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The Synthesis of Magnesium-aluminium Spinel for Catalytic Hydrolysis of Carbonyl Sulphur at the Middle Temperature

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Abstract. The influences of the physical and chemical properties for the catalyst materials on the hydrolysis catalytic activity of carbonyl sulphur (COS) and the anti-oxygen property will be crucial to removing COS from gas at moderate temperature. The magnesium-aluminium spinel for catalytic hydrolysis of COS was synthesized by the dry mixing of pseudo boehmite with MgO. The performances of the prepared catalyst were characterized by XRD, nitrogen isothermal adsorption (BET), CO₂-TPD, and the COS hydrolysis activities were measured in fix-bed reactor with the change of space velocity, temperature, COS concentration and O₂. The results showed that the MgAl₂O₄ synthesized by mixing of pseudo boehmite with MgO and then calcining at 873K is feasible. By comparison with γ -Al₂O₃ catalyst, the synthesized MgAl₂O₄ catalyst possesses more pore volume and diameter so as to improve the diffusion rate of reactant and product of COS hydrolysis. MgAl₂O₄ spinel catalyst showed the better catalytic activity of COS hydrolysis, combining the advantages of γ -Al₂O₃ and MgO. As a result, MgAl₂O₄ catalyst in itself not only helps to improve the catalytic activity of COS, but also helps to enhance the anti-oxygen poisoning property.

1. Introduction

In order to reduce the emission of sulphur compounds, the removing sulphur compounds from gas is one of the key processes in application of fossil fuel. Sulphur compounds contain inorganic and organic sulphur. By comparison with inorganic sulphur, organic sulphur such as carbonyl sulphur (COS) is more difficult to remove from gas. The existing methods for removing COS include two types of removal by direct absorption and indirect conversion absorption. The removing COS by direct absorption consists of wet absorption method and dry adsorption method, and among these the indirect conversion absorption comprises hydrogenation conversion, hydrolysis conversion and oxidation conversion. In comparison with direct removal absorption, the indirect conversion absorption has the advantage of high operation temperature, easy to run, big capture capacity and low operating cost. The indirect conversion adsorption means that COS is firstly converted to H₂S over a catalyst, and then the produced H₂S is desorbed using a desulfurization sorbent [1]. Among the indirect conversion absorption method, the step of COS catalytic conversion is its core. At present, γ -Al₂O₃ and TiO₂ had been regarded as the catalyst carrier for COS hydrolysis at lower temperature [2]. However, it was found that they completely ignore a defect in stability for catalytic hydrolysis of COS at middle temperature. For example, if there is a small amount of oxygen in gas, the catalytic conversion of COS over catalyst will rapidly decrease due to catalyst poisoning by sulphation. Therefore, the developing a novel catalyst material will play in an important role in the removing COS from gas at middle temperature. The compound metal oxygen such as magnesium-aluminium spinel [3-5] was put forward as catalyst material for COS catalytic hydrolysis at middle temperature. In this paper, a



magnesium-aluminium spinel for catalytic hydrolysis of COS was synthesized by the dry mixing of pseudo boehmite with MgO. The performances of the synthesized catalyst were characterized by XRD, nitrogen isothermal adsorption (BET), CO₂-TPD and the COS hydrolysis activity was measured in fixed bed reactor with the change of space velocity, temperature, COS concentration and O₂.

2. Experimental

2.1. Synthesis of Magnesium-aluminium Spinel for Catalytic Hydrolysis of COS

The magnesium-aluminium spinel for catalytic hydrolysis of COS was synthesized by the dry mixing of pseudo boehmite with MgO. Firstly, pseudo boehmite, MgO and K₂CO₃ were weighed, which the proportion for their contents is 70 wt. %, 20 wt. % and 10 wt. % in raw material, respectively. Second, the pseudo boehmite, MgO and K₂CO₃ were mixed by stirring. Finally, the pure water was added into the mixture and then crushed, shaped, dried at normal atmospheric temperature for 4h, and calcined at 823K for 4h to obtain the experimental catalyst samples.

2.2. Analysis and Characterization of the Catalyst

The crystal structures of the synthesized catalyst material for COS hydrolysis were detected by X-ray diffractometer (XRD). A DX-2700 X-ray diffractometer using Cu K α radiation ($\lambda=0.15406$) was used to scan the prepared catalyst samples. The intensity data were collected over 2θ range of 5° to 85° with a scanning speed of 10°/min. The pore structures for the synthesized catalyst samples were performed by N₂ adsorption-desorption method (BET) using Micromeritics Tristar 3000. The surface basicity for the synthesized catalyst samples were characterized by CO₂ temperature programmed desorption (CO₂-TPD) using AutoChem- II2920.

2.3. Performance Test of COS Hydrolysis for Catalyst

Catalytic performances for COS hydrolysis over the synthesized magnesium-aluminium spinel catalyst were performed in a fixed-bed micro-reactor. The experimental apparatus consists of gas inlet unit, reaction unit and detecting unit. Gases were controlled by flow meter and then introduced into a vertically quartz tube that was placed in a tube furnace. The inner diameter of the reaction quartz tube was 15 mm. 10 ml of catalyst sample was packed in the tube to a height of about 4.5 cm, and then heated to the reaction temperature in a mixed gas flow. The mixed gas contains N₂, O₂ and COS. The reaction temperature was range from 423 to 523K.

3. Results and Discussions

3.1. Crystalline Phase for the Synthesized Catalyst Samples

The phase identification of the synthesized both γ -Al₂O₃ catalyst and MgAl₂O₄ catalyst samples was carried out by XRD. XRD spectrum of two catalyst samples was shown in Figure 1.

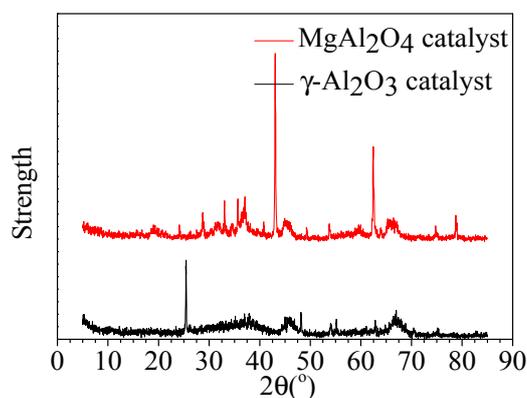


Figure 1. XRD spectrum of the Al₂O₃ catalyst and MgAl₂O₄ catalyst samples synthesized

The diffraction peak of the synthesized γ - Al_2O_3 catalyst were 45.84° , 45.90° and 67.00° , and MgAl_2O_4 catalyst were 36.9° , 44.8° , 62.5° and 77.1° , respectively. Crystalline phases for these catalysts were identified by comparison with the reference data from JCPDS Database, the synthesized catalyst samples were γ - Al_2O_3 and MgAl_2O_4 spinel, respectively. The diffraction peak of active component K_2CO_3 had been found in XRD spectrum, which shows that loading K_2CO_3 was dispersed evenly in γ - Al_2O_3 and MgAl_2O_4 carrier and formed amorphous phases. The higher in the strength of diffraction peak and the sharper in shape of diffraction peak show that MgAl_2O_4 catalyst has better crystallinity.

3.2. Pore Structure for the Synthesized Catalyst Samples

The pore structures of the synthesized both γ - Al_2O_3 and MgAl_2O_4 catalysts were carried out by N_2 adsorption-desorption method. The pore size distribution of two catalysts was shown in Figure 2.

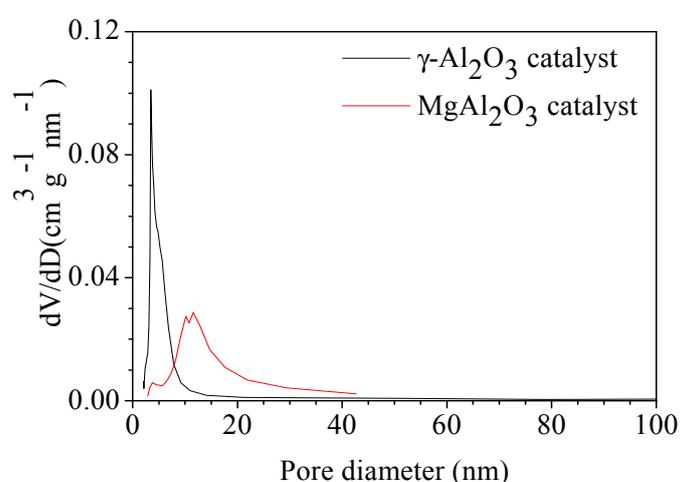


Figure 2. Pore size distribution of the synthesized γ - Al_2O_3 and MgAl_2O_4 catalyst samples

From Figure 2, it was seen that the peak temperature of the synthesized MgAl_2O_4 spinel catalyst is higher, and the area is smaller by comparison with the synthesized γ - Al_2O_3 catalyst, which was further determined in the following Table 1. The pore parameters of the synthesized both γ - Al_2O_3 and MgAl_2O_4 catalyst samples were shown in Table 1.

Table 1. Pore parameters of the synthesized both γ - Al_2O_3 and MgAl_2O_4 catalyst samples

Sample name	BET surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore diameter (nm)
γ - Al_2O_3 catalyst	141.16	0.34	5.68
MgAl_2O_4 catalyst	123.65	0.50	14.09

As seen in Table 1, the BET surface area of the synthesized MgAl_2O_4 catalyst decreases by comparison with the synthesized γ - Al_2O_3 catalyst, but its pore volume and diameter increase. The change of pore structure is beneficial to improving catalytic performance in COS hydrolysis. As a result of the heterogeneous reaction of COS hydrolysis happen in surface of solid catalyst, and the pore diffusion influences the rate of COS hydrolysis. The improving pore diameter may decrease the pore resistance of reactants and products in gas-solid heterogeneous reaction, that is, increase the rate of the adsorption of COS, H_2O and desorption of H_2S and CO_2 .

3.3. Surface Basicity for the Synthesized Catalyst Samples

The surface basicity of the synthesized both γ - Al_2O_3 and MgAl_2O_4 catalyst samples were measured by CO_2 -TPD. The result of two catalysts is shown in Figure 3.

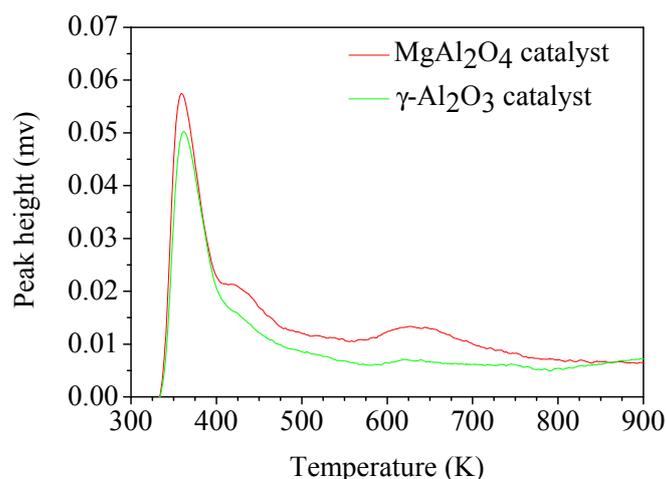


Figure 3. Surface basic distribution of the γ - Al_2O_3 and MgAl_2O_4 catalyst samples synthesized

There are two types of CO_2 desorption peak corresponding to surface basicity over the synthesized γ - Al_2O_3 and MgAl_2O_4 catalyst. The temperature of the first desorption peak for MgAl_2O_4 catalyst is the same as γ - Al_2O_3 catalyst, however, the second is lower. Table 2 gives the detail data of CO_2 -TPD for the synthesized γ - Al_2O_3 and MgAl_2O_4 catalyst samples.

Table 2. The temperature and area of CO_2 -TPD for the synthesized γ - Al_2O_3 and MgAl_2O_4 catalyst

Sample	Desorption temperature (K)		Desorption area (cm^2g^{-1})	
	First	Second	First	Second
γ - Al_2O_3 catalyst	361	897	9.38	4.00
MgAl_2O_4 catalyst	362	627	10.07	8.45

As seen in Table 2, although there are two types of surface basicity over the synthesized both γ - Al_2O_3 and MgAl_2O_4 catalyst samples, but two catalysts has obvious difference in the area and temperature of the second peak for CO_2 -TPD. The temperature of the second peak of CO_2 -TPD for MgAl_2O_4 catalyst decrease and the area increase, which show the increase of middle surface basicity MgAl_2O_4 catalyst by comparison with γ - Al_2O_3 catalyst. The increase of surface basicity may be benefit to improving the rate of COS hydrolysis, due to COS hydrolysis being base catalysis reaction.

3.4. COS Hydrolysis Activity for the Synthesized Catalyst Samples

3.4.1 Influence of Space Velocity on COS Hydrolysis Conversion. In conditions of COS concentration of $80\text{mg}/\text{m}^3$, a temperature of 573K and atmospheric pressure, the influences of space velocity on COS hydrolysis conversion were carried out at a space velocity of 3000, 4000, 5000, 7000, 9000, 11000h^{-1} , respectively. The results were shown in Figure 4.

As seen in Figure 4, COS hydrolysis conversion over the synthesized γ - Al_2O_3 and MgAl_2O_4 catalyst samples at middle temperature gradually decrease with the increase of space velocity, but the difference in COS hydrolysis conversion for two catalyst samples become apparent. At the same space velocity, the conversion of COS hydrolysis over MgAl_2O_4 spinel catalyst is bigger than that over γ - Al_2O_3 catalyst sample. The result may be related to the improvement of pore structure of MgAl_2O_4 catalyst. The big pore diameter is benefit to the adsorption of COS and increases the speed of COS hydrolysis.

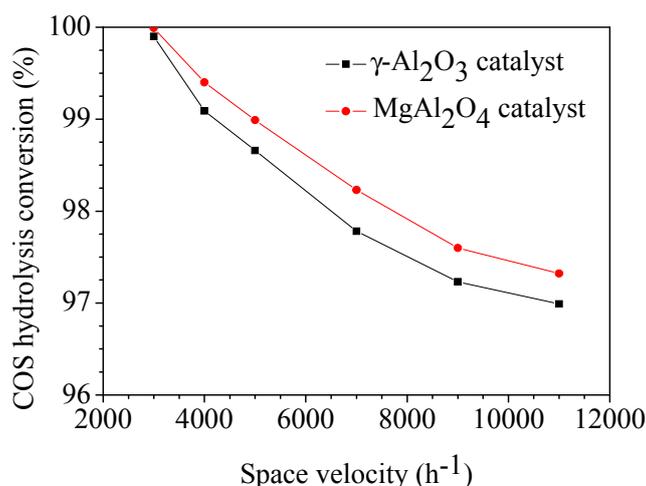


Figure 4. Influences of space velocity on COS hydrolysis conversion over the synthesized $\gamma\text{-Al}_2\text{O}_3$ and MgAl_2O_4 catalyst samples

3.4.2 Influence of Temperature on COS Hydrolysis Conversion. In conditions of COS concentration of 80mg/m^3 , a space velocity of 9000h^{-1} and atmospheric pressure, the influences of temperature on COS hydrolysis conversion were carried out at a temperature of 423, 473, 523, 573, 623K, respectively. The results were shown in Figure 5.

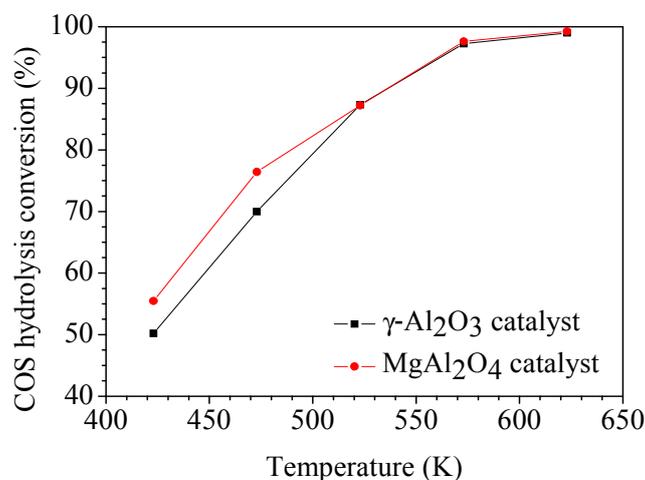


Figure 5. Influences of temperature on COS hydrolysis conversion over the synthesized $\gamma\text{-Al}_2\text{O}_3$ and MgAl_2O_4 catalyst samples

COS hydrolysis conversion over the synthesized $\gamma\text{-Al}_2\text{O}_3$ and MgAl_2O_4 catalyst samples gradually increase with the increase of temperature, but the difference in COS hydrolysis conversion for two catalysts become little while temperature is high. The result may be related to the improvement of surface basicity of MgAl_2O_4 catalyst.

3.4.3 Influence of COS Concentration on COS Hydrolysis Conversion. In conditions of a temperature of 573K, a space velocity of 9000h^{-1} and atmospheric pressure, the influences of COS concentration on COS hydrolysis conversion were carried out at a COS concentration of 40, 80, 120, 180, 220mg/m^3 , respectively. The results were shown in Figure 6.

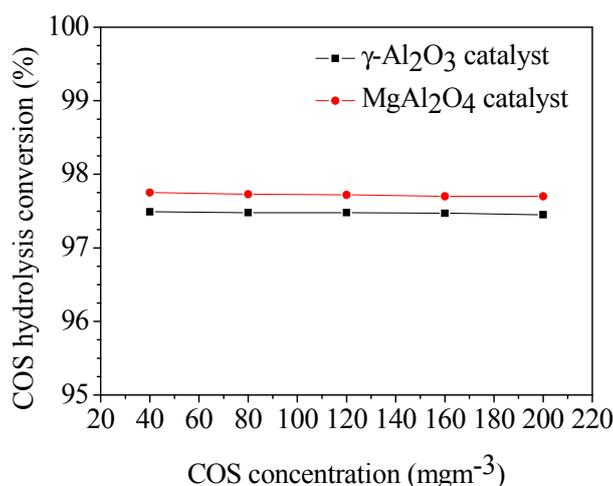


Figure 6. Influences of COS concentration on COS hydrolysis conversion over the synthesized γ -Al₂O₃ and MgAl₂O₄ catalyst samples

COS hydrolysis conversion over the synthesized γ -Al₂O₃ and MgAl₂O₄ catalyst samples keep constant with the increase of COS concentration, which shows that the reaction of COS hydrolysis is first order reaction kinetics. However, the difference in COS hydrolysis conversion over the synthesized γ -Al₂O₃ and MgAl₂O₄ catalyst samples is not the same, that is, the conversion of COS hydrolysis over MgAl₂O₄ catalyst is more than that over γ -Al₂O₃ catalyst. The results further demonstrate that MgAl₂O₄ catalyst has better the surface basicity and pore structure by the comparison with γ -Al₂O₃ catalyst.

3.4.4 COS Concentration on O₂ Concentration on COS Hydrolysis Conversion. In conditions of a temperature of 573K, a space velocity of 9000h⁻¹, COS concentration of 2000mg/m³, O₂ concentration of 0.5 vol.% and atmospheric pressure, the change of COS hydrolysis conversion were carried out with reaction time increasing. The results were shown in Figure 7.

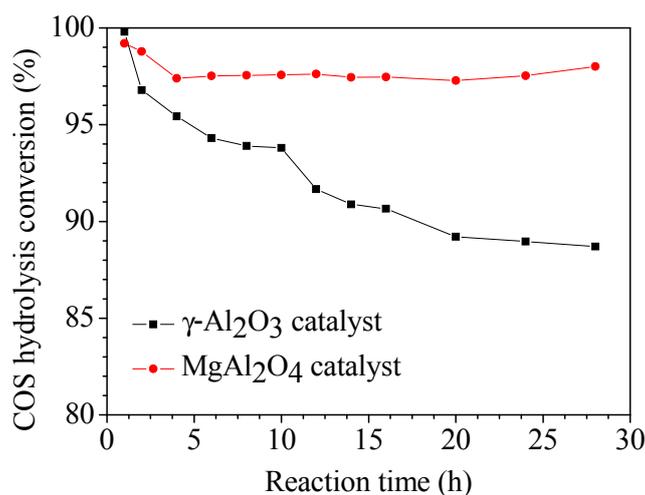


Figure 7. The change of COS hydrolysis conversion over the synthesized γ -Al₂O₃ and MgAl₂O₄ catalyst samples with the increasing reaction time

From Figure 7, it was that the conversion of COS hydrolysis over the synthesized MgAl₂O₄ catalyst sample keep constant, but that over γ -Al₂O₃ catalyst sample decline dramatically with increasing time in atmosphere containing oxygen. The reasons are that big pore diameter for MgAl₂O₄ catalyst

accelerates the speed of desorption of H₂S produced, and large surface basicity hinders the further oxidation of sulphur compound to sulphate. The MgAl₂O₄ structure helps to improve the anti-oxygen poisoning property.

4. Conclusions

The synthesis of MgAl₂O₄ spinel catalyst by the mixing of pseudo boehmite with MgO and then calcining at 873K is feasible. MgAl₂O₄ spinel catalyst possess more pore volume and diameter so as to improve the diffusion rate of COS hydrolysis by comparison with γ -Al₂O₃ catalyst. The MgAl₂O₄ spinel catalyst has the catalytic activity of COS hydrolysis, combining the advantages of γ -Al₂O₃ and MgO. MgAl₂O₄ spinel catalyst in itself not only helps to improve the catalytic activity of COS hydrolysis, but also helps to improve the anti-oxygen poisoning property.

5. Acknowledgments

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6. References

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