

Preparation of supported nano-copper oxide and its sulfation kinetics

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Received 10 August 2009; accepted 15 September 2009

Abstract: CuO/ γ -Al₂O₃ sorbents were prepared by means of impregnation. Thermogravimetric technique was used to study the sulfation of CuO/ γ -Al₂O₃ sorbents. The sulfation tests were performed using gas containing 0.1%–0.9% SO₂, 5% O₂, 3% H₂O steam, and N₂ as the balance. Experimental conditions including temperature, SO₂ concentration and pore structure were studied. The sulfation experiment results show that the sulfation reaction rate increases with increasing temperature and SO₂ concentration, and the surface and pore volume decrease after sulfation. Sulfation kinetics analysis shows that the reaction between CuO/ γ -Al₂O₃ and SO₂ obeys pore-blocking model well. Proportionality (pore-blocking constant) $1/\lambda$ decreases with increasing temperature. The activation energy and reaction order with respect to SO₂ obtained are 37.9 kJ/mol and the first order, respectively. The existing state of CuO exerts an influence on activation energy.

Key words: CuO; SO₂; sulfation; pore-blocking model; flue gas desulfurization

1 Introduction

Air pollution arising from the emission of SO_x from combustion of fossil fuels has increasingly been recognized as a problem[1–3]. Currently, flue gas desulfurization (FGD) is being carried out mainly using two basic FGD processes: regenerable and throwaway. Throwaway process uses inexpensive scrubbing media that are cheaper to replace than to regenerate, but a lot of waste disposals are needed. With increasing severe environmental regulations, there is a strong incentive worldwide to the application of efficient processes for dry and recycling solid sorbents. The removal of SO₂ by CuO/ γ -Al₂O₃ sorbent, a dry and regenerable means to remove SO₂, has received much attention recently[4–8].

To use gas-solid reaction models in modeling of SO₂ retention in boilers, it is necessary to know the sulfation kinetics. CENTI et al[9] proposed that SO₂ interacted CuO sites to give rise to the formation of SO₃ that in turn reacted with a further copper site to form a

bidentate sulfate, and an integral kinetic model based on two parallel pathways of formation of copper- or alumina-sulfate was obtained. In the case of industrial copper-on-alumina pellets for industrial applications[10], a grain model modified was used for the simulation of sulfation behavior in fixed-bed flow reactor tests. Most grain models are based on the assumption that the initial structure is maintained throughout and is not affected by the progress of the reaction[11–12]. These models generally require a numerical solution. In recent years, the regeneration of sulfated CuO/ γ -Al₂O₃ sorbents indicated that the surface area and pore volume of sorbent decreased after sulfation due to the pore plugging caused by the formation of sulfates[13]. Furthermore, few literatures reported the sulfation of nano-CuO. Based on considerations above, a more general and easily resolved model, i.e. the “pore-blocking” model was believed to be a logical choice to give satisfactory predictions in sulfation reactions.

The aim of the present work is to prepare nano-scale CuO supported on γ -Al₂O₃. The effects of SO₂

Foundation item: Project(u0837604) supported by United Foundation of Natural Science Foundation of China and Yunnan Province; Project(08Z0017) supported by the Provincial Education Department of Yunnan Province, China; Project(2008ZC011M) supported by the Applied Fundamental Research of Yunnan Province, China; Project(2008-06) supported by the Scientific Research Foundation of Kunming University of Science and Technology

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concentration and temperature were investigated by thermogravimetric technique. The sulfation kinetics of CuO/ γ -Al₂O₃ sorbent was studied using pore-blocking model, and the change of kinetic parameters was discussed.

2 Experimental

2.1 Instruments and materials

Instruments included a self-made thermogravimetric setup[14], an muffle furnace (SX2–12–10), a surface adsorption and desorption instrument (AUTOSORB–1C), an X-ray diffractometer (D/max–RBX), and a scanning electron microscopy (JSM–5800).

The gas composition was 2.86–25.74 g/m³ SO₂, 5% O₂, 3% H₂O steam, and N₂ as the balance. Cu(NO₃)₂·3H₂O (A.R.) and γ -Al₂O₃ (BET surface area 277.8 m²/g) were used.

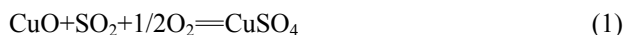
2.2 Experimental procedure

CuO/ γ -Al₂O₃ sorbent was prepared by wet impregnation with a known mass of γ -Al₂O₃ and a solution containing a calculated amount of Cu(NO₃)₂·3H₂O. Being kept in static conditions at room temperature for 1 h, followed by evaporating at 90 with stirring, the samples were dried in oven at 120 for 24 h, and subsequently calcined at 450 in stagnant air for 5 h in muffle furnace to convert the impregnated Cu(NO₃)₂ to CuO. In this way, sorbents containing 0.30 g CuO, 0.40 g CuO and 0.5 g CuO per gram γ -Al₂O₃ were obtained, respectively.

A sample pan loaded with 50 mg of sorbent was placed into the reaction zone of the thermogravimetric setup and then heated to the desired temperature. Humidified mixture of H₂O steam, N₂ and O₂ with a rate of 300 mL/min flew into the reactor. When the mass change of the sample reached a steady state, SO₂ was introduced into the reactor. The mass gain was recorded automatically.

2.3 Data evaluation

The chemical reaction taking place during the sulfation of sorbents is as follows:



Data of mass gain vs time during sulfation are obtained from the TG results. $\Delta m = m_t - m_0$ is calculated at each time, 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 . The conversion of CuO to CuSO₄, X , defined as $\Delta m / \Delta m_{\max}$ is calculated for each time and plotted as a function of time. $\Delta m_{\max}$ calculated according to Eq.(1) is the maximal mass gain.

2.4 Kinetic model

Pore-blocking model was derived by EVANS[15] based upon the reaction rate influenced by the products in a given pore set up compressional stresses in the solid, causing blockage of neighboring pores. The conversion of copper oxide (X) is expressed by

$$X = \lambda \ln(1 + K_d t / \lambda) \quad (2)$$

where t is time; $1/\lambda$ is proportionality constant (pore-blocking constant) that depends only on the basic pore structure and should be independent of gas concentration; K_d is constant. Eq.(2) can be transformed to the following equation:

$$\exp(X/\lambda) = 1 + K_d t / \lambda \quad (3)$$

The pore-blocking model given by Eq.(3) can be tested by the range of λ , which gives a straight line at each temperature on plotting $\exp(X/\lambda)$ against t . K_d influenced by temperature and gas concentration can be expressed as

$$K_d = a \cdot k \cdot f(C_{\text{SO}_2}) \quad (4)$$

where a is the stoichiometry coefficient ($a=1$ in this system); k is the rate constant; C_{SO_2} is the SO₂ concentration in the bulk; and f designates the concentration dependence. According to Arrhenius equation:

$$\ln k = -E/(RT) + B \quad (5)$$

where B is a constant, and R is the gas constant.

The slope is then used to calculate activation energy.

3 Results and discussion

3.1 XRD characterization

XRD patterns were used for nano-CuO identification. Fig.1 shows XRD patterns of the samples, indicating the peaks of CuO at 35° and 38°.

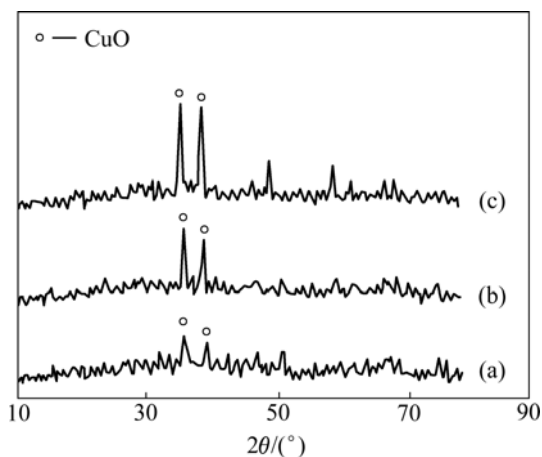


Fig.1 XRD patterns of CuO supported on γ -Al₂O₃: (a) 0.3 g CuO/g (γ -Al₂O₃); (b) 0.4 g CuO/g (γ -Al₂O₃); (c) 0.5 g CuO/g (γ -Al₂O₃)

The intensities of peaks increase with increasing the amount of CuO loading. γ -Al₂O₃ is noncrystallite and cannot be detected by XRD. Scherer's formula (Eq.(6)) was used for the calculation of CuO crystallite sizes.

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (6)$$

where D is the crystallites size; λ is the X-ray wavelength used; β is the broadening of diffraction line measured as half of its maximum intensity; and θ is the corresponding angle. Based on Eq.(6), an estimated crystallite size of 0.3 g CuO/g(γ -Al₂O₃) found to be 85 nm was used in the following sulfation experiments.

3.2 Sulfation experiments

3.2.1 Effect of SO₂ concentration

SO₂ concentrations were chosen as follows: 2.86, 5.72, 14.30, 25.74 g/m³. The effect of the SO₂ concentration on the conversion at 400 °C is shown in Fig.2.

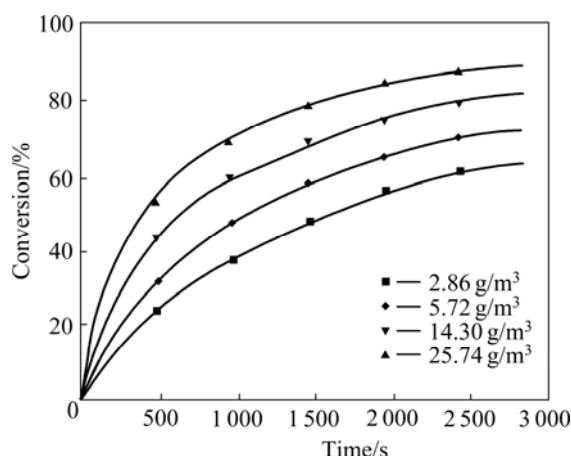


Fig.2 Curves of conversion vs time at different SO₂ concentrations

The reaction rate increases with an increase in the SO₂ concentration. The curves exhibit two regions: a rapid reaction region, and a slow reaction region in which the conversion either levels off or continues at a slow rate. The decreasing slope may be attributed to the decreasing pores and the increasing diffusional resistance through pores.

3.2.2 Effect of temperature

The experiments were carried out at SO₂ concentration of 14.30 g/m³ in the temperature range of 250–450 °C. The conversion vs time at different temperatures is shown in Fig.3.

The sulfation curves were characterized by an initial increase in conversion with increasing temperature. Due to size expansion from CuO to CuSO₄ and possibly pore plugging by the formed CuSO₄, a slow rate is found in

the final stage of sulfation, which is similar to the curves of conversion vs time at different SO₂ concentrations shown in Fig.2.

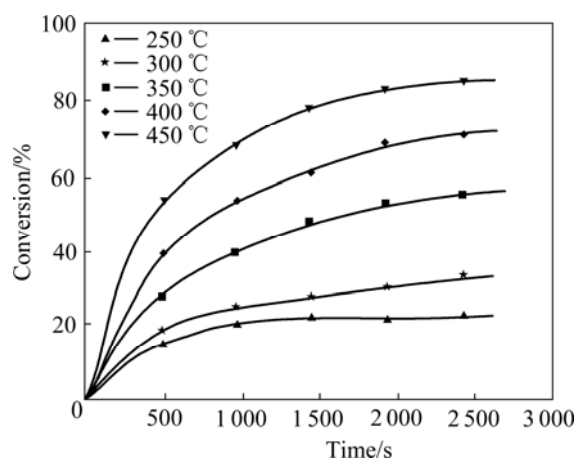


Fig.3 Curves of conversion vs time at different temperatures

3.2.3 Effect of pore structure

In order to study the effect of sulfation on pores, pore structure parameters of CuO/ γ -Al₂O₃ sorbent before and after the sulfation were tested using N₂ isothermal adsorption method. The pore size distribution is shown in Fig.4.

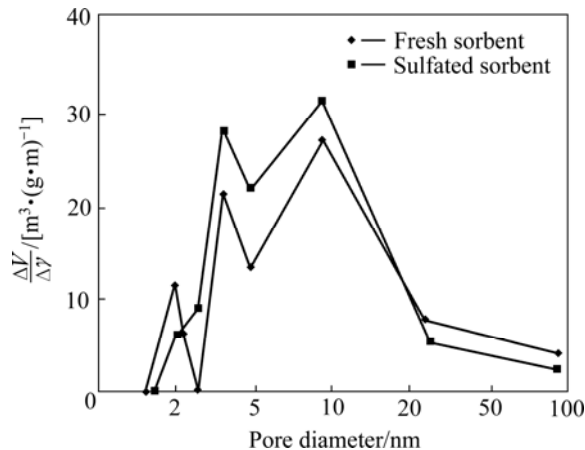


Fig.4 Pore-size distribution of 0.3 g (CuO)/g(γ -Al₂O₃) sorbent before and after sulfation

The pore size distribution shifts to smaller pores with a decrease of surface area during sulfation reaction.

The total average pore diameter is smaller than 20 nm. Most pores of the sorbent are mesopores and micropores. Pore volumes of sulfated samples are observed to decrease, indicating that the reaction takes place inside the pores and the reaction products (CuSO₄) formed on the pore walls have larger molar volumes than the solid reactants. The surface area decreases after sulfation of CuO/ γ -Al₂O₃ sorbent because sulfates may plug the pores of the alumina support, as confirmed by Table 1.

Table 1 Pore structure parameters of 0.3 g (CuO)/g(γ -Al₂O₃) sorbent before and after sulfation

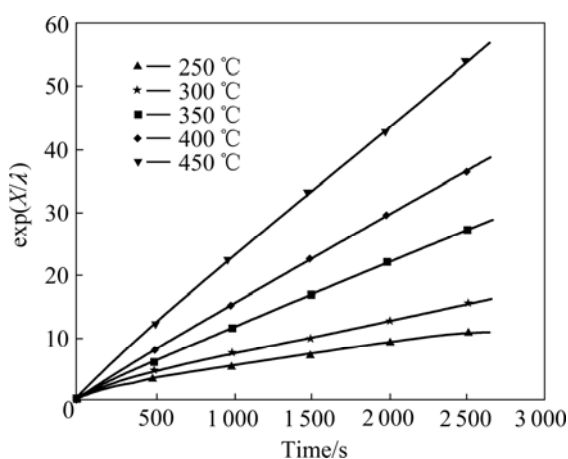
Sorbent	Surface area/ (m ² ·g ⁻¹)	Pore volume/ (cm ³ ·g ⁻¹)	Average pore diameter/mm
Fresh	1.412	0.498 7	14.59
Sulfated	1.326	0.433 6	13.87

3.3 Kinetic analysis

In order to check the validity of pore-blocking model, experimental data at different temperatures were analyzed according to Eq.(3). λ and K_d determined by nonlinear regression analysis[16] are shown in Table 2. A straight line at each temperature on plotting $\exp(X/\lambda)$ vs t is obtained, as shown in Fig.5, which means that the pore-blocking model fits the sulfation of nano-CuO well.

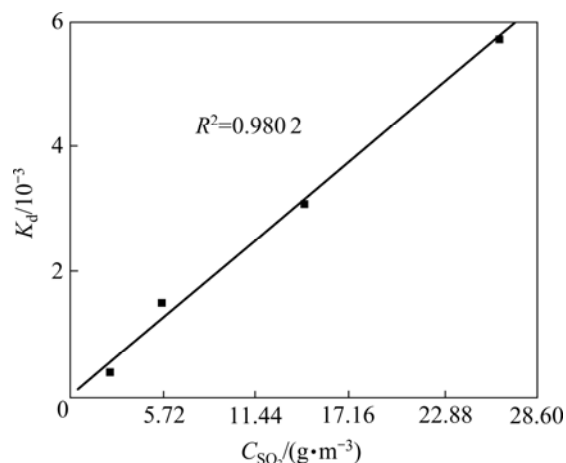
Table 2 λ and K_d at different temperatures

Temperature/	$1/\lambda$	$K_d/10^{-3}$	R^2
450	3.57	5.28	0.994 3
400	4.00	3.20	0.995 6
350	4.76	1.98	0.992 4
300	5.88	0.71	0.992 1
250	6.25	0.54	0.990 3

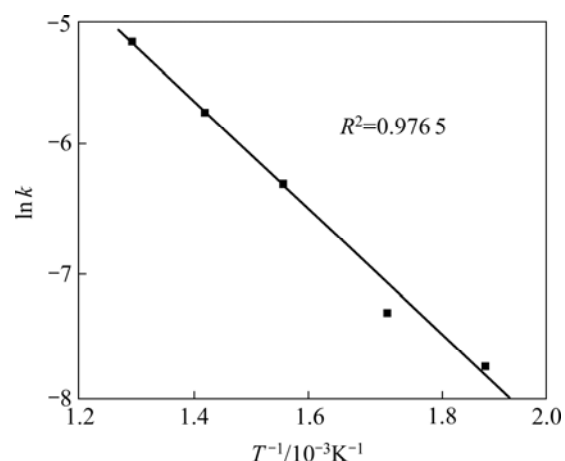
**Fig.5** Plots of $\exp(X/\lambda)$ vs time at different temperatures

The chemical reaction was confined to the external crystallites of the individual particle at the initial stage. However, at higher temperatures, the penetration of SO₂ increases, and the reaction takes place within the interior structure of the particle. These phenomena are supported indirectly by the higher pore-blocking rate constants. $1/\lambda$ is obtained at lower temperatures and shown in Table 2. As supported by the data for CuSO₄ crystallite size listed in Table 1, larger $1/\lambda$ is undoubtedly associated with a larger size of CuSO₄ crystallites locally formed in the external layer of CuO particles.

According to Eq.(4), a plot of K_d vs C_{SO_2} yields a straight line passing through the origin, as shown in Fig.6, indicating that the reaction is of the first order with respect to SO₂ concentration in the gas phase. It should be pointed out that O₂ concentration is far more than SO₂ concentration, and the complete reaction of SO₂ only consumes less than 3% of the total oxygen. Therefore, it is reasonable to assume that O₂ concentration is unchangeable.

**Fig.6** Plot of K_d vs SO₂ concentration

In order to obtain the activation energy, rate constants (k) at different temperatures were calculated according to Eq.(4) and K_d in Table 2. Then, substituting k into Eq.(5), the plot of $\ln k$ vs $1/T$ is a straight line relationship, as shown in Fig.7. The slope of the straight line through the experimental points corresponds to an activation energy of 37.9 kJ/mol and the frequency factor is 13 360 s⁻¹.

**Fig.7** Arrhenius plot of $\ln k$ vs $1/T$

Due to the influence of heat transfer and mass transfer on the phase surface, kinetic parameters of gas-solid reaction vary with many factors, such as the change of reaction condition and crystal form. DEBERRY and SLADEK[17], and YU et al[18] reported

that the reaction activation energies of pure CuO and highly dispersed CuO with SO₂ were 112.44 and 19.98 kJ/mol, respectively. There exists a dramatical decrease of activation energy in the case of nano-scale reductants compared with the normal sized CuO. This is normally attributed to the excessive energy stored in the phase boundaries of nano-CuO. The reaction activation energy of highly dispersed CuO is even lower than that of nano-CuO, since the highly dispersed CuO has higher surface energy than nano-CuO. The existing state of CuO exerts an influence on its reaction activity.

4 Conclusions

1) Under the studied conditions, the sulfation reaction rate increases with increasing temperature and SO₂ concentration, and the surface area and pore volume decrease after sulfation.

2) The sulfation reaction between CuO/ γ -Al₂O₃ and SO₂ obeys pore-blocking model well. Proportionality (pore-blocking constant) $1/\lambda$ decreases with increasing temperature. Activation energy and reaction order with respect to SO₂ obtained are 37.9 kJ/mol and the first order, respectively.

3) The activation energy of nano-CuO supported on γ -Al₂O₃ decreases much compared with that of pure CuO, and a little higher than that of highly dispersed CuO supported on γ -Al₂O₃. The existing state of CuO exerts an influence on its reaction activity.

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(Edited by CHEN Wei-ping)