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Sulfation behavior of CuO/γ-Al$_2$O$_3$ sorbent for the removal of SO$_2$ from flue gas

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Abstracts: CuO/γ-Al$_2$O$_3$ has been considered as a promising and recycling sorbent to remove sulfur dioxide from flue gas. In this study, a series of CuO/γ-Al$_2$O$_3$ sorbents with different CuO loadings were prepared by impregnation. The monolayer coverage of CuO supported on γ-Al$_2$O$_3$ determined by X-ray quantitative analysis was 0.275 g CuO/g (γ-Al$_2$O$_3$). Below the monolayer coverage, CuO was found highly dispersed on γ-Al$_2$O$_3$. Thermogravimetric technique was used to study sulfation kinetics and sulfation recycling. It was found that the Langmuir kinetic adsorption model described well the experimental data at the rapid sulfation region of the CuO/γ-Al$_2$O$_3$ sorbent. The adsorption activation energy was 19.98 kJ/mol and the pre-exponential factor was 9.97×10^{-5} s^{-1}·Pa^{-1}. The CuO/γ-Al$_2$O$_3$ sorbent has shown good performance on regeneration, but long sulfation time might cause the deactivation of the CuO/γ-Al$_2$O$_3$ sorbent. It was also seen that the sulfated γ-Al$_2$O$_3$ support could not be reduced at 400°C.

Key words: sulfation; copper oxide; kinetics; monolayer

1. Introduction

In recent years, a great deal of attention has been given to the problem of reducing the level of atmospheric pollution caused by sulfur dioxide emission [1]. Currently, the primary method of SO$_2$ disposal from flue gas is a scrubbing process with calcium-based sorbents, in which the solid product produced as a result of scrubbing SO$_2$ has to be disposed. This, of course, results in additional operating costs. It has been found that CuO/γ-Al$_2$O$_3$ is a promising adsorbent to remove SO$_2$ from flue gas. Most current power plants use two separate facilities or technologies to reduce SO$_x$ and NO$_x$ emissions. The copper oxide technology can reduce both SO$_x$ and NO$_x$ in a single unit, which has the advantage of lower costs than separate technologies when high SO$_x$ and NO$_x$ removals are required. The copper oxide technology will also be able to turn the captured SO$_x$ into high valued by-products such as sulfuric, ammonia sulfate, and concentrated SO$_2$ gas, which can compensate the

process costs. Finally, because the copper oxide technology is a dry and regenerable process it will not generate solid waste that leads to landfill. It has been shown that metal oxides dispersed as monolayer on a support can have different activities from bulk materials [2]. Centi *et al*. [3-4] reported that there existed a catalytic function of CuO when the CuO supported on γ-Al$_2$O$_3$ was sulfated at 250-350°C. They reported that the conversion ratio of all CuO to CuSO$_4$ was above 1.0 in thermobalance experiments. And they also indicated that the reason was direct participation of the support in the reaction. The mechanism could be described as a stage of catalytic oxidation of SO$_2$ to SO$_3$ with two consecutive parallel pathways of the formation of copper sulfate or aluminum sulfate. According to the reaction mechanism, an integral kinetic model, which included the sulfation of γ-Al$_2$O$_3$, was proposed. After the adsorption of SO$_2$, the CuO supported on γ-Al$_2$O$_3$ is converted into CuSO$_4$ and must be regenerated for reusing. The regeneration efficiency is closely related to subsequent sulfur removal activity and sta-

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bility of the sorbent. Till date, the regeneration methods for the sulfated CuO/γ-Al$_2$O$_3$ sorbent are mainly thermal decomposition and reductive regeneration [5]. Because thermal decomposition has to be carried out at a temperature much higher than that of sulfation, the sorbent suffers from the loss of sulfur removal activity and shortening of life span. The reductive regeneration is regarded to be better than the thermal decomposition because of relatively low regeneration temperatures.

Although the sulfation kinetics has been studied, the kinetic model is too complicated. Further study shows that Langmuir adsorption kinetics model can be used to describe the sulfation of sorbent. In addition, sulfation time plays an important role in the regeneration of sulfated sorbent. In the present work, the dispersion of CuO supported on γ-Al$_2$O$_3$ was characterized by X-ray diffraction (XRD). Sulfation kinetics and sorbent recycling through reductive regeneration were investigated by thermogravimetry technology.

2. Experimental

2.1. Materials and preparation of sorbents

Cu(NO$_3$)$_2$·3H$_2$O and KCl were of high purity and commercially available. γ-Al$_2$O$_3$ (the Brunauer-Emmett-Teller (BET) specific surface area: 277.8 m^2/g) was obtained from SINOPEC. The CuO/γ-Al$_2$O$_3$ sorbent was prepared by impregnating a known mass of γ-Al$_2$O$_3$ with the solution containing a calculated amount of Cu(NO$_3$)$_2$·3H$_2$O. It was kept in static condition for 1 h at room temperature, followed by evaporation at 90°C with stirring. Then, the samples were dried in an oven at 120°C for 24 h, and subsequently calcined at 450°C in stagnant air for 5 h in a muffle furnace to convert Cu(NO$_3$)$_2$ to CuO. Thus, the sorbents containing 0.12, 0.35, 0.40, 0.50, and 0.55 g CuO per gram γ-Al$_2$O$_3$ were obtained, which were labeled as 0.12CuAl, 0.35CuAl, 0.40CuAl, 0.50CuAl, and 0.55CuAl, respectively. The calculated typical gas composition was 0.2vol% SO$_2$, 5vol% O$_2$, 3vol% H$_2$O, and N$_2$ was used as the balance. About 50 mg of sorbent particles in 20-80 μm were used in each run. Under these conditions mass transfer effects were negligible.

2.2. Experimental procedure and measurements

Sulfation tests were carried out in a thermogravimetric setup as shown in Fig. 1. The experimental setup consists of four sections: reactor, feeding system, analytical balance, and heating system. The output signals corresponding to weight changes are automatically recorded in a computer. A sample pan loaded with 50 mg of sorbent was placed into the re-

action zone and then was heated to the desired temperature. Through a gas feeding system, a protective gas Ar flew into the room of the analytical balance and the humidified mixture of N$_2$ and O$_2$ flew into the reactor. After the weight change of the sample reached a steady state, SO$_2$ was introduced into the reactor.
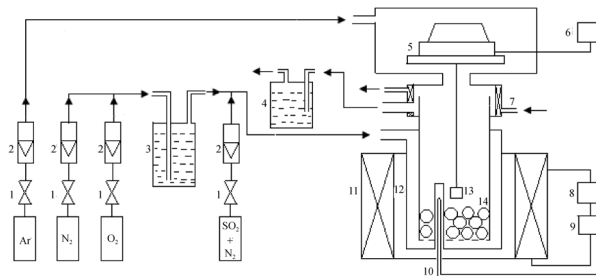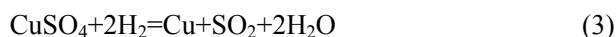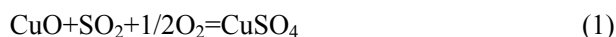

Fig. 1. **Diagram showing the experimental setup: 1—pressure indicator; 2—flowmeter; 3—humidifier; 4—SO$_2$ trapper; 5—mettler AT100; 6—recorder; 7—water cooling inlet; 8—power supply; 9—controller; 10—thermocouple; 11—tubular furnace; 12—quartz reaction reactor; 13—quartz pan; 14—quartz spheres.**

The regeneration of the sulfated CuO/γ-Al$_2$O$_3$ sorbent was carried out in the same apparatus in 5vol% H$_2$/Ar at the desired reduction temperatures for approximately 3000 s. After regeneration, the reactor was purged with Ar and the temperature was adjusted to a desired sulfation temperature, and Ar was then changed to a humidified mixture of N$_2$ and O$_2$. When the weight change of the sample recovered to a steady state, SO$_2$ flew into the reactor for the consecutive sulfation.

XRD patterns were recorded in the range of 10°≤2θ≤80° by using a D/MAX-γA diffractometer with a Cu K$_\alpha$ radiation (40 kV, 50-100 mA). The Fourier transform infrared spectroscopy (FT-IR, U.S. Nicolet, Avatar 360) was measured in the range of 500-4000 cm^{-1}.

2.3. Data evaluation

The chemical reactions taking place during sulfation and reduction of sorbents are as follows:

$$CuO+SO_2+1/2O_2=CuSO_4 \qquad (1)$$

$$Al_2O_3+3SO_2+3/2O_2=Al_2(SO_4)_3 \qquad (2)$$

$$CuSO_4+2H_2=Cu+SO_2+2H_2O \qquad (3)$$

$$Cu+1/2O_2=CuO \qquad (4)$$

$$Al_2(SO_4)_3+12H_2=Al_2S_3+12H_2O \qquad (5)$$

Δm ($\Delta m=m_t-m_0$) is calculated at each time value, where m_0 is the mass of the sorbent at the start of sulfation, and m_t is the mass of the sorbent at time t. Δm_{max} calculated according to reaction (1) is the maximum weight gain. The conversion ratio $\Delta m/\Delta m_{max}$, corresponding to the surface coverage ra-

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tio θ, is calculated for each time value and plotted as a function of time.

3. Results and discussion

3.1. XRD characterization

Fig. 2 shows the XRD patterns of the CuO/γ-Al$_2$O$_3$ sorbents with different CuO loadings. There are no characteristic peaks seen both in the γ-Al$_2$O$_3$ support and sorbents with a lower CuO loading (curves (1) and (2)). This result indicates that the disappearance of the CuO peaks in the low CuO loading sorbents is because of the high dispersion of the supported species. However, when the CuO loading exceeds a critical value, *i.e.*, the monolayer coverage, the characteristic peaks of crystalline CuO can clearly be detected and the peak intensities increase with increasing CuO loading (curves (3)-(6)). KCl is used as the standard reference material. The monolayer coverage of copper oxide determined by XRD quantitative analysis [6] is 0.275 CuAl. As the metal loading increases, the microparticles of metal oxides form on the γ-Al$_2$O$_3$ support above a monolayer coverage [7], and these microparticles are found to be less active in the sulfation process. Theoretically, monolayer dispersion is highly desired to maximize the amount of active species that can react with SO$_2$, and enhance their sorption capacity for SO$_2$. However, as a result of the size expansion of Cu compound [8], from CuO to CuSO$_4$, and possibly pore plugging by the formed CuSO$_4$, the optimal CuO loading is not at the monolayer coverage. In this study, the 0.12 CuAl sorbent was used in the sulfation kinetics and sorbent recycling experiments.
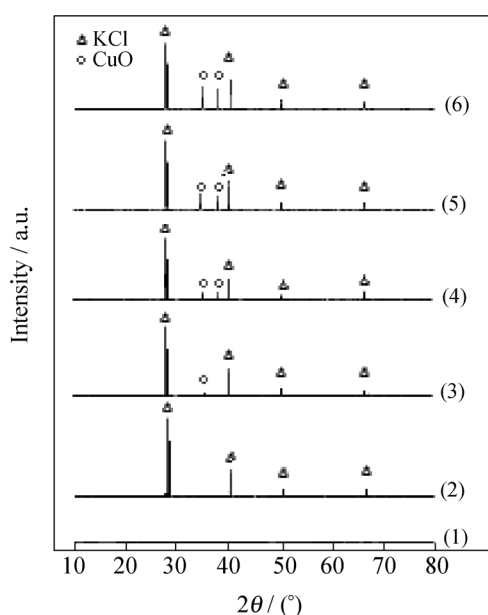

Fig. 2.   XRD patterns of the CuO/γ-Al$_2$O$_3$ samples with different CuO loadings: (1) γ-Al$_2$O$_3$; (2) 0.12 CuAl; (3) 0.35 CuAl; (4) 0.40 CuAl; (5) 0.50 CuAl; (6) 0.55 CuAl.

3.2. Sulfation kinetics of the CuO/γ-Al$_2$O$_3$ sorbent

Fig. 3 shows the influence of temperature on the conversion ratio *versus* time of 0.12 CuAl at a constant SO$_2$ content of 0.2vol%. The sulfation curves exhibits two regions: a rapid sulfation region, which is generally confined to the first 3000 s of sulfation, and a slow sulfation region in which the conversion either levels off or continues at a slow rate because of the bulk sulfation of alumina. The sulfation of CuO and γ-Al$_2$O$_3$ follows reactions (1) and (2), respectively. The sulfation rate of the 0.12 CuAl sorbent increases when the temperature is raised.
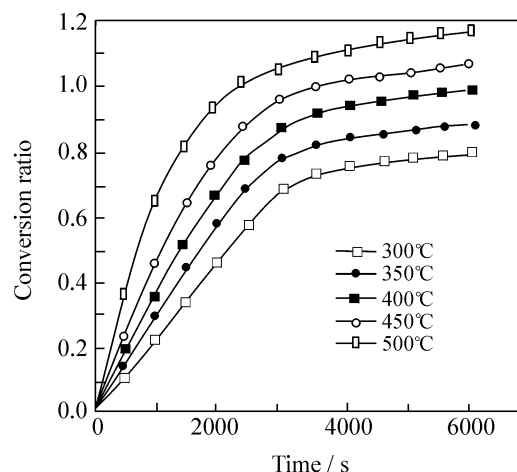

Fig. 3.   Influence of temperature on the conversion ratio.

Several model equations were proposed to describe the solid-gas adsorption kinetics [9]. These models can be grouped into three main categories: (1) Langmuir model, (2) Elovich model, and (3) Banham model.

The sulfation process is a special form of gas-solid reaction. Sulfur dioxide molecules are adsorbed and react with CuO in the presence of oxygen molecules. The increase in mass at the rapid sulfation region can be attributed to the formation of a monolayer of the product. The simple Langmuir kinetics adsorption model, based on localized monolayer adsorption, is expected to describe the SO$_2$ adsorption kinetics data in the rapid sulfation region. The Langmuir kinetics model can be simplified as follows:

$$d\theta/dt = K_{ad}P(1-\theta) \qquad (6)$$

Integrating Eq. (6) gives the following equation for the adsorption curve:

$$\ln(1-\theta) = -K_{ad}Pt \qquad (7)$$

where θ is the surface coverage ratio, K_{ad} the adsorption rate constant, P the partial pressure of SO$_2$, and t the adsorption time.

According to Eq. 6, the reduction of the conversion

ratio can be as a result of the increasing coverage of the surface with a monolayer of the product, which is consistent with the experimental data (Fig. 3). The modeling of the conversion caused by the reaction between CuO and SO₂ is achieved using Eq. (7) (Fig. 4). A plot of the left-hand side of Eq. (7) *versus* time should yield a straight line. Table 1 gives the resulting kinetic constants and the correlation coefficients from the straight lines least square fit.
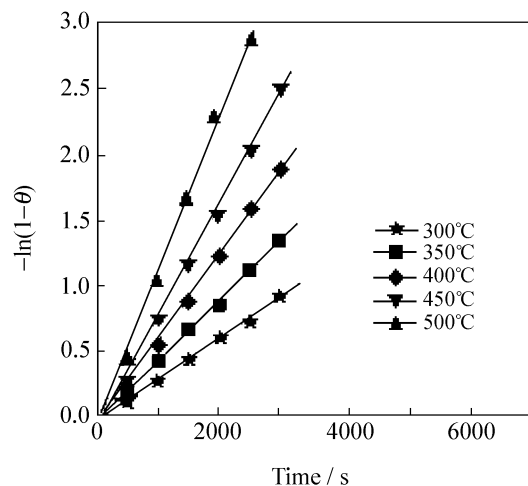

Fig. 4. Influence of temperature on $-\ln(1-\theta)$ *versus* time.

Table 1. Comparison of correlation coefficients for different temperatures

Temperature / °C	K_{ad} / (s⁻¹·Pa⁻¹)	Correlation coefficient
300	1.43×10^{-6}	0.97
350	2.08×10^{-6}	0.98
400	3.12×10^{-6}	0.98
450	3.57×10^{-6}	0.97
500	6.10×10^{-5}	0.99

The values of the correlation coefficients indicate that the least square fits are good. One can see that the slope increases with increasing temperature, expressing the values of K_{ad} as an Arrhenius function.

$$K_{ad} = K_{ad0} \cdot \exp(-E_a/RT).$$

Thus, the adsorption activation energy, E_a, of 19.98 kJ/mol, and a pre-exponential factor, K_{ad0}, of 9.97×10^{-5} s⁻¹·Pa⁻¹ can be obtained.

3.3. Sorbent recycling

To determine the regeneration performance of the CuO/γ-Al₂O₃ sorbent, recycling tests were done. Fig. 5 shows the 0.12 CuAl sorbent subjected to 3 consecutive recycling at 350°C. Reduction of the sulfated CuO/γ-Al₂O₃ sorbent was carried out in 5vol%H₂ at 400°C. There is little difference among these three sulfation curves before 3500 s, which means that copper sulfate can be reduced entirely. Under reducible at-

atmosphere, CuSO₄ will be reduced to Cu according to reaction (3), and Cu will be oxidized to CuO before the next sulfation process occurs according to reaction (4).
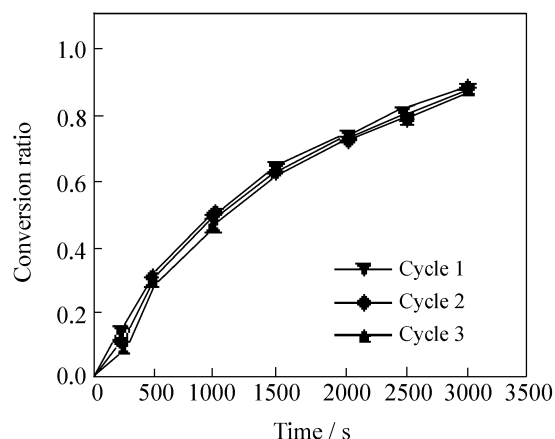

Fig. 5. Influence of sulfation recycling of the 0.12CuAl sorbent.

To allow the participation of γ-Al₂O₃ support in the sulfation process, the sulfation time of the 0.12CuAl sorbent was prolonged under the same conditions. The experimental results are shown in Fig. 6. It clearly indicates that γ-Al₂O₃ participates in the sulfation process. A reasonable explanation is that the sulfation of CuO begins first, followed by the bulk sulfation of γ-Al₂O₃ in a long sulfation time, which cannot be reduced. Then, the bulk sulfation pore volume of the sulfated sorbent decreases due to pore plugging caused by the formation of alumina sulfates [10]. The reaction between CuO and SO₂ is inhibited in the second sulfation process. Alumina sulfate can be reduced at 490°C [11] according to reaction (5), but sulfur still remains in Al₂S₃. Therefore, it is rational to control sulfation time to lower the sulfation of γ-Al₂O₃ support.
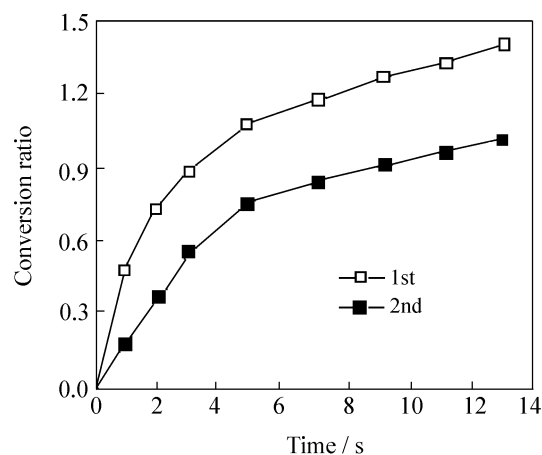

Fig. 6. Effect of the prolonged time on sulfation cycles of the 0.12CuAl sorbent.

3.4. IR analysis

If the reactants are very strongly adsorbed on the

active sites, it will clearly be unreactive, as the chemisorption bond is too strong to be broken. SO_2 can be adsorbed on the Cu sites of the sorbent in the presence of O_2 and the sulfated sorbent can be reduced by H_2. These results show that the chemisorption bond between CuO and SO_2 is appropriate. In the case of 0.12 CuAl sorbent, CuO loading is below the monolayer coverage, and a lot of naked hydroxyls are left on the surface. The γ-Al_2O_3 support can be sulfated upon SO_2 adsorption. SO_2 chemisorbs weakly at basic surface hydroxyls and O^{2-} sites; in the latter case adsorbed sulphites are formed, which can be converted to sulfates upon oxidation [12].

Fig. 7 presents the results of the FT-IR investigation of the 0.12 CuAl sorbent. The IR spectra can be divided into two spectral ranges: the first one extends from 4000 to 1500 cm^{-1} and the second one from 1500 to 400 cm^{-1}. The high-frequency spectral of a wide band around 3423 cm^{-1} and a shoulder around 1600 cm^{-1} are the characteristic of the presence of molecular water probably in the batch composition. Sulfation species shows characteristic vibrational bands in the 1000-1500 cm^{-1} region. The frequency band at 606 cm^{-1} is attributed to the asymmetric vibration of Al$-$O$-$Al bonds. However, a low characteristic vibrational peak of 1142 cm^{-1} exists in curve (c) in Fig. 7, which shows that the sulfated γ-Al_2O_3 support formed in a long sulfation time cannot be reduced at 400°C.

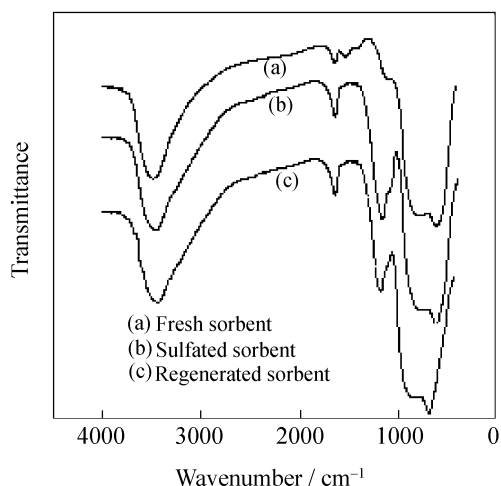**Fig. 7.   FT-IR spectra of the 0.12 CuAl sorbent.**

4. Conclusions

(1) The monolayer coverage of CuO supported on γ-Al_2O_3 determined by X-ray quantitative analysis is 0.275 gCuO/g(γ-Al_2O_3). Below the monolayer coverage CuO is found highly dispersed on γ-Al_2O_3.

(2) The Langmuir kinetics adsorption model is found to predict well the experimental data at the rapid sulfation region of the CuO/γ-Al_2O_3 sorbent. The adsorption activation energy is 19.98 kJ/mol, and the preexponential factor is 9.97×10^{-5} $s^{-1}\cdot Pa^{-1}$.

(3) The CuO/γ-Al_2O_3 sorbent has shown good performance on regeneration. Long sulfation time would cause deactivation of the CuO/γ-Al_2O_3 sorbent.

(4) The sulfated γ-Al_2O_3 support cannot be reduced at 400°C.

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