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The Influence of Ammonia Regeneration for CuO/γ-$A1_2O_3$ Catalyst of Desulfurization Performance

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Abstract: In order to investigate the effects of performance of catalyst desulfurization on the different regeneration conditions, different ammonia flow, reduction temperature, and reduction time were selected for catalyst regeneration by using ammonia as a reducing gas. The results of experiment displayed :With the increase of ammonia flow, reduction temperature and reduction time, the desulfurization performance of catalyst regeneration showed incresing trend, and the optimum reduction conditions of Cu O/γ-$A1_2O_3$ catalysts were that ammonia flow rate was 200 ml/min, the reduction temperature was 400 °C, the reduction time was 1 h.

Keywords: ammonia regeneration; catalyst; the desulfurization performance

1. Introduction

Coal processing and combustion are the main cause of air pollution in our country. With the development of industry, the coal consumption and SO_2 emissions will further increase, acid rain and acid fog of SO_2 do harm to environment greatly[1], thus the control of coal-combustion flue gas and SO_2 emission is the urgent problems of our country ecological environment and the healthy development of the national economy[2].

At present,the flue gas desulfurization technology in accordance with the morphology of adsorbent can be divided into dry process and semi-dry method and wet method at home and abroad [3]. In the field of atmosphere pollution prevention the technology of metal oxide supported sorbents for desulfurization of dry flue gas because of its simplification equipment, convenience of operation and management and low production costs has become an essential aspect in the frontier research[4]. But supported metal oxide catalysts are particularly susceptible to poisoning and need frequent regeneration and adverse influence for the life of the catalysts and the follow-up of the desulfurization performance may be generated by frequent warming and cooling [5] , so reduction method for catalyst regeneration is selected.

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H_2 and CH_4 are often used as a reducing agent for the regeneration of the catalyst by reduction method, strong reducibility of H_2 is more likely to cause excessive load on the oxide reduction in the regeneration process and generate some metal simple substance attached to the catalyst to reduce efficiency in the regenerated catalyst desulfurization and increase consumption of H_2[6]. Reducibility of CH_4 is lower than that of H_2, but effective temperature of catalyst regeneration must be above 500 °C, it is difficult to achieve regeneration at the same temperature of desulfurization regeneration. Adverse influence for the life of the catalysts and the follow-up of the desulfurization performance may be generated by frequent warming and cooling. So NH_3 is choosed as the re generant reducing gas due to reduction performance between H2 and CH_4. The catalyst after regeneration can maintain the stability of the physical structure, the high and stability efficiency of desulfurization, and NH_3 and SO_2 generated within the reactor generate directly sulfur amine salt solid, the realization of utilization of sulfur ,the lowering of the operating costs and improvement the economic benefits is impossible[7].

2. Experiment Part

2.1. Experimental Design

Load copper oxide bore on the carrier of γ-$A1_2O_3$ is crystallized as the active ingredient, and the catalyst after poisoning desulfurization experiments are completed. Then poisoned catalyst after desulfurization is restored by using ammonia to study the impact on the activity of catalyst regeneration with different ammonia flow, reduction temperature and reduction time. In the experiment, load was 7%, the calcinations temperature is 350 °C, roasting time is 3 h and the reaction temperature is 180 °C. By using a single variable method and flue gas analyzer, the change of SO_2 in flue gas desulfurization experiment is compared with the former content that is the comparison of desulfurization rate. The tube furnace is used to restored poisoning catalyst , then the effect of the different reduction factors of catalyst and the optimum reduction conditions is concluded by using the flue gas analyzer for testing.

2.2. Evaluation Device of Catalyst Activity

Catalyst performance testing is carried out in constant temperature in the fixed bed adsorption column. Adsorption column is a quartz tube for inside diameters of 20 mm and length of 50cm. Performance testing device of catalyst is shown as in figure 2.1.

2.3. Deactivation and Regeneration of Catalyst

CuO loaded on the γ-Al_2O_3 catalysis with SO_3 generated by react of O_2 and SO_2 to achieve desulfurization purpose. When the active components absorb SO_2 to reach saturation, the active component of the deactivation can use NH_3 to reinstate the regeneration and once again get copper oxide or elemental copper, and Cu meets free of O2 in flue gas and generates Cu O. The deactivation of the catalyst is included in the tube furnace, and different ammonia flow rate (100 ml/min, 200 ml/min and 300 ml/min), reduction temperature (300 °C, 400 °C, 500 °C), the reduction time (0.5 to 1.5 h, 1 h, h), are selected to investigate influence of different reduction conditions on the desulfurization performance. Installation diagram is shown in figure 2.2.

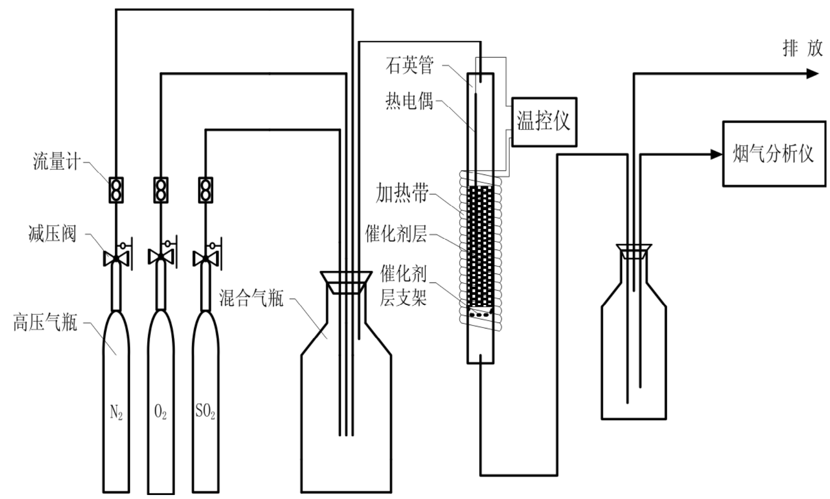

Figure 2.1: Performance testing device of catalyst

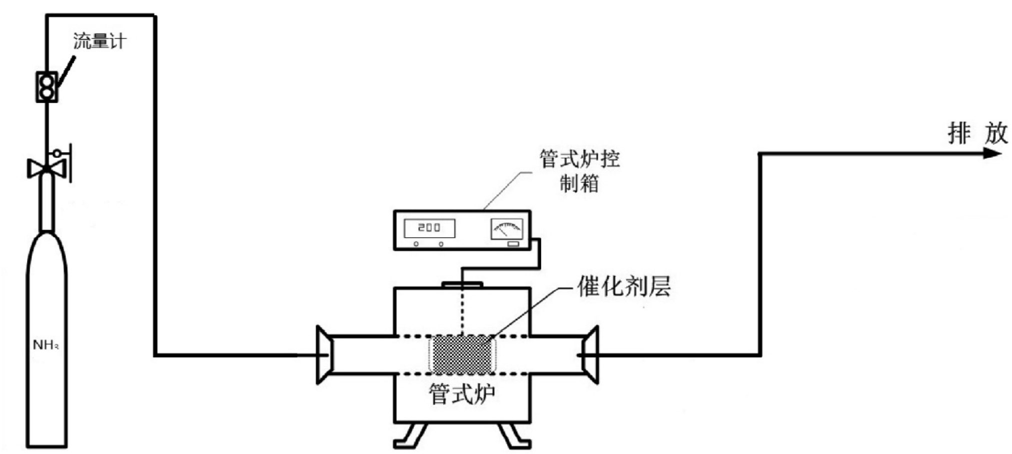

Figure 2.2: Reduction device of catalyst

3. Results and Discussion

3.1. Research on the Influence of Desulfurization Performance on different Ammonia Flow Rate

As can be seen from the figure 3.1, previously the effect of reduction is poor when the ammonia flow rate is 300 ml/min, the effect of flow rate of 300 ml/min is more than 100 ml/min in the middle period, and in the whole process better effect of reduction is achieved

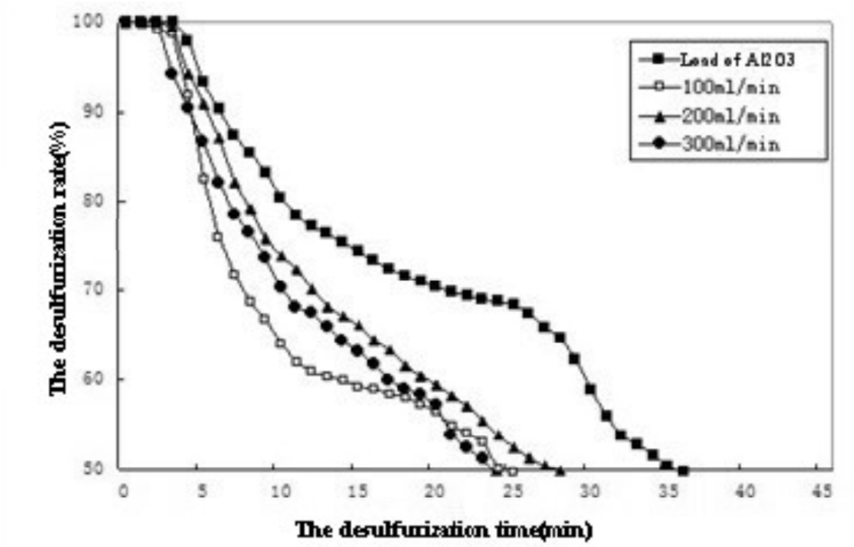

Figure 3.1: Desulfurization Rate under different Ammonia Flow

on 200 ml/min of flow rate . The conclusion is that the high ammonia reduction degree of 300 ml/min leads to generate the Cu, and this is due to early oxygen content reduces quickly in the desulfurization process. Due to the copper oxide generated in the reaction, the effect of flow rate of 300 ml/min is more than 100 ml/min in the middle period. From the whole curves ammonia flow of 200 ml/min should be choose d as the best flow to the reduction of the next step.

3.2. Research on the Influence of Desulfurization Performance on Different Reduction Temperature

As can be seen from the figure 3.2, in the early period of the desulfurization process, the desulfurization effect under the condition of the reduction temperature of 500 °C is the worst, in the mid period effect of 500 °C is better than that of other temperature, and effect of 400 °C is in a leading position in the process of desulfurization. The reason is that in the early period of the desulfurization process temperature is too high, copper oxide are restored into copper and obvious reddish brown of the catalyst appears, black copper oxide basic no longer exists. In the mid-term, because of oxygen in desulfurization process copper oxide is oxidized into copper oxide, and copper oxide of new generation acts as a catalyst for the desulfurization reaction. So desulfurization effect of 500 °C is very good and the effect of the 300 ! is the worst. In the entire process the desulfurization effect of 400 °C is so better that choose it as the best temperature for the reduction of the next step.

3.3. Research on the Influence of Desulfurization Performance on different Reduction Time

At the optimum flow rate of 200ml/min and the temperature of 400 °C the reduction time is respectively 0.5 hours, 1 hour, 1.5 hours, and three reduction curves of different temperatures are shown in figure 3.3.

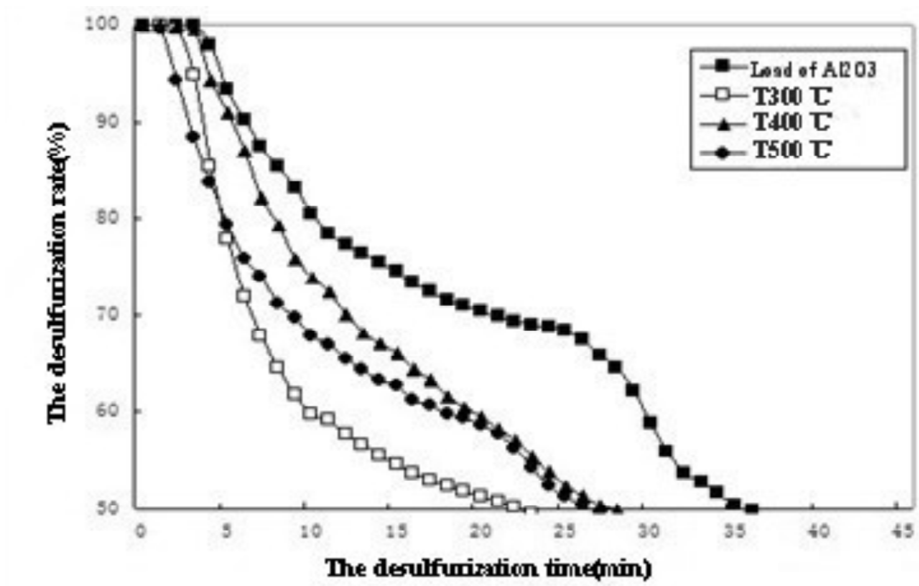

Figure 3.2: Desulfurization Rate under different Reduction Temperature

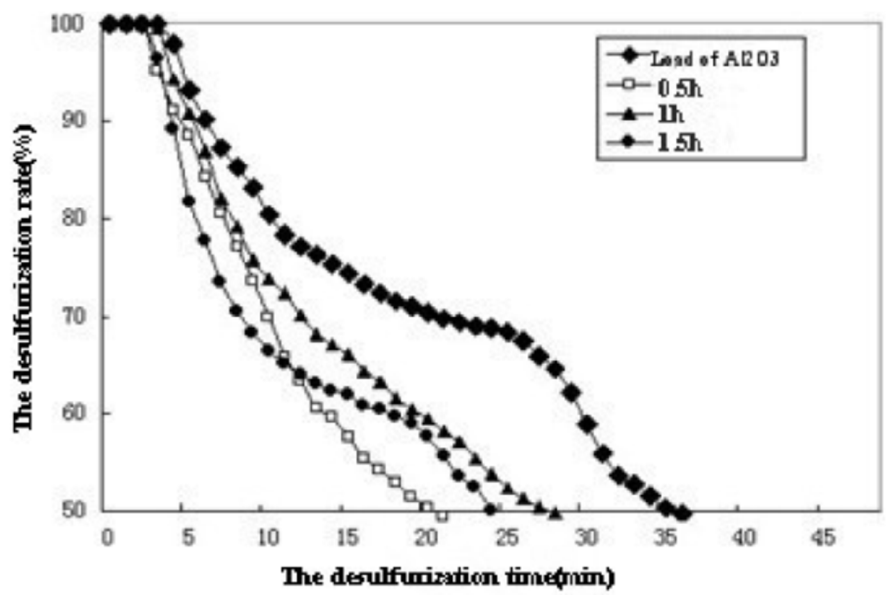

Figure 3.3: Desulfurization Rate under Different Reduction Time

Early the desulfurization effect of reduction time of 1.5 hours is the worst, the curve of 1.5 hours later has a clear warming trend, in the whole process the reduction time of the best desulfurization effect should be 1 hour. In the early period reduction time is long, and reduction product copper oxide is excessively restored into copper. Copper has not a catalytic effect in the process of desulfurization thus of desulfurization effect of reducing time of 1.5 hours is the worst. Copper oxide continues to serve as a catalyst in desulfurization due to that copper is oxidized to copper oxide in the late desulfurization process, so the curve of 1.5 hours has obvious warming trend and the better effect than 0.5 hours. Reduction effect of 1 hour should be the best one in the entire process.

4. Conclusion

Desulfurization efficiency of CuO/gamma $A1_2O_3$ after regeneration with ammonia can maintain high and stable. With the increase of ammonia flow desulfurization performance of catalyst showed a trend of increasing and optimal ammonia flow of Cu O/γ-$A1_2O_3$ is 200 ml/min; With the increase of temperature, catalyst regeneration effect is also increasing and the best temperature is 400 °C; with the increase of reduction time the catalyst regeneration effect is also increasing, reduction time of the best effect is 1 hour. The optimal condition of ammonia reduction screened from experiment is the flow rate of 200 ml/ min, temperature of 400 °C and reduction time of 1 hour.

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