

Regeneration of Sulfated Alumina Support in CuO/ γ -Al₂O₃ Sorbent by Hydrogen

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Introduction

Sulfur dioxide (SO₂) and nitrogen oxides (NO_x) are major air pollutants which have to be removed before emitting flue gases to the atmosphere. Numerous processes have been developed to remove these pollutants (Shin et al., 1994) and CuO/ γ -Al₂O₃ sorbent is known to be one of the efficient methods to remove SO₂/NO_x (Yoo et al., 1994; Centi et al., 1992; Harriot and Markussen, 1992).

Recently, Yoo et al. (1994) reported that SO₂ removal capacity of CuO/ γ -Al₂O₃ sorbent varied with sulfation temperature and the amount of CuO loading. Based on the sulfation degree of alumina support, sulfation phenomena of the sorbent can be classified into three types (surface, slightly deep, and bulk sulfations). The maximum capacity of SO₂ removal by bulk sulfation can be 10 times higher than that by the surface sulfation since alumina support continually participates in sulfation reaction.

In the present study, the effects of reduction temperature, sulfate types and the numbers of sulfation-regeneration cycles on the regeneration of sulfated CuO/ γ -Al₂O₃ sorbent have been determined in a thermogravimetric analyzer.

Experimental Section

Sorbent Preparation. The sorbent was prepared by impregnating copper precursor solution into γ -Al₂O₃ cylindrical pellets of 3 mm × 3 mm (STREM Chemical, U.S.A). First, the alumina support was dried at 110 °C for 24 h and allowed to cool in a desiccator. The copper precursor solution, Cu(NO₃)₂·3H₂O, was mixed with the dried pellets in a rotary vacuum evaporator. After complete evaporation of distilled water for 5 h in a rotary vacuum evaporator, the impregnated alumina pellet was taken out and then calcined at 600 °C in a thermobalance reactor under air flow. Copper oxide concentration as measured by atomic adsorption spectroscopy in the calcined sorbent was 8 wt % based on dry alumina. After calcination, the uniformity of CuO distribution in CuO/ γ -Al₂O₃ was verified by using SEM and Energy Dispersive X-Ray Spectroscopy (EDX). The BET surface area of the calcined sorbent was found to be 184.7 m²/g.

Experimental Procedure. Sulfation and regeneration reactions were carried out in a thermogravimetric (TG) analyzer (TGDTA92 thermoanalyzer, SETARAM, France) as shown in Figure 1. The experimental equipment consists of three sections: reactor, weight detector, and gas analyzer. A sample basket was loaded with 30 mg of calcined sorbent and then was placed into the reaction zone of thermogravimetric analyzer. After reaction temperature reached steady state with a given air flow, SO₂ gas was introduced into the reactor to maintain the concentration of 1.5 vol % SO₂ with a flow rate of 900 cc/min.

Upon completion of sulfation, the reaction mixture was switched to reduction gas of H₂/N₂ for regeneration of the sorbent in a thermogravimetric analyzer. The weight variation of sample with reaction time was recorded in a personal computer. The product gases evolved from regeneration reactions were analyzed by mass spectrometry (SX300, Vacuum Generators Limited). The regenerated sorbents were cooled in N₂ atmosphere and their crystal structures and elements on the sorbent were analyzed by X-ray diffractometer (XRD), X-ray photoelectric spectroscopy (XPS) and EDX. The pore size distributions of sorbent were measured by the BET method.

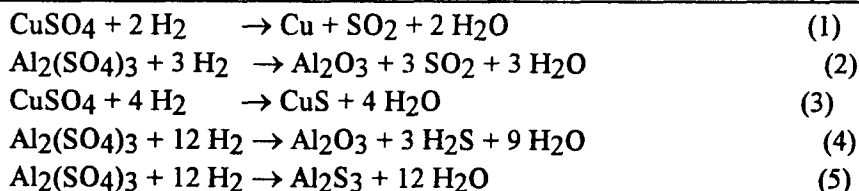
Results and Discussion

The regeneration of bulk sulfated sorbent (7 h at T_s = 500 °C) with 5 vol % H₂ as a function of regeneration time is shown in Figure 2. Regeneration conversion of sulfated sorbent is defined as the mole ratio of reduction to sulfation reaction as

$$X_r = \frac{\Delta m_{r, SO_3}}{\Delta m_{s, SO_3}} \quad (1)$$

where Δm represents the number of SO₃ moles changed during sulfation (subscript s) and reduction (subscript r). In the above equation, the formation of sulfide can be neglected since the amount of sulfide is relatively small compared to the amount of sulfate. The reduction of sulfate on copper and alumina sites follows the reactions (1) and (2) in Table 1, respectively.

Table 1. Chemical reactions involved in the regeneration of sulfated CuO/γ-Al₂O₃



The reduction rate is fast during the first few minutes and then slows down. The final degree of regeneration increases sharply with increasing temperature above 400 °C. This may indicate that reduction of sulfate on alumina site starts to

occur above 400 °C. However, the completion of regeneration reaction cannot be achieved even at 500 °C due to the presence of residual sulfur compound on alumina site. Thus, it can be claimed that the reduction temperature of bulk sulfate should be at least 400 °C and most of the bulk sulfate can be reduced at 500 °C.

The pore size distributions of the sorbents after sulfation and regeneration are shown in Figure 3. The pore volume and surface area of the fresh sorbent are found to be 0.39 cc/g and 185 m²/g, respectively. After bulk sulfation, pore volume of the sulfated sorbent decreases to 0.16 cc/g due to the pore plugging caused by the formation of Al₂(SO₄)₃ with the decrease of surface area (76 m²/g). When the regeneration temperature increases up to 500 °C, both pore volume and surface area of the regenerated sorbent approach the values of the fresh sorbent. However, pore volume of the regenerated sorbent at 500 °C is somewhat smaller than the fresh sorbent due to partial pore plugging caused by residual sulfur rather than thermal sintering. Without thermal regeneration, the average pore diameters remains nearly constant since the regeneration temperature of sulfated sorbent by H₂ is lower than the sintering temperature of γ-Al₂O₃. As can be seen in Figure 3, however, thermal regeneration of sulfated sorbent causes an increase in the average pore diameter from 84 to 120 angstroms due to the sintering of alumina support.

The effect of number of sulfation-regeneration cycles on sulfur removal capacity of 8 wt % CuO/γ-Al₂O₃ sorbent is shown in Figure 4. Sulfur removal capacity of surface sulfated sorbent (T_s = 300 °C; T_r = 500 °C) decreases up to 2 cycles and thereafter the activity remains constant until cycle number reaches 7 times (Figure 4). The cycle test of bulk sulfation-regeneration (T_s = 500 °C; T_r = 500 °C) was performed up to 30 times. It has been found that sulfur removal capacity in bulk sulfation is higher than that in surface sulfation. As can be seen in Figure 4, however, sulfur removal capacity of the sorbent (T_s = 500 °C; T_r = 500 °C) slightly decreases up to 30 cycles. This result may indicate that degradation of active sites on the sorbent occurs at 500 °C. Also, it should be noticed that sulfur removal capacity of the sorbent is enhanced by the addition of NaCl.

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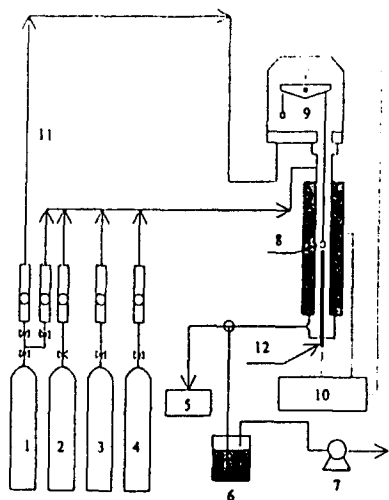


Fig. 1. The schematic diagram of thermogravimetric analyzer; 1. N_2 , 2. air, 3. SO_2 , 4. H_2 , 5. gas chromatography, 6. SO_2 trap, 7. fan, 8. basket, 9. balance, 10. controller, 11. buffering line, 12. thermocouple.

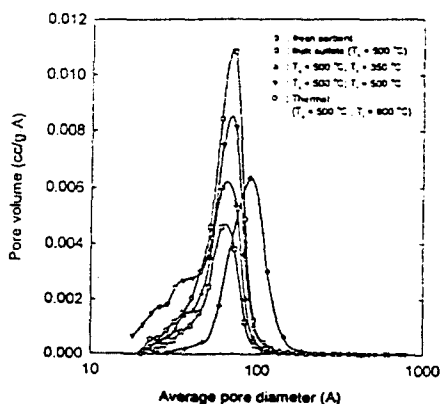


Fig. 3. Pore size distribution of the sorbent after sulfation and regeneration.

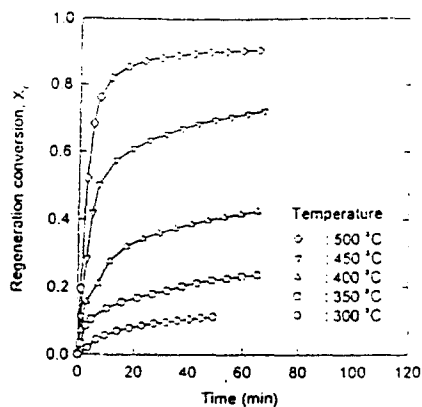


Fig. 2. Regeneration conversion of bulk sulfated sorbent (7 h at $T_s = 500^\circ\text{C}$) as a function of time with variation of regeneration temperature.

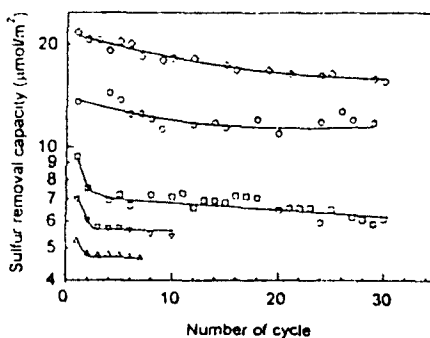


Fig. 4. Effect of number of sulfation-regeneration cycle on sulfur removal capacity.
 ○ : 5 wt% NaCl/8 wt% CuO/γ-Al₂O₃ ($T_s = 500^\circ\text{C}$; $T_r = 500^\circ\text{C}$),
 □ : 5 wt% NaCl/8 wt% CuO/γ-Al₂O₃ ($T_s = 440^\circ\text{C}$; $T_r = 440^\circ\text{C}$),
 △ : 8 wt% CuO/γ-Al₂O₃ ($T_s = 500^\circ\text{C}$; $T_r = 500^\circ\text{C}$),
 ▽ : Centi et al. (1992) 5 wt% ($T_s = 300^\circ\text{C}$; $T_r = 470^\circ\text{C}$)
 ▲ : 8 wt% CuO/γ-Al₂O₃ ($T_s = 300^\circ\text{C}$; $T_r = 500^\circ\text{C}$)