L/h.

Table 3.17: H₂S treatment capacity of material

Treatment	H ₂ S concentration in	
time (h)	outlet (ppm)	
1	< 0,100	
3	0,120	
5	0,120	
7	0,120	
8	0,120	

Results of hydro sulfide treatment $ZnOnano/\gamma$ -Al₂O₃/monlithe with are shown in Table 3.17. Experimental results show that the H₂S treated flow contains very low H₂S content (about 0.1 ppm). Moreover, the material has a stable activity. The capacity of material was hydro stable with sulfide content unchanged after 8 hours of continuous operation.

3.5.4.2. Material nano ZnO-CuO-Fe₂O₃/γ-Al₂O₃/Monlith

 Table 3.18. H₂S treatment capacity

 of material

Treatment	H_2S concentration in outlet (ppm)
1	0.1-0.2
5	0,1-0,2
10	0,1-0,2
20	0,1-0,2
40	0,1-0,2
60	0,1-0,2

Experimental evaluation of material activity and stability was carried out in a continuous flow system with a gas mixture containing 10 ppm H2S in N2 under mild conditions: the absorption temperature of 25°C, gas flow of 6 L/h gas. The results are shown in Table 3.18. It shows that the H₂S flow at the outlet reaches the 0.1 and 0.2 ppm detected by the test kit. Materials have a stable activity: the activity unchanged after 60 hours of work.

Thus, for both moduls using active phase ZnO nanoparticles and ZnO modified by CuO, Fe₂O₃ supported on γ -Al₂O₃/monolithic, the post-treatment sulfur content decreased to 0.1-0.2 ppm.

CONCLUSION

The thesis has the following main contents:

1. Have studied the optimum conditions for successful synthesis of ZnO nanostructured with wurzite crystal phase, high purity and nanoflower, nanoparticles or nanotube morphology as following:

- The nanoflower ZnO, which is hydrothermally synthesized, has a S_{BET} surface area of 70 m²/g and each "nanoflower" (size 1-2 μ m) owns flower petals with diameter of 10-20nm.

- The nanoparticles ZnO, having a diameter of about 100 nm, were prepared by hydrothermal crystallization method from micro ZnO with grain size particle about 5μ m and in presence of H₂O₂. The most important parameter in the synthesis process is the ZnO/H₂O₂ ratio: the smaller the ratio, the smaller the particle size obtained. In particular, the best synthesis condition for the fit between particle size and synthetic yield is the ratio of 1g ZnO/50 ml H₂O₂.

- The ZnO nanotubes, about 50 nm in diameter, 300-600 nm in length, were synthesized by hydrothermal method at 180° C for 24 h.

2. Successfully synthesized surface modified ZnO: ZnOnanoflower/ZnOmicro. The sulfur sorption tests showed that the maximum absorbed content (% S) was 29.7; 39.8; 45, 1 and 51.5 for the

nanoflower ZnO, respectively for number of impregnation cycle 1, 5, 10, 100. The results reveals that the maximum sorption capacity of the nanoflowerZnO/microZnO material has been significantly improved, with the increase of 28.8% in comparison with commercial micro ZnO.

3. Successfully synthesized ZnO modified by Al_2O_3 : ZnO- Al_2O_3 . The typical results show that ZnO is in the wurzite phase and Al_2O_3 in the amorphous structure with $S_{BET} = 82-84 \text{ m}^2/\text{g}$. The conversion of COS to H_2S on this material was investigated in function of Al_2O_3 content and the results showed that 10% of Al_2O_3 (in weight) was optimal content with 80% of COS converted under experimental conditions. In addition, the sulfur sorption capacity attained is 45.2%.

4. The CuO-ZnO-Al₂O₃ composite was studied in accordance with working conditions at high temperature and the CuO-Fe₂O₃-ZnOnano/ZnOmicro suitable for working at ambiance temperature. Among studied materials, the CuO-ZnO-Al₂O₃ material, with composition of 11.51% CuO, 78.65% ZnO, 9.79% Al₂O₃, had the highest specific surface area and sulfur sorption capacity about 31% of mass, at 300°C. The CuO-Fe₂O₃-ZnOnano/ZnOmicro composite, with content of 3.9% CuO, 4% Fe₂O₃, 7% ZnO nanoparticles and 85% ZnO micro, has a specific surface area of 19 m²/g and sulfur sorption capacity about 17.36% in mass, at room temperature.

5. Have studied the impregnation of acive phases above on monolithic honeycomb materials, ZnO/γ -Al₂O₃/monolith and CuO-Fe₂O₃-ZnO/ γ -Al₂O₃/monolith, and the sulfur sorption capacity of these new "devices" in order to lower H₂S content in gas flow down to range 0.1-0.2 ppm. The results obtained are following:

- Among three method to impregnate γ -Al₂O₃ layer on monolith (using aluminum sol, the mixture of bohemite suspension and aluminum sol and only aluminum bohemite suspension), the method using aluminum bohemite suspension formed γ -Al₂O₃ layer with thickness of 150 µm, corresponding to 21.4% (in weight) of "device". This oxide layer showed good mechanical strength, no cracking phenomena, good adhesion to monolith surfaces and porous surfaces.

- The "device" 0,4%ZnO/ γ -Al₂O₃/monolith enable to decrease the H₂S content until 0.1 ppm for 8 hours continuous operation, at a temperature of 300°C and the one 0,008% CuO-0,009% Fe₂O₃-0,178% ZnO/ γ -Al₂O₃/Monolith lowered H₂S content until 0.1-0.2 ppm for 60 hours continuously working, at room temperature.