

Sulfation of Al_2O_3 in Flue Gas Desulfurization by $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ Sorbent

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Deep sulfation of alumina support in flue gas desulfurization by $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ sorbent causes a detrimental effect on stability and regeneration of the sorbent since regeneration of sulfated sorbent requires higher temperatures. To define the sulfation characteristics of alumina support in $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$, the effects of temperature, CuO loading, and addition of NaCl on sulfation of alumina support have been determined in a thermobalance reactor. The sulfation degree of alumina support in terms of the amount of sulfate ions present on the support can be classified into three types (surface, slightly deep, and bulk sulfations) as a function of reaction temperature and CuO loading. Surface sulfation (sulfate ions $< 2.0 \times 10^{18}$ ions/ m^2) occurs at CuO loading between 2 and 11 wt % at reaction temperature 250–350 °C, slightly deep sulfation (2.0×10^{18} ions/ $\text{m}^2 < \text{sulfate ions} < 3.4 \times 10^{18}$ ions/ m^2) occurs with the loading below 4 wt % at 350–600 °C, and bulk sulfation (3.4×10^{18} ions/ $\text{m}^2 < \text{sulfate ions}$) occurs at the loading above 6 wt % at 450–600 °C. The bulk sulfation of alumina occurs in the presence of SO_3 decomposed from CuSO_4 . The main product of deep sulfation is $\text{Al}_2(\text{SO}_4)_3$ which is identified by the X-ray diffraction peak at $2\theta = 25.4$. With an addition of 5 wt % NaCl , bulk sulfation occurs at lower temperature by 50 °C and lower CuO loading by 2 wt % CuO .

Introduction

Emission of SO_x from combustion of fossil fuels causes air pollution problems. Various sorption processes are under operation to remove SO_x from flue gases. Dry regenerative processes using sorbents are considered as alternatives to the once-through limestone scrubbing process (Kiel et al., 1992). It has been found that $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ sorbent is the effective means to remove SO_2 since sulfation and regeneration reactions readily occur (Dautzenberg and Nader, 1971; Lowell et al., 1971; McCrea et al., 1970).

Several investigators (Dassori et al., 1988; Cho and Lee, 1983; McCrea et al., 1970) studied the sulfation reaction of $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$. In previous studies, however, the participation of alumina support in sulfation reaction is neglected with the assumption that all the sulfates formed on CuO . Recently, Centi et al. (1990) paid special attention to the catalytic function of CuO when $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ sorbent is sulfated at 250–350 °C. They reported that deep sulfation of alumina occurred above 320 °C to form aluminum sulfate which cannot be regenerated by 2% H_2 gas below 420 °C (Centi et al., 1992). Thus, higher reaction temperatures and concentrations of H_2 are needed to regenerate sulfated alumina. However, these severe reaction conditions are unfavorable because of the large difference between sulfation and regeneration temperatures which may result in thermal shock of sorbent and higher operating cost (McCrea et al., 1970). In the commercial Shell process (Dautzenberg and Nader, 1971), sulfation temperature is same as the regeneration temperature at 400 °C. Thus, it is important to identify the conditions at which deep sulfation of alumina occurs in order to design the efficient SO_2 removal and regeneration systems. However, the criteria and causes of the surface and deep sulfations have not yet been defined.

In this study, the effects of CuO loading, sulfation temperature, and addition of NaCl on the deep sulfation of alumina support in a $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ sorbent have been determined. Also, the criteria between the surface and deep sulfations are identified.

Experimental Section

Sorbent Preparation. The support used for sulfation reaction was 3-mm \times 3-mm cylindrical pellet type $\gamma\text{-Al}_2\text{O}_3$ (STREM Chemical, USA). It was dried at 110 °C for 24 h and allowed to cool in a desiccator. The copper ions were impregnated in a rotary vacuum evaporator which contained a known mass of dried $\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ for 5 h. The impregnated alumina pellet was calcined at 600 °C in a thermobalance reactor under air flow. Copper oxide loading in the calcined sorbent was varied between 2 and 11 wt % based on dry alumina. The uniformity of CuO distribution in $\gamma\text{-Al}_2\text{O}_3$ was verified by using SEM and EDAX. The BET surface area of the calcined sorbent was found to be in the range of 130–210 m^2/g .

Experimental Procedure. Sulfation reaction was carried out in a thermobalance reactor as shown in Figure 1. The experimental system consists of two sections: reactor and weight detector. The details of the thermobalance reactor can be found elsewhere (Kwon et al., 1988). When the system reached steady state at a desired temperature and an air flow rate, calcined sorbent (1.5 ± 0.05 g) suspended in a sample basket was lowered into the reaction zone of the thermobalance reactor using a winch assembly. After drying the sorbent for 10 min in the reaction zone, pure SO_2 gas was introduced into the reactor to maintain the concentration of 1.0 vol % SO_2 . An electronic balance was used to monitor the weight variation of the sample with time. The signal from the balance was recorded on a personal computer. After completion of sulfation reaction, physical properties of sulfated samples (surface area, pore volume, pore size distribution) and their crystal structures were determined by the BET and XRD techniques, respectively.

Results and Discussion

Physical and Chemical Characteristics of Fresh and Sulfated Sorbent. Surface area and pore volume of the sorbents with different CuO loadings are summarized in Table 1. The loading of CuO is assumed to be a linear function of copper nitrate concentration in the solution

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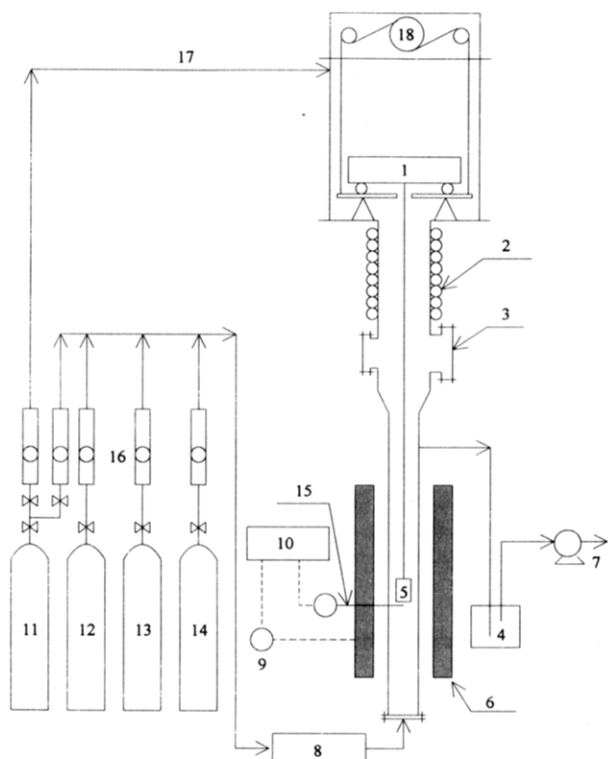


Figure 1. Schematic diagram of the thermobalance: 1, electronic balance; 2, cooling line; 3, hatch; 4, SO₂ trap; 5, sample basket; 6, electrical heater; 7, vent line; 8, preheater; 9, variable transformer; 10, temperature controller; 11, N₂; 12, air; 13, SO₂; 14, H₂; 15, thermocouple; 16, flowmeter; 17, purge line; 18, winch assembly.

Table 1. Physical Properties of Calcined Sorbent

	surf. area (m ² /g)	measd pore vol (cm ³ /g)	calcd pore vol (cm ³ /g)	% reduc- tion of pore vol ^a	Cu ions per unit area (ions/m ²)
pure alumina	196.5	0.427			
2 wt % CuO	196.1	0.422	0.424	0.47	0.8×10^{18}
4 wt % CuO	190.4	0.416	0.421	1.20	1.6×10^{18}
6 wt % CuO	186.6	0.407	0.418	2.70	2.3×10^{18}
8 wt % CuO	173.0	0.384	0.415	8.10	3.1×10^{18}
11 wt % CuO	163.0	0.366	0.410	12.0	4.3×10^{18}

^a (Calculated - measured)/measured \times 100.

for impregnation. Based on the surface area of pure alumina, the number of copper ions on alumina support can be calculated. Small reduction of surface area indicates that most of the impregnated CuO is located within the pores. Pore volume of the sorbents can be calculated from the measured pore volume (0.427 cm³/g) of pure alumina and the density of CuO (6400 kg/m³). The difference of pore volume between the measured and calculated values becomes larger with CuO loading above 8 wt % due to the pore blockage at the entrance of small pores.

Variation of surface area of the 2 and 8 wt % CuO sorbents with sulfation time at 500 °C is shown in Figure 2. Variation of surface area is influenced by the sorption of SO₂ due to the volume expansion of CuO and Al₂O₃ (Nam et al., 1986). The surface area of 2 wt % CuO sorbents decreases about 20% up to 60 min; thereafter it remains constant without further sorption of SO₂. However, the surface area of the sorbent decreases continuously with reaction time with 8 wt % CuO loading. As sulfur content in the sorbent is increased, surface area reduces by ca. 65% with 18.8 wt % sulfur. This may indicate that sulfation of alumina occurs in the sorbent as Nam et al. (1986) previously observed with V₂O₅/alumina catalyst in that surface area decreases continuously over 90% with 12 wt % sulfur due to sulfur absorption by alumina support.

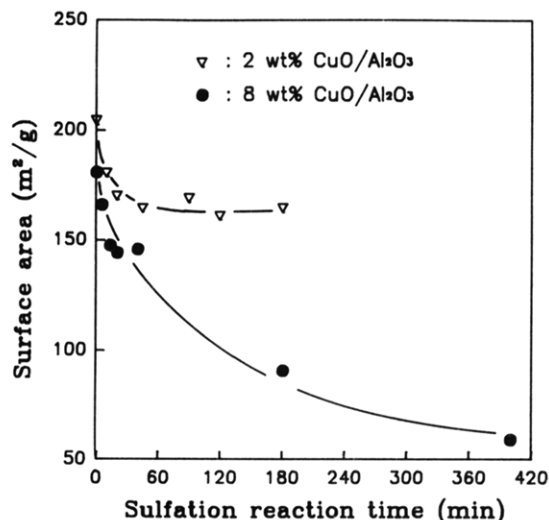


Figure 2. Variation of surface area of sorbent impregnated with 2 and 8 wt % CuO as a function of sulfation time.

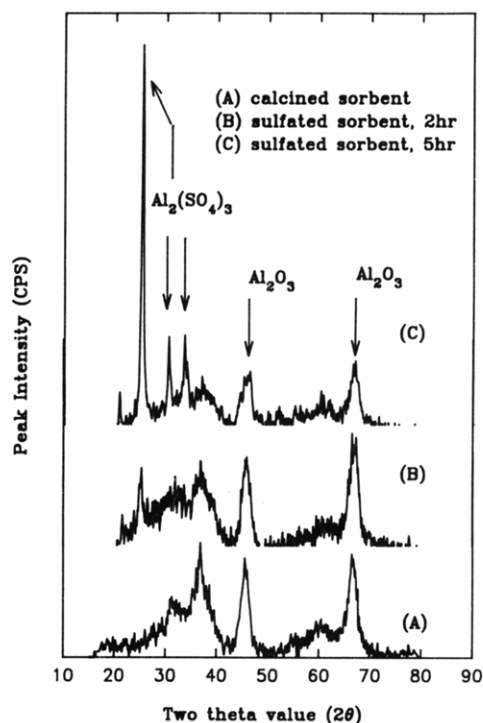


Figure 3. X-ray diffraction peaks of fresh and sulfated sorbent loaded with 8 wt % CuO at 500 °C with sulfation reaction time.

The X-ray diffraction peaks of the fresh and sulfated sorbent of 8 wt % CuO at 500 °C are shown in Figure 3. The peaks of CuO appear at $2\theta = 35.6, 36.7,$ and 38.8 with the CuO loadings above 4 wt % Cu/(100 m²/g sorbent) in CuO/ γ -Al₂O₃ sorbent. As can be seen in Figure 3A, however, a definite crystal phase of CuO does not appear in the calcined sorbent (3.2 wt % Cu/(100 m²/g sorbent)) due to low content and high dispersion of CuO as previously observed by Strohmeier et al. (1985). In Figure 3B,C, the characteristic peak of Al₂(SO₄)₃ begins to appear at $2\theta = 25.4$ after 2 h of sulfation. The peak intensity of Al₂(SO₄)₃ becomes larger and that of alumina (peaks at $2\theta = 45.7$ and 66.5) becomes smaller as sulfation reaction proceeds for 5 h. Therefore, we may conclude that the crystal structure of alumina surface is changed from γ -Al₂O₃ to Al₂(SO₄)₃ phase, which results in an expansion of crystal lattice. This expansion makes new alumina surface accessible to SO₃ that is formed from the decomposition of CuSO₄ (Table 2, reaction 4). The formation of

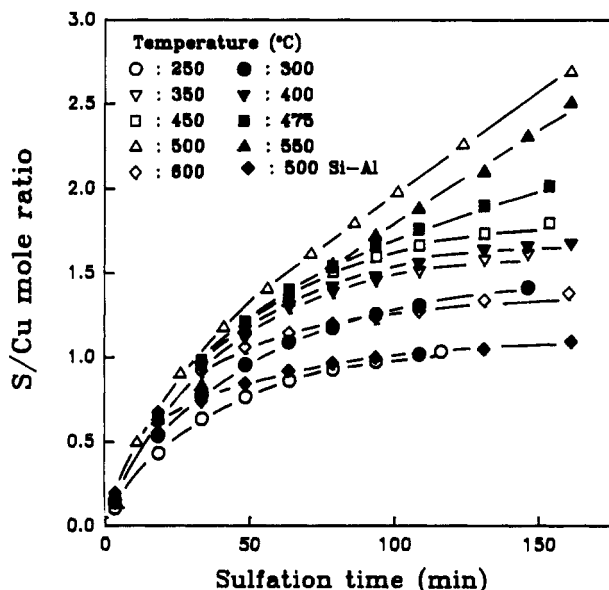


Figure 4. S/Cu mole ratio as a function of reaction time at 250–600 °C with CuO loading of 8 wt %.

Table 2. Basic Reaction Equations of CuO/Al₂O₃

$\text{CuO} + \text{SO}_2 + (1/2)\text{O}_2 \rightarrow \text{CuSO}_4$	(1)
$\text{CuO} - \text{SO}_2 + \text{Al}_2\text{O}_3 \rightarrow \text{Cu} + \text{Al}_2\text{O}_3 - \text{SO}_3$	(2)
$\text{Cu} + (1/2)\text{O}_2 \rightarrow \text{CuO}$	(3)
$\text{CuSO}_4 \leftrightarrow \text{CuO} + \text{SO}_3$	(4)
$\text{Al}_2\text{O}_3 + \text{SO}_3 \rightarrow \text{Al}_2(\text{SO}_4)_3$	(5)
$\text{SO}_3 \rightarrow \text{SO}_2 + (1/2)\text{O}_2$	(6)

aluminum sulfate causes hardening of sulfated sorbent which is not easily regenerated with 2% H₂ in the mild regeneration condition. However, it can be rapidly regenerated above 550 °C with 5% H₂ in N₂ atmosphere, which is confirmed by the disappearance of the peak at $2\theta = 25.4$.

Effect of Temperature on Sulfation Reaction. Variation of the S/Cu mole ratio of the 8 wt % CuO sorbent with reaction time at 250–600 °C is shown in Figure 4 in which S/Cu mole ratio is calculated by the following equation

$$\text{S/Cu} = \frac{(W - W_0)/M_{\text{SO}_3}}{(W_0 C_0)/M_{\text{CuO}}} \quad (1)$$

where W is weight of sorbent at reaction time t , W_0 is initial weight of sorbent, C_0 is weight fraction of loaded CuO, and M_i is molecular weight of species i .

As can be seen in Figure 4, a S/Cu mole ratio of larger than 1.0 is observed in CuO/ γ -Al₂O₃ sorbent at reaction temperature above 250 °C. However, the extent of sulfation of the 8 wt % CuO supported on silica-alumina does not exceed 1.0 since silica support is found not to react with SO₂ (Kiel et al., 1992). Thus, it is concluded that alumina support participates in sulfation reaction above 250 °C with 8 wt % CuO/ γ -Al₂O₃ sorbent as can be seen in Figures 2 and 3.

At reaction temperature below 450 °C, a rapid initial uptake of SO₂ is followed by a somewhat slow reaction and eventually the uptake is saturated. At the reaction temperature between 450 and 600 °C, the sorption rate of SO₂ remains constant after 60 min for the next 4 h and no saturation of S/Cu mole ratio has been observed. This may indicate that the formation of Al₂(SO₄)₃ sharply increases with sulfation time. Above 600 °C, sulfation reaction rate slows down again and sulfation of sorbent does not proceed any more.

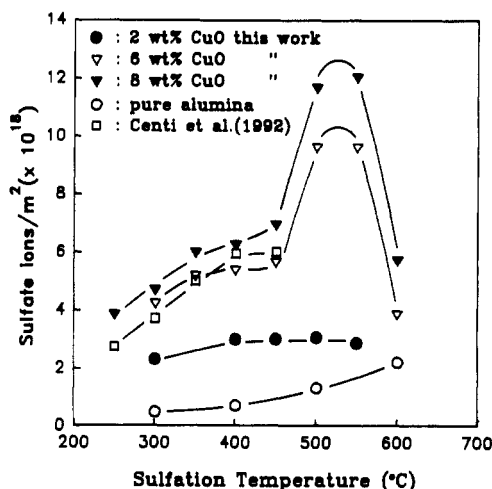


Figure 5. Effect of sulfation temperature on sulfate ions per unit surface area with different CuO loadings.

The effect of sulfation temperature on the SO₂ removal capacity (number of sulfate ions/unit area of sorbent) with different CuO loadings is shown in Figure 5. The removal capacity of pure alumina increases up to 2.0×10^{18} sulfate ions/m² as reported by Nam and Gavalas (1989). The sulfate ions removed by 2 wt % CuO (0.8×10^{18} Cu ions/m²) sorbent increases marginally with increasing temperature up to 400 °C with saturation of sulfate ion at 3.0×10^{18} ions/m². This value is higher than the amount of sulfate species that can be removed by CuO and alumina independently due to the catalytic function of CuO which has been characterized by the deep sulfation in a previous study (Centi et al., 1992).

The deep sulfation starts to occur above 400 °C with the 2 wt % CuO sorbent, whereas it starts to occur above 350 °C with CuO loading above 6 wt %. However, the removed amount of sulfate ions by the sorbent loaded CuO above 6 wt % (2.3×10^{18} Cu ions/m²) varies widely through two different processes, namely, slightly deep and continual deep sulfations, depending on the sulfation temperature. To differentiate the continual deep sulfation from the slightly deep sulfation with saturation, we define the continual deep sulfation phenomena as the bulk sulfation.

In the slightly deep sulfation, SO₂ removal capacity of alumina support is saturated in the range of $(2.0\text{--}3.4) \times 10^{18}$ sulfate ions/m² at the reaction temperature 350–450 °C. In the continual deep or bulk sulfation, the SO₂ removal capacity of alumina is not saturated at 450–600 °C. The amount of sulfate ions reaches the value of $(10\text{--}11) \times 10^{18}$ ions/m², which exceeds significantly the limiting value (2.0×10^{18} ions/m²) of pure alumina.

Reaction Mechanism of CuO/ γ -Al₂O₃ Sulfation. Centi et al. (1992) proposed that the sulfation of alumina can be characterized by surface transfer of SO₃ from Cu to Al sites (Table 2, reactions 2 and 3) with CuO catalyst. It is known that CuO catalyzes the reaction $\text{SO}_2 + (1/2)\text{O}_2 \rightarrow \text{SO}_3$ and eventually becomes inactive copper sulfate (Lowell et al., 1971). When the sulfation reaction proceeds below 450 °C, the inactive copper sulfate forms so that the surface transfer of SO₃ does not occur. Consequently, sulfation reaction of alumina support cannot proceed further. However, above 450 °C, decomposition of inactive CuSO₄ begins to start to produce CuO and SO₃ (Ingraham, 1965). This produced SO₃ reacts with alumina and CuO restores its catalytic activity.

It should also be noticed that the formation of Al₂(SO₄)₃ is continued in the sorbent but not formed in pure alumina

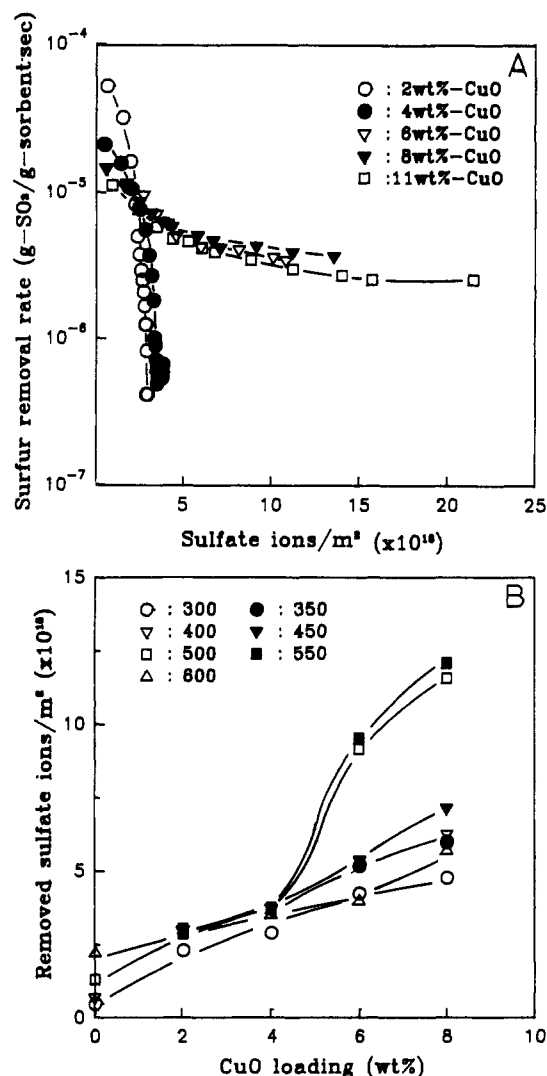


Figure 6. (A) Effect of sulfate ions per unit surface area on sulfur removal rate with different CuO loadings at sulfation temperature 500 °C. (B) Effect of CuO loading on sulfur removal capacity.

at 450–600 °C. In the present study, we also find that bulk sulfation of CuO/ γ -Al₂O₃ sorbent occurs even below 450 °C with SO₃/O₂/N₂ which is obtained from the reaction of SO₂/O₂/N₂ mixture on V₂O₅/K₂SO₄/SiO₂ catalyst (Xie and Nobile, 1985). Even with pure alumina, bulk sulfation also occurs at 500 °C using SO₃/O₂/N₂ mixture as observed by Chang (1978). Thus, it can be claimed that SO₃ plays an important role in the bulk sulfation of alumina.

Based on the present and previous studies (Centi et al., 1992), a qualitative reaction model can be proposed. Surface sulfate is formed by catalytic function of CuO through reaction 2 (CuO-SO₂ + Al₂O₃ → Cu + Al₂O₃-SO₃) and reaction 3 (Cu + (1/2)O₂ → CuO), and sulfation reaction is terminated by reaction 1 (CuO + SO₂ + (1/2)O₂ → CuSO₄) as shown in Table 2. At higher temperatures, the decomposition of CuSO₄ into CuO and SO₃ is in equilibrium by reaction 4 (CuSO₄ ↔ CuO + SO₃) and the bulk sulfation reaction proceeds by reaction 5 [Al₂O₃ + SO₃ → Al₂(SO₄)₃] in Table 2.

Effect of CuO Concentration on Bulk Sulfation Reaction. The effect of sulfate ions per unit surface area on the sulfur removal rate with different CuO loadings at 500 °C is shown in Figure 6A. With the sorbent loaded with CuO below 4 wt %, the sulfur removal rate decreases rapidly with increasing sulfate ions per unit surface area, and the removed amount of sulfate ions is slightly higher than the sum of copper and alumina ions. Above 6 wt %

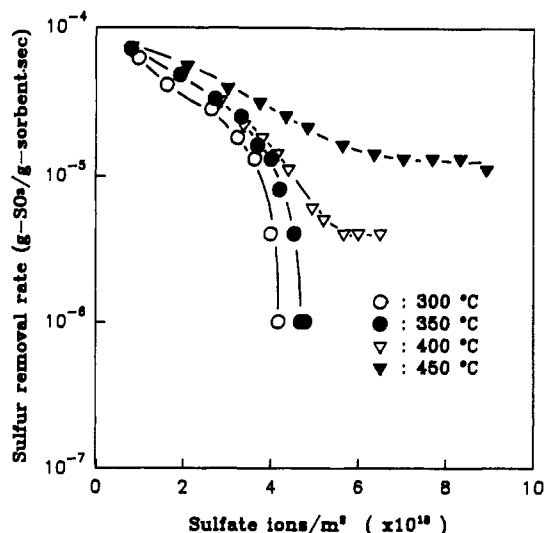


Figure 7. Effect of sulfate ions per unit surface area on sulfur removal rate of 8 wt % CuO/ γ -Al₂O₃ adding 5 wt % NaCl with sulfation temperature.

CuO loading in the sorbent, however, the sulfur removal rate decreases exponentially down to 10⁻⁵ (g of SO₃/(g of sorbent-s)) thereafter it remains constant. As can be seen in Figure 6A, slightly deep sulfation of alumina occurs in the sorbent with CuO loading below 4 wt % and bulk sulfation takes place in the sorbent with CuO loading above 6 wt % at 500 °C.

The effect of CuO loading on the sulfur removal capacity is shown in Figure 6B. Bulk sulfation is dominant with higher CuO loadings at higher reaction temperatures. The effect of CuO loading on bulk sulfation can be attributed to crystallite size of CuO and strong bonding interaction between Cu and Al. The crystallite size of CuO decreases as CuO loading is decreased (Strohmeier et al., 1985). Thus, the amount of isolated copper ions increases and decomposition of copper sulfate through cupric oxysulfate does not proceed further with decreasing CuO loading. These small CuO particles in the sorbent interact with alumina support and form copper aluminate-like species (Strohmeier et al., 1985). If the sulfate is bridged to both the Cu and Al sites instead of directly bonding to the copper site only, the decomposition of sulfate species to SO₃ is retarded since the bond strength between alumina and SO₂ is stronger than that between CuO and SO₂. The sulfate bridged on both Cu and Al sites in CuAl₂O₄ spinel structure is also observed by Waqif et al. (1991). Without SO₃, no bulk sulfation occurs even at higher temperatures. With lower CuO loadings, SO₃ cannot be obtained even at higher temperatures due to strong interaction between CuO and alumina. Thus, in the present study, SO₃ is formed when CuO loading is higher than 6 wt %.

Effect of Alkali Salt Addition on Bulk Sulfation Reaction. It has been found that the addition of NaCl on the sorbent reduces the decomposition temperature of sulfate compound and consequent increase in the rate of decomposition (Mu and Perlmutter, 1981). Therefore, the decomposition temperature of copper sulfate may be reduced so that the bulk sulfation occurs at lower temperature by the addition of NaCl.

The sulfur removal rate as a function of sulfate ions per unit surface area with the sorbent loaded with 8 wt % CuO and 5 wt % NaCl is shown in Figure 7. The removal rate decreases with increasing sulfate ions per specific surface area below 400 °C, but the rate remains constant above 400 °C. Therefore, the bulk sulfation occurs at lower

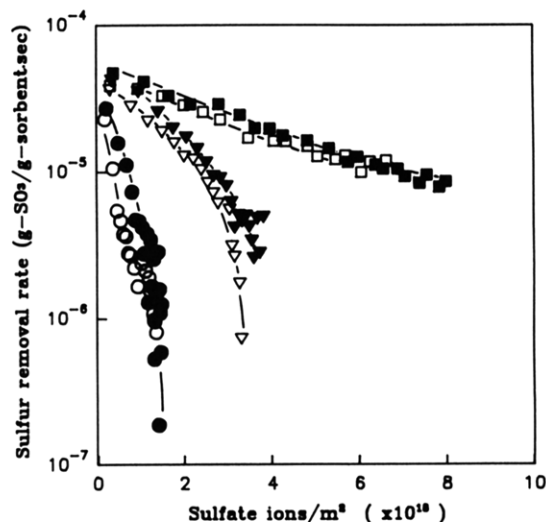


Figure 8. Effect of sulfate ions per unit surface area on sulfur removal rate with variation of NaCl loading: (○) pure γ - Al_2O_3 ; (●) pure γ - Al_2O_3 + 5 wt % NaCl; (▽) 4 wt % CuO/ γ - Al_2O_3 ; (▼) 4 wt % CuO/ γ - Al_2O_3 + 2 wt % NaCl; (□) 4 wt % CuO/ γ - Al_2O_3 + 5 wt % NaCl; (■) 4 wt % CuO/ γ - Al_2O_3 + 8 wt % NaCl.

temperatures since the decomposition temperature of copper sulfate decreases with the addition of NaCl.

The decomposition temperature of pure CuSO_4 is found to be 600 °C, and that of $\text{Al}_2(\text{SO}_4)_3$ is above 700 °C in N_2 atmosphere. On the other hand, an equal mixture of NaCl and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ decompose above 400 °C as observed by Mu and Perlmuter (1981). On the basis of these findings, we can claim that the addition of NaCl lowers the decomposition temperature of copper sulfate and enables the production of SO_3 even above 400 °C.

The effect of sulfate ions per unit surface area on the sulfur removal rate (sulfation reaction rate) with different NaCl loadings is shown in Figure 8. Since the sorbent loaded with 5 wt % NaCl has the same sulfation rate as the pure alumina, NaCl has no reactivity on desulfurization reaction. In case of 4 wt % CuO/ γ - Al_2O_3 sorbent, the reaction rate is higher than that of pure alumina due to the catalytic activity of CuO. The addition of 2 wt % NaCl to the sorbent slightly enhances the rate of sulfation reaction. With increasing NaCl loading up to 5 wt %, the surface sulfation is shifted to the bulk sulfation with the same removal rate of 8 wt % CuO sorbent (10^{-5} g of SO_3 /(g of sorbent-s)). The change of reaction type in the sorbent may be caused by the reduction of bonding interaction between copper and aluminum ions since the addition of sodium ions to alumina increases the dispersion of loaded copper ions. Thus, an interaction between copper and alumina decreases with the addition of NaCl, and SO_3 is easily formed by the decomposition of CuSO_4 .

The effects of sulfation temperature and CuO loading on the sulfation types of the sorbent are shown in Figure 9A along with the data of Centi et al. (1992). Sulfate ions removed by alumina increase with increasing sulfation temperature and CuO loading which are represented by a three-dimensional diagram as shown in Figure 9B. The degree of sulfation of alumina support in terms of the amount of sulfate ions present on the support can be classified into three types (surface, slightly deep, and bulk sulfations) as a function of reaction temperature and CuO loading. Surface sulfation (sulfate ions $< 2.0 \times 10^{18}$ ions/ m^2) occurs at CuO loading between 2 and 11 wt % at reaction temperature 250–350 °C; slightly deep sulfation (2.0×10^{18} ions/ $\text{m}^2 <$ sulfate ions $< 3.4 \times 10^{18}$ ions/ m^2) is dominant with CuO loading below 4 wt % at reaction

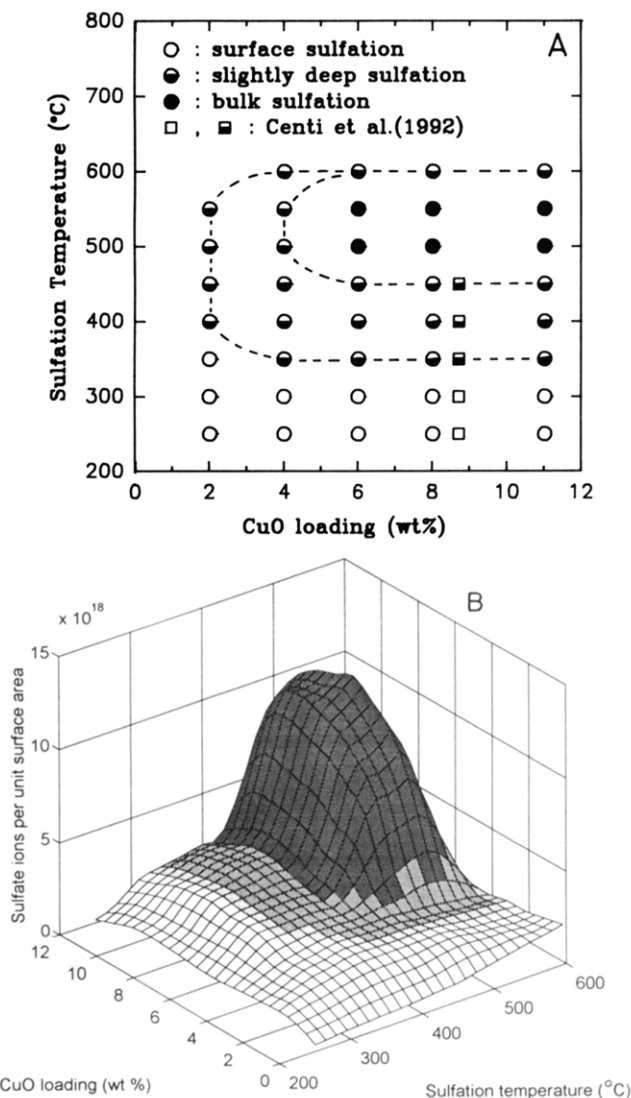


Figure 9. (A) Effect of temperature and CuO loading on sulfation types of CuO/ γ - Al_2O_3 sorbent. (B) Three-dimensional diagram for sulfation of alumina as a function of reaction temperature and CuO loading.

temperature 350–600 °C. With the loading above 4 wt %, the range of reaction temperature is narrowed down to 350–450 °C. Finally, the bulk sulfation (3.4×10^{18} ions/ $\text{m}^2 <$ sulfate ions) proceeds with CuO loading above 6 wt % at reaction temperature between 450 and 600 °C.

Conclusions

Three different types (surface, slightly deep, and bulk sulfations) of sulfation reactions of alumina in CuO/ γ - Al_2O_3 have been determined as a function of CuO loading and reaction temperature. Surface sulfation (sulfate ions $< 2.0 \times 10^{18}$ ions/ m^2) occurs at CuO loading between 2 and 11 wt % at reaction temperature 250–350 °C, slightly deep sulfation ($2.0 \times 10^{18} <$ sulfate ions $< 3.4 \times 10^{18}$ ions/ m^2) occurs with the loading below 4 wt % at 350–600 °C, and bulk sulfation (3.4×10^{18} ions/ $\text{m}^2 <$ sulfate ion) occurs at the loading above 6 wt % at 450–600 °C. The temperature range of slightly deep sulfation is narrowed down to 350–450 °C with CuO loading above 4 wt %. With the addition of 5 wt % NaCl, bulk sulfation begins to occur at lower temperature by 50 °C and lower loading by 2 wt % CuO. Regardless of the addition of NaCl, the bulk sulfate is mainly composed of $\text{Al}_2(\text{SO}_4)_3$ of which the XRD peak appears at $2\theta = 25.4$. The surface area reduction of the sorbent in bulk sulfation is larger than that in the surface sulfation.

Acknowledgment

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