Effects of Particle Size and Gas Velocity on Bulk Sulfation of Al₂O₃ Support in CuO/γ-Al₂O₃ Sorbent

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Abstract: The effects of particle size and gas velocity on sulfation of alumina support of CuO/γ-Al₂O₃ sorbent have been determined in a thermogravimetric analyzer (TGA). Sulfation rate of alumina support of CuO/γ-Al₂O₃ increases with increasing gas velocity up to 0.2 m/s and then decreases with a further increase in gas velocity. The bulk sulfation rate of alumina support decreases with decreasing particle size and sample weight. The slight increase of gas velocity enhances the sulfation rate via reduction of gas film resistance but the outward diffusion rate of SO₂ also increases. As a result maximum rate of bulk sulfation appears at about 0.2 m/s. The concentration of SO₂ in pores of CuO/γ-Al₂O₃ pellet and bulk sulfation rate of alumina support decrease with decreasing particle size.

Keywords: CuO/γ-Al₂O₃ sulfation, TGA, diffusion resistance, gas-solid reaction

Introduction

It is widely recognized that emission of sulfur oxides (SOₓ) from combustion of fossil fuels causes serious air pollution problem. One of the methods to remove SOₓ is to utilize a sorbent with high sorption capacity and faster reactivity with SO₂ gas [1,2]. It is also required that the sulfated sorbent can be easily regenerated and the sorbent maintains the sulfation reactivity after repeated sulfation-regeneration cycles [3-6]. In this regards, CuO/γ-Al₂O₃ sorbent is one of the promising sorbent/catalyst to remove SOₓ from flue gases.

The early studies for sulfation reaction with CuO/γ-Al₂O₃ sorbent have been carried out [7-9] based on the principal assumption that the alumina support is inactive to SO₂ gas. This assumption is valid for lower concentrations of SO₂ gas and lower reaction temperatures. Recently, it has been reported that the alumina support participates in sulfation reaction via catalytic action of the loaded CuO [10] and sulfate species on alumina site play a key role in selective catalytic reduction (SCR) of NOₓ [3,11,12,22]. Sulfation characteristics of CuO/γ-Al₂O₃ sorbent have been classified into three types [1] namely surface, deep, and bulk sulfations according to the reaction temperature and CuO loading. The maximum sulfation capacity of CuO/γ-Al₂O₃ sorbent by the bulk sulfation can be attained about 10 times higher than that by the surface sulfation.

The bulk sulfation of CuO/γ-Al₂O₃ sorbent occurs by the reaction of Al₂O₃ support with SO₂ from decomposition of CuSO₄. Since gas species of SO₂ may diffuse from the internal surface of pellet to the main gas stream, the intraparticle or gas film diffusion resistance may affect the bulk sulfation. Therefore, in this study, the effects of particle size and gas velocity on the bulk sulfation rate of CuO/γ-Al₂O₃ sorbent have been determined in a thermogravimetric analyzer (TGA).

Experimental

Sorbent Preparation

The sorbent was prepared by impregnating copper precursor solution into γ-Al₂O₃ 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 solution of Cu(NO$_3$)$_2$·3H$_2$O was mixed with the dried pellets in a rotary vacuum evaporator. After complete evaporation of distilled water in a rotary vacuum evaporator, alumina pellet was removed and then calcined at 600°C in a thermobalance reactor with air-flow. The calcined samples were crushed and sieved to separate a proper size of CuO/γ-Al$_2$O$_3$ sorbent. Copper oxide concentration was selected at 8 wt% based on the dried alumina since this concentration is high enough to form all three types of sulfates depending on the sulfation temperatures [1]. The concentration of loaded CuO was measured by atomic absorption spectrophotometer (A.A). After calcination, the samples were characterized by SEM and electron probe micro analysis (EPMA) to verify the homogeneity of the prepared CuO/γ-Al$_2$O$_3$ samples.

**Experimental Procedure**

Sulfation reaction was carried out in a thermogravimetric analyzer (TGDTA92 thermoanalyzer, SETARAM, France) as shown in Figure 1. The experimental system consists of three sections; reactor, weight detector, and gas analyzer. A sample basket was filled with 30 mg of calcined sorbent and was lowered into the reaction zone of thermogravimetric analyzer. After reaction temperature reached steady state with air-flow, SO$_2$ gas (15000 ppm) was introduced into the reactor with a variation of air-flow rate. The weight variation of sample with reaction time was recorded in a personal computer.

**Results and Discussion**

**Bulk Sulfation**

Variation of sulfur removal capacity of the different sorbents as a function of reaction time at 500°C is shown in Figure 2. The sample weight of 8 wt% CuO/silica-alumina (87:13 wt%) pellet (3 mm × 3 mm) increases with increasing reaction time. The sample weight does not vary after 2 h since all copper oxide is converted to CuSO$_4$ and silica-alumina support is inactive to SO$_2$ gas. Also, sulfation reaction of alumina support does not occur after 2 h. The sulfur removal capacity of alumina support is about 0.05 g-SO$_2$/g-alumina, that is a similar value as found previously [13]. However, SO$_2$ removal capacity of CuO/γ-Al$_2$O$_3$ sorbent is much higher than that of other sorbents and sulfation rate by CuO/γ-Al$_2$O$_3$ sorbent remains constant after 1 h for the next 4 h without saturation. This is caused by the reaction of
Figure 2. Variation of SO$_2$ removal capacity of different sorbents as a function of reaction time at 500°C and 1.5% SO$_2$.

Figure 3. S/Cu mole ratio of 8 wt% CuO/γ-Al$_2$O$_3$ sorbent as a function of reaction time with a variation of gas flow rate at 550°C.

alumina support with SO$_2$ decomposed from CuSO$_4$, which is defined as the bulk sulfation in our previous study [1].

Effect of Gas Velocity

The S/Cu mole ratio of 8 wt% CuO/γ-Al$_2$O$_3$ sorbent as a function of reaction time with a variation of gas flow rate at 550°C is shown in Figure 3. With increasing gas flow rate, S/Cu mole ratio of the sorbent after 2 h increases up to 800 cc/min ($U_g = 0.23$ m/s). Also, the bulk sulfation of CuO/γ-Al$_2$O$_3$ does not occur at 2000 cc/min ($U_g = 0.57$ m/s) and sulfation of alumina does not proceed.

The effect of $U_g$ on the initial and bulk sulfation rates of 8 wt% CuO/γ-Al$_2$O$_3$ is shown in Figure 4. The initial sulfation rate of CuO/γ-Al$_2$O$_3$ increases up to $U_g = 0.23$ m/s and then remains constant with a further increase in gas velocity. This may imply that gas film resistance of the reactant particles decreases with increasing $U_g$ and disappears at higher $U_g$ as in case of conventional gas-solid reactions [14]. As can be seen in Figure 4, the initial sulfation rate qualitatively agrees with the reported data of previous studies [14-16].

The bulk sulfation rate is defined as SO$_2$ removal rate of the sorbent after sulfation time of two hours because sulfation of CuO/γ-Al$_2$O$_3$ sorbent occurs mainly at the alumina support. However, it exhibits a maximum value at $U_g$ around 0.23-0.34 m/s and then decreases with a further increase in $U_g$. This indicates that the effect of $U_g$ on bulk sulfation of CuO/γ-Al$_2$O$_3$ sorbent is different from that of conventional gas-solid reactions. As reported by Yoo and coworkers [1], the bulk sulfation is caused by the reaction of alumina support with SO$_2$ that is decomposed from CuSO$_4$. Therefore, slight increase of $U_g$ enhances diffusion rate of SO$_2$ into the sorbent and consequent increase in bulk sulfation rate up to $U_g = 0.23$ m/s (800 cc/min). Also, with increasing $U_g$ above 0.23 m/s, the outward diffusion rate of SO$_2$ increases from intraparticles of the sorbent and concentration of SO$_2$ in pores of CuO/γ-Al$_2$O$_3$ sorbent becomes lower. This leads to the decrease of the bulk sulfation rate of the sorbent and may implicate that the bulk sulfation of CuO/γ-Al$_2$O$_3$ sorbent could be controlled by the outward diffusion of SO$_2$. 

Figure 4. Effect of gas velocity on the initial and bulk sulfation rates of 8 wt% CuO/γ-Al$_2$O$_3$ sorbent at 550°C.
Effect of Particle Size (dp)

The effect of particle size on the initial sulfation rate of 8 wt% CuO/γ-Al₂O₃ sorbent at 550°C with 1.5% SO₂ is shown in Figure 5. The initial sulfation rate increases with decreasing dp as reported previously [17]. The difference of the absolute value between the present and previous studies of Centi and coworkers [17] may come from the different concentration of CuO loading. Reduction of dp reduces the value of Thiele modulus that consists of particle radius, the rate constant and gas diffusivity [R(κ/Dp)₁/₂] and SO₂ concentration in pore surface of particles becomes similar to that of the main stream. Therefore, large reduction of dp can cause the change of rate controlling step from the product layer diffusion to the chemical reaction step [18].

The S/Cu mole ratio of 8 wt% CuO/γ-Al₂O₃ sorbent (dp = 220 μm) at 900 cc/min as a function of reaction temperature is shown in Figure 6. Since the bulk sulfation occurs quite rapidly, gas flow rate is determined based on the results of Figure 4. As can be seen, the amount of captured SO₂ by CuO/γ-Al₂O₃ sorbent increases with increasing the reaction temperature up to 450°C and then remains constant. This result shows that bulk sulfation of alumina support does not occur at 500°C with dp of 220 μm, which suggests that particle size of CuO/γ-Al₂O₃ sorbent affects the bulk sulfation rate of alumina support.

The effect of particle size on sulfur removal capacity of 8 wt% CuO/γ-Al₂O₃ sorbent at 550°C with 1.5% SO₂ is shown in Figure 7 with the data of previous studies [17,19,20] at Uₘ of 0.23 m/s (800 cc/min) to eliminate gas film resistance of the sample. As can be seen, SO₂ sorption capacity of the calcined limestone decreases with increasing dp due to the formation of solid product in external surface of the calcined limestone particles. This result reflects the increase of intraparticle diffusion resistance reduces the inward diffusion rate of SO₂ gas [19,20]. In the results of Centi and coworkers [17], SO₂ removal capacity of CuO/γ-Al₂O₃ sorbent decreases with increasing dp because the continual sulfation reaction of alumina support does not occur below 350°C. However, SO₂ removal capacity of CuO/γ-Al₂O₃ sorbent at 550°C increases with increasing dp up to 3500 μm, that
is a reverse phenomenon of the typical gas-solid reaction. It has been known that particle size is an important factor to determine the rate-controlling step of gas-solid reactions. In the intraparticle diffusion control regime, diffusion resistance inside the particles governs the overall reaction rate of sulfation at a sharp interface between the reacted and the unreacted zones. Therefore, SO₂ removal capacity of sorbent decreases with increasing \( d_p \) as much as the diffusion rate decreases. Bulk sulfation of alumina support is caused by reaction of SO₂ species with alumina support. Therefore, increasing \( d_p \) also inhibits outward diffusion of SO₂ species, which provide more reaction time with alumina. Consequently, sulfur removal capacity by the bulk sulfation increases with increasing \( d_p \).

The effect of sample weight on the S/Cu mole ratio with 8 wt% CuO/γ-Al₂O₃ sorbent (\( d_p = 220 \mu m \)) at 500°C is shown in Figure 8 with the data of a packed bed reactor. As can be seen, the initial sulfation rate decreases with increasing sample weight of CuO/γ-Al₂O₃ up to 56 mg that is consistent with the data of previous studies [14,21]. As shown in Figure 6, bulk sulfation of CuO/γ-Al₂O₃ (\( d_p = 220 \mu m \)) does not occur at \( U_g = 0.26 \text{ m/s (900 cc/min).} \) However, the bulk sulfation rate of CuO/γ-Al₂O₃ sorbent (\( d_p = 220 \mu m \)) increases up to the sample weight of 56 mg. It is also noted that the bulk sulfation rate becomes higher when \( U_g \) decreases to 0.028 m/s (100 cc/min). In a packed bed reactor test, bulk sulfation of CuO/γ-Al₂O₃ (\( d_p = 220 \mu m \)) is also observed. As can be seen in Figure 8, the initial sulfation rate of CuO/γ-Al₂O₃ (space velocity = 15000 hr⁻¹) is significantly lower

in a packed bed reactor, however, the amount of captured SO₂ by CuO/γ-Al₂O₃ sorbent becomes higher with increasing sulfation time. Therefore, we can conclude that the bulk sulfation of alumina support can be achieved with increasing sample weight that increases the external mass transfer resistance.

**Conclusions**

The effects of particle size and gas velocity on bulk sulfation of alumina support in CuO/γ-Al₂O₃ sorbent have been determined in a thermogravimetric analyzer (TGA). The maximum bulk sulfation rate of CuO/γ-Al₂O₃ sorbent appears at gas velocity of 0.23 m/s and the bulk sulfation rates become slower at higher gas velocities. Bulk sulfation of alumina support is determined from concentration of SO₂ in pores of CuO/γ-Al₂O₃ particle based on the competition of outward diffusion rate of SO₂ with sulfation rate between Al₂O₃ and SO₂ through product layer of Al₂(SO₄)₃. Therefore, reduction of external gas film resistance of particles at higher gas velocities enhances the rate of outward diffusion of SO₂ and lowers the concentration of SO₂ in pores of particles. Bulk sulfation rate of CuO/γ-Al₂O₃ sorbent increases with increasing particle size and sample weight. Consequent increase of intraparticle and external diffusion resistances enhances bulk sulfation of the alumina support at lower gas velocities.

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**References**