

The Study of the Preparation of Catalysts for Carbonyl Sulfide Hydrolysis under Moderate Temperature

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Abstract

Multifunctional composite catalyst for carbonyl sulfide hydrolysis under moderate temperature was prepared by impregnation method. The hydrolysis and deoxidation ability of the prepared catalyst was investigated in a fixed bed reactor. It was found that deoxidation ability of the prepared catalyst was raised by the increase of the content of potassium loading catalyst and reaction temperature. And the concentration of H₂S had no effect on deoxidation while COS improved the deoxidation ratio. And deoxidation rates were nearly scaled up with concentration of H₂. The hydrolysis ability was decreased by the decrease of the surface basicity.

Keywords

Carbonyl Sulfide Hydrolysis, Deoxidation, Catalyst, Moderate Temperature

1. Introduction

In the process of coal coking, through a series of complex physical and chemical reactions, coal was generated into the coke oven gas eventually. Coke oven gas contains a lot of sulfide, hydrogen chloride, hydrogen fluoride and other gases, and trace amount of these compounds can result in the deactivation of the following catalysts and lead to corrosion of the following reaction equipment [1]-[6]. The amount of sulfur in the gas must be decreased to a standardized scope. So the sulfide in coke oven gas must be removed before used. Coke oven gas contains not only hydrogen sulfide (H₂S) but also other sulfurous gases including carbonyl sulfide (COS). In comparison to H₂S, COS is more difficult to remove due to its low reactivity in many desulfurizers. Therefore, the formation

of COS in coke oven gas will reduce the coke oven gas desulfurization efficiency. Many studies of COS removal by sorption, catalytic hydrolysis and hydrogenation conversion have been reported in order to overcome this limitation [7] [8] [9] [10]. An alternative technology has been used for the removal of COS, and this is based on the formation of H₂S by hydrolysis: $\text{COS} + \text{H}_2\text{O} = \text{H}_2\text{S} + \text{CO}_2$.

Liu *et al.* [11] studied the heterogeneous reaction of COS on metal oxides. The results showed that the activity series for heterogeneous hydrolysis of COS decreased in the following sequence: $\text{Al}_2\text{O}_3 > \text{CaO} > \text{MgO} > \text{TiO}_2 > \text{ZnO} > \text{Fe}_2\text{O}_3 > \text{SiO}_2$. The specific surface area and surface basicity of these oxides have great effect on the catalytic activity. Shangguan *et al.* [12] prepared the catalyst containing Al_2O_3 and K_2CO_3 at low temperature and an improved desulfurization performance was reported. Loading K_2CO_3 can increase the basicity of catalyst, which increases the COS hydrolysis ability. However, some desulfurization process must be carried out under intermediate temperatures, and in this temperature, Al_2O_3 is easy to be sulfated which will decrease the catalytic activity. Liujun *et al.* [13] thought reduce catalytic activity was due to oxygen existed in gas. The oxygen can make H₂S transform into SO_{42} —on the surface of catalyst and this reaction can sulfate the Al_2O_3 , thereby decreasing the basicity of catalysts.

To overcome the pernicious effect of Al_2O_3 that oxygen brings in, something that can remove oxygen must be introduced into catalyzer. Hydrodeoxygenation has been reported as a feasible way to remove the oxygen. Hydrodeoxygenation refers to the reaction of O₂ and H₂ generate into H₂O to remove oxygen under the influence of deoxidizers. Cu-based deoxidizer has been widely used, but it has low deoxidization accuracy and oxygen capacity. Pd-based deoxidizer has wide operating temperature range and high deoxidization accuracy, but it is expensive and needs strict impurity in the raw material gas. Mn-based deoxidizer cannot be used in sulfur-containing atmosphere while coke oven gas contains a lot of sulfur. Ni-based deoxidizer has very high hydrodeoxygenation catalytic activity, however Ni can react with CO and coke oven gas has some CO. Mo-based deoxidizer has high hydrodeoxygenation catalytic activity, and it still work even in high temperature. In sulfur-containing atmosphere, Mo can generate MoS₂ which has better hydrodeoxygenation catalytic activity, so Mo-based deoxidizer can add into middle temperature hydrolysis catalysts to avoid oxygen poisoning.

By considering the deoxidization ability of middle temperature COS hydrolysis catalysts added MoO₃ and the change law of the deoxidization ability in different reaction conditions, some researches were investigated in this paper.

2. Experimental

2.1. Preparation and Pre-Sulfidation of Catalysts

The COS hydrolysis catalysts doped with MoO₃ were prepared using impregnation method. Different mass ration of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 6\text{H}_2\text{O}$ and K_2CO_3 were dissolved in some distilled water that accorded with the water absorption of

supports. Then the corresponding mass of Al_2O_3 supports was added into the above solution. The mixture was maintained for 12 h at room temperature. Then put the mixture into the drying oven for 4 h at 120°C . Finally put them into muffle furnace for calcination activation at 550°C for 5 h.

2.2. Pre-Sulfidation

Catalyst was heated to 200°C in a N_2 atmosphere, and then H_2 and H_2S was inlet. H_2 concentration was 50% - 60% and H_2S concentration was 2000 - 2500 mgS/m^3 with N_2 balanced.

2.3. Hydrodeoxygenation Tests

Hydrodeoxygenation tests 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 rotameter 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 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 H_2 , N_2 , O_2 and H_2S or COS . The reaction temperature was range from 200°C to 300°C .

2.4. Determination of the Deoxidization Ability

The concentration of O_2 in inlet and outlet were determined through CG7900. The changes in the concentration of O_2 in inlet and outlet indicate the deoxidization ability of the catalysts.

3. Results and Discussion

3.1. The Pre-Sulfidation of Catalysts

At the time of preparing catalysts, Mo was the form of ionic state in the impregnating solution firstly, then transformed into oxidation state when the catalysts were roasting and activating. However, only if molybdenum oxides were transformed into MoS_2 can catalysts get more deoxidization ability. The reaction that occurs during the pre-sulfidation process is $\text{MoO}_3 + 2\text{H}_2\text{S} + \text{H}_2 = \text{MoS}_2 + 3\text{H}_2\text{O} + 48.1 \text{ kJ}$.

When the H_2S was at a low concentration, the time of pre-sulfidation would be grown. This will take more time for pre-sulfidation process in practical application. When the temperature of pre-sulfidation was too high, H_2 would transform Mo oxides into Mo simple substance which could make the active component of hydrodeoxygenation loss. So, the concentration of H_2S in sulfidation gas was 2000 - 2500 mgS/m^3 and the temperature was 200°C .

3.2. The Pre-Experiment of Catalysts Hydrodeoxygenation

The change of the ratio of deoxidization for catalyst without Mo was shown in **Figure 1** with the increase of time. As shown in **Figure 1**, the deoxidization ratio

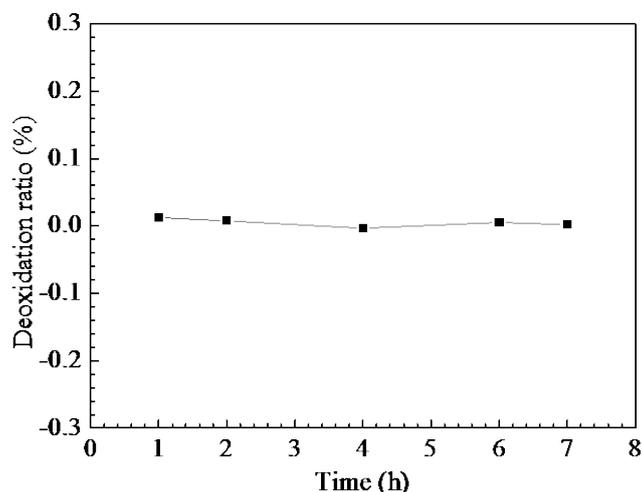


Figure 1. The change of the ratio of deoxidization for catalysts without Mo with the time increasing.

of the catalysts without Mo was nearly zero, and it could be proved that the catalysts without Mo did not have the ability of deoxidization and the oxidation of H_2S could not have effect on the determination of deoxidization ratio.

3.3. The Effect of the Molybdenum Content on the Hydrolysis Ability of the Catalysts

The change of the COS hydrolysis conversion for the catalysts was shown in **Figure 2** with the increase of time. As shown in **Figure 2**, A referred to the catalyst without Mo doped, and B referred to the catalyst with 10 wt.% Mo doped, and C was the catalyst that doped with 10 wt.% Mo after pre-sulfurized. The temperature of reactions were 300°C , and the concentration of H_2 was 20%. The hydrolysis ability of the catalyst was decreased with the Mo doped in and this phenomenon was more significant when the catalyst was pre-sulfurized. Because the COS hydrolysis reaction was a base-catalysis, while the Mo doped in made the surface basicity decrease and decreased the hydrolysis ability eventually. And the pre-sulfidation made the surface basicity decrease further. It might be that after the pre-sulfidation the S_2 -occupied lots of surface space and made the COS difficult to combine with surface basic sites. Though the hydrolysis ability decreased with addition of Mo, it can make the catalyst have the ability of deoxidization to avoid the pernicious effect of Al_2O_3 that oxygen brought in.

3.4. The Effect of Temperature and the Potassium Content on the Deoxidization Ability of the Catalysts

Influences of temperature and the content of potassium on the ratio of deoxidization of catalyst were shown in **Table 1**.

As shown in the **Table 1**, it can be concluded that the deoxidization ability raised with the increase of reaction temperature and the potassium content. From the thermodynamics, the hydrodeoxygenation reaction is an exothermic

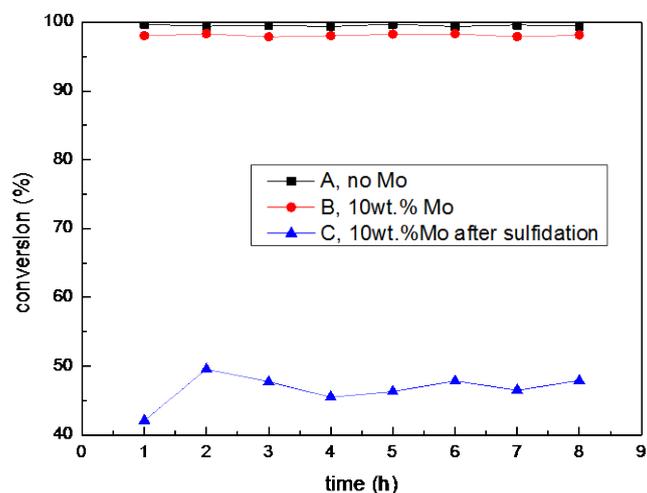


Figure 2. The change of the COS hydrolysis conversion ratio for catalysts in different forms of Mo-based with the time increasing.

Table 1. Influences of different Temperature and different potassium content on the ratio of deoxidization of catalyst.

Content of potassium (%)	Ratio of deoxidization in different temperature (%)		
	200°C	250°C	300°C
5	1.12	2.58	3.14
10	1.37	4.73	6.83
15	9.67	30.39	50.41

process, so deoxidization ability should be decreased with the increase of the reaction temperature. However, the actual deoxidization ratio showed the opposite tendency, this may be because that the hydrodeoxygenation reaction is away from the chemical equilibrium, catalyst improves the chemical reaction rate and the reaction rate increase with the temperature raising. As for potassium content, the H^+ in surface hydroxyl was replaced by K^+ with the potassium added in which could reduce the phase change of Al_2O_3 and accelerate electron transfer of activated oxygen and activated hydrogen. And K^+ not only could prompt Mo^{4+} into stable Mo^{5+} but also was the active center of oxidation-reduction reaction.

3.5. The Effect of Sulfur-Containing Atmosphere the Deoxidization Ability of the Catalysts

The change of the ratio of deoxidization for catalyst in different sulfur containing atmosphere was shown in **Figure 3** with the increase of time. As shown in **Figure 3**, the 80, 200, 700, 1100 referred to the concentration of H_2S , and that were 80 mgS/m^3 , 200 mgS/m^3 , 700 mgS/m^3 , 1100 mgS/m^3 . And the concentration of COS was 700 mgS/m^3 . The temperature of reactions were 300°C, and the concentration of H_2 was 20%. The ratio of deoxidization did not significantly changed with the increased of the concentration of H_2S , however in COS

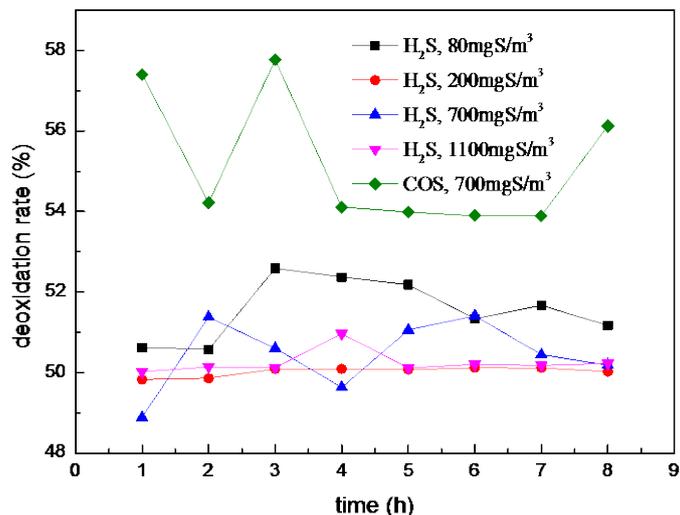


Figure 3. The ratio of deoxidization of catalysts in different sulfur containing atmosphere with the time increasing.

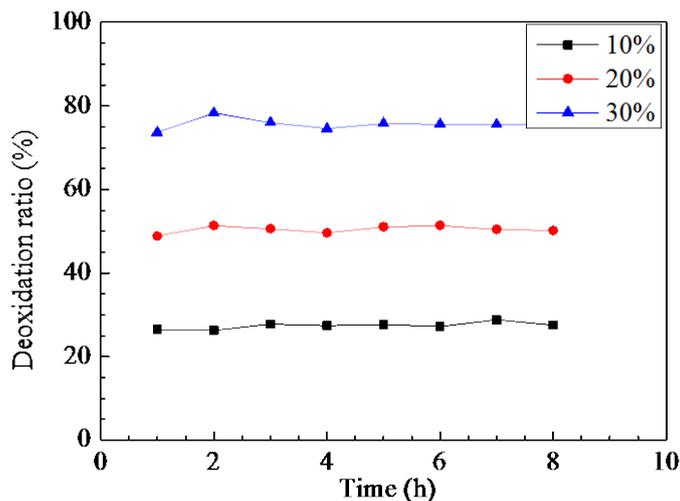


Figure 4. The ratio of deoxidization of catalysts in different concentration of H₂.

atmosphere the ratio of deoxidization was raised a lot. That may be in COS atmosphere, the COS hydrolysis reaction can raise the concentration of surface O₂⁻ in Al₂O₃ which is beneficial to the absorption of H₂ and finally increase the ratio of deoxidization. In COS atmosphere the conversion of COS and H₂S may make the deoxidization unstable.

3.6. The Effect of the Concentration of H₂ on the Deoxidization Ability of the Catalysts

The change of the ratio of deoxidization for catalyst in different concentration of H₂ was shown in **Figure 4** with the increase of time. As shown in **Figure 4**, the ratio of deoxidization of catalyst were raised with the increase of the concentration of H₂. The ratio of deoxidization were nearly scaled up with concentration

of H₂, so it can be concluded that the controlling process of hydrodeoxygenation reaction was connected with H₂ and that process might be a second order reaction.

4. Conclusion

At the process of catalyst deoxidization, the potassium can improve the deoxidization ability of the catalysts, and the improvement raised with the increase of potassium contents while at the process of hydrolysis the surface basicity decrease make the hydrolysis ability decrease. Catalyst improves the deoxidization rate and the deoxidization rate increase with the temperature raising. In the H₂S containing atmosphere the ratio of deoxidization did not change with the change of the concentration of H₂S, however in the COS atmosphere the ratio of deoxidization raised a lot. The ratio of deoxidization scaled up with the increased of the concentration of H₂ and that may be a second order reaction.

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