SO₂ REMOVAL BY CuO ON γ -ALUMINA

MOO HWAN CHO AND WON KOOK LEE

Department of Chemical Engineering, Korea Advanced Institute of Science & Technology,
Seoul 131 Korea

Removal of SO₂ gas from simulated flue gases was carried out, using copper oxide adsorbent. The copper oxide adsorbent is made by impregnation of γ -alumina tablet in a solution of copper (II) nitrate, followed by oxidation.

SO₂ breakthrough curves were obtained by changing temperature and initial concentration in a tubular packed bed reactor. The kinetic parameters were determined by fitting breakthrough curves to the theoretical kinetic model, and the rate equation was obtained.

The saturation capacities were calculated by the numerical integration of breakthrough curves, and the equation representing breakthrough curves was obtained. By means of this equation, the influence of space time on breakthrough curves was estimated.

1. Introduction

SO₂ emission control is becoming a serious problem due to the projected increase in use of high-sulfur coal to meet energy requirements in this country. A large effort has emerged in the last few years to develop processes for fuel or waste gas desulfurization. Over 50 processes for waste gas desulfurization have been proposed. Many of them are summarized by Slack.¹⁰⁾

Wet throwaway processes, such as alkali or limestone scrubbing, are currently being predominantly developed on a commercial scale.¹⁰⁾ However, dry recovery processes, based either on regenerative adsorption or on catalytic oxidation or reduction, would be far more advantageous since they would produce a useful product and would avoid both flue gas reheating and the crystallization phenomena usually encountered in flue gas scrubbing.

In one of the dry recovery processes the waste gas is brought into contact with CuO-on-support, whereupon the SO₂, present at low concentration, reacts with O₂ to produce CuSO₄. Among the porous supports γ -alumina has been reported as the most favorable.¹³⁾ CuO-on- γ -alumina is a strong adsorbent that can be regenerative at lower temperature with either low heat or reducing gas consumption.⁹⁾

The removal of SO₂ with CuO is not new. Bienstock, *et al.*¹⁾ described a precipitated adsorbent in 1961. More recent work has been sponsored by NAPAC at Avco Corp. and Tracor, Inc.⁸⁾ In addition, a patent covering impregnation of copper into supports was issued to Shell International Research^{2,13)} in 1969. In the present study attention was focused on the search for a rate equation for the

CuO-SO₂-O₂ reaction system that may be useful in the design of commercial devices.

2. Theoretical Considerations

2.1 Reaction mechanism

The kinetics and mechanism of the reaction among SO₂, O₂ and CuO appear to have received scant attention. The reverse process, the thermal decomposition of copper sulfate, has been extensively studied, however, and its thermodynamics and features are well understood.^{4,5)}

The principal product is anhydrous copper sulfate when copper oxide comes in contact with SO₂ and O₂ at temperatures lower than 600°C.

A great number of mechanisms may be postulated for the reaction. One possible reaction pathway that explains the empirically determined rates, and that is also confirmed by observations of other investigators,⁷⁾ is as follows:

The diffusion resistance of the external mass transfer is negligible by calculation from Acetis and Thodos' correlation,¹⁴⁾ and the internal diffusion resistance is also negligible by the criteria of pore diffusion.¹⁵⁾

Received May 31, 1982. Correspondence concerning this article should be addressed to W. K. Lee. M. H. Cho is now at Dept. of Chem. Eng., Yonnam Univ., Taegu, Korea.

2.2 Kinetic model

Consider a packed bed through which the gas passes in plug flow and assume that the inlet concentration C_{Ai} of reactant gas, SO_2 , is so low that any reduction in its concentration causes a negligible change in the overall volumetric flow rate, F . Assume further that reaction occurs by a four-step mechanism represented by Eqs. (2) to (5).

On the basis of these assumptions the design equation for the system becomes

$$\frac{V}{F} = - \int_{C_{Ai}}^{C_{Ao}} \frac{dC_A}{r_A} \quad (6)$$

Consider the reaction mechanism expressed by Eqs. (2) to (5), and suppose that the step of sulfate formation is rate-determining (Eq. (5)). Then we have

$$r_A = k_r(\text{CuO} - \text{SO}_3^*) \quad (7)$$

Other steps are in equilibrium:

$$\frac{(\text{CuO} - \text{SO}_2^*)}{(\text{CuO}^*)(\text{SO}_2)} = K_1 \quad (8)$$

$$\frac{(I - \text{O}^*)}{(\text{O}_2)^{1/2}(I)} = K_2 \quad (9)$$

$$\frac{(\text{CuO} - \text{SO}_3^*)(I)}{(\text{CuO} - \text{SO}_2^*)(I - \text{O}^*)} = K_3 \quad (10)$$

Substituting concentrations for the chemisorbed species in Eq. (7), we have

$$r_A = K_1 K_2 K_3 K_r (\text{O}_2)^{1/2} (\text{SO}_2) (\text{CuO}^*) \quad (11)$$

Assuming that the concentration of O_2 , in large excess in the system studied, is taken to be constant throughout, we have

$$r_A = K_r C_A (1 - X_R) \quad (12)$$

where $K_r = K_1 K_2 K_3 K_r (\text{O}_2)^{1/2} (\text{CuO}^*)_0$, $C_A = (\text{SO}_2)$, X_R = conversion of CuO^* , and $(\text{CuO}^*)_0$ = original concentration of CuO^* .

Rate equations of the same form as Eq. (12) can also be derived on other assumptions of rate-determining step. Therefore the real rate-determining step cannot be determined in this study.

The rate of consumption of the active site, CuO^* , can be expressed as¹⁶⁾

$$\frac{dX_R}{dt} = K_d (1 - X_R) \quad (13)$$

Integration of Eq. (13) gives

$$1 - X_R = \exp(-K_d t) \quad (14)$$

Inserting Eq. (14) into Eq. (12) yields

$$r_A = K_r \exp(-K_d t) C_A \quad (15)$$

which on substitution into Eq. (6) gives

$$\frac{V}{F} = - \int_{C_{Ai}}^{C_{Ao}} \frac{dC_A}{K_r \exp(-K_d t) C_A} \quad (16)$$

This may be integrated to give

$$\frac{C_{Ao}}{C_{Ai}} = \exp \left[- \frac{V}{F} K_r \exp(-K_d t) \right] \quad (17)$$

By measuring the gas breakthrough from a suitable differential fixed bed reactor, it is possible for this particular reaction mechanism to determine the rate coefficients K_r and K_d . Values of these two unknowns, K_r and K_d , were calculated to minimize

$$S_E^2 = \sum_{j=1}^n e_j^2(K_r, K_d) = \sum_{j=1}^n [f_j(K_r, K_d) - F_j]^2 \quad (18)$$

where f_j is the value of (C_{Ao}/C_{Ai}) calculated from Eq. (17) for a time t_j , and F_j is the corresponding experimental point.

By the Rosenbrock minimization technique,⁶⁾ the sum, S_E^2 , of the squares of the errors, e_j^2 , between the theoretical and experimental points on the breakthrough curve was reduced to below 0.01 for each breakthrough curve; this represents a standard error of observation of about ± 0.02 in all cases.

3. Experimental Section

3.1 Adsorbent preparation

Adsorbents prepared by impregnation into inert supports were used, since any acceptable adsorbent had to be resistant to physical attrition. Early efforts to fabricate strong, stable pellets from precipitates, coprecipitates with alumina, or powders were not successful.²⁾

The support used for the solid adsorbent was 3''/16 $\times$ 1''/18 tablet type of porous γ -alumina manufactured by United Catalyst Inc. The properties of γ -alumina are shown in Table 1.

Before impregnation, the alumina was dried at 160°C for 24 hours and allowed to cool in a desiccator.

A solution of copper(II) nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, in deionized water was prepared and the alumina was immersed in the solution for 48 hours. Considering both capacity and rate, the optimum concentration is from 4 to 6 wt% Cu.²⁾ The impregnated alumina was removed from the nitrate solution and quickly rinsed to remove any solution trapped between the particles. The particles were dried at 80°C for 48 hours and the particles were heated to 450°C with flowing air for another 24 hours to decompose the copper nitrate to copper oxide. A copper concentration on alumina of 5 wt% was aimed for and was checked by reverse calculations of saturation capacities of adsorbents.

X-Ray diffraction was used to analyze the components of the support, the adsorbent, and the product qualitatively after reaction.

Table 1. Properties of γ -alumina (3''/16 $\times$ 1''/18 Tablet)

Crystalline compounds	γ -Al ₂ O ₃
Mean crystallite size	49 Å
Surface area	165 m ² /g
CCl ₄ pore volume [ml/g]	0.29 at 800 Å 0.28 at 140 Å
Hg porosimeter	
Pore volume [ml/g]	Pore diameter [μ]
0.01	175–1.75
0.03	1.75–0.08
0.10	0.08–0.014
0.29	0.014–0.0029

3.2 Experimental apparatus and methods

The experimental equipment consisted of gas cylinders, the gas feed system, flow meters and manometer, moisture removal column, preheaters, a reactor bed, and monitoring equipment. A schematic representation of the equipment is presented in Fig. 1. A differential packed bed reactor consisting of a stainless steel screen tube of 40 mesh size, 1.5 cm in diameter and 13 cm long, was used as the adsorption vessel. All gases employed were pure grade (99.9%), manufactured by Matheson Gas Products Co.

The reactor was first loaded with a charge of solid copper oxide on alumina, 5.1 grams, which had previously been dried in a desiccator and weighed on an analytical balance. The flow rate of a mixture of oxygen and nitrogen to the reactor was adjusted to the desired operating conditions. After steady-state temperature had been reached in the bed, sulfur dioxide was introduced and the starting time was recorded. Analysis of the reactor effluent was made at about 5-minute intervals to determine relative percentages of oxygen, nitrogen, and sulfur dioxide. Sampling continued until saturation of the copper oxide was obtained. The same routine operations were performed at different temperatures and concentrations. The inlet SO₂ concentrations used in this study ranged from 0.3 vol% to 1.0 vol%, since the concentration of SO₂ in flue gases is about 3000 ppm and the upper limit is about 10000 ppm. Oxygen concentrations varied from 4.5 vol% to 5.0 vol%. The balance was pure nitrogen. The total flow rate of the gas stream was 1000–1100 ml/min, and the reactor temperature ranged from 250°C to 450°C with an interval of 50°C for each run.

Analyses of the gas stream were accomplished by use of a Varian Model 1400 gas chromatograph with a thermal conductivity detector.

4. Results and Discussion

4.1 SO₂ breakthrough curves

SO₂ concentration in the output stream from the bed was recorded continuously from the start of each run until it reached the inlet concentration, at which

Fig. 1. Schematic diagram of apparatus. A, calcined alumina; B, packed bed reactor; C, moisture removal tube; F₁–F₄; rotameters; G, gas chromatograph; J, insulation; K, kanthal wire; M, manometer; P, furnace preheater; R, preheater tube; T, temperature controller.

time the solid adsorbent was completely converted to copper sulfate. Graphs of the fractional output concentration, C_{Ao}/C_{Ai} , vs. time are termed “breakthrough curves.”

SO₂ breakthrough curves were obtained for different operating conditions of temperature and initial concentration. It was found that the effect of initial concentration over the range of this study on the breakthrough curves was negligible compared with that of temperature. Therefore, the data points of the breakthrough curves for various initial concentrations at the same temperature could produce one average breakthrough curve for the corresponding temperature.

One of the breakthrough curves is shown in Fig. 2. Figure 3 shows Arrhenius plots of the two kinetic parameters as a function of temperature. From these values, the apparent activation energies and pre-exponential factors for the two kinetic parameters were calculated.

4.2 Effect of temperature on breakthrough curves

Breakthrough curves for various temperatures, shown in Fig. 4, demonstrate the effect of temperature on these curves.

As the temperature increases, the slope of the tangential line at $t=0$ increases, and the value of C_{Ao}/C_{Ai} at $t=0$ decreases. These results show that the initial adsorption rates increase with temperature. When elapsed time exceeds 30 minutes, the temperature effect is nearly negligible. The reason may be said to be that as time increases, the fraction of occupied CuO* active sites increases exponentially by Eq. (14), and the time effect on breakthrough curves is predominant over the temperature effect at $t > 30$ min.

4.3 Effect of temperature on saturation capacity

Calculations of saturation capacity were carried

Fig. 2. SO₂ breakthrough curve, $T=350^{\circ}\text{C}$ and $V/F=0.36\text{ s}$.

Fig. 3. Arrhenius plot of kinetic parameters.

Fig. 4. Effect of temperature on SO₂ breakthrough curve.

out as

$$\begin{aligned} & \text{Saturation capacity (g-SO}_2\text{/g-adsorbent)} \\ &= \frac{\text{AREA}}{\text{g-adsorbent}} \times \frac{\text{g-SO}_2 \text{ fed}}{\text{min}} \end{aligned} \quad (19)$$

where AREA shown in Fig. 5 can be considered as the adsorbed fraction of g-SO₂ fed during the time t_a , and was calculated by the method of numerical integration. The calculated values of saturation capacities

Fig. 5. Calculation of saturation capacity.

Fig. 6. Effect of temperature on saturation capacity.

with temperatures are shown in Fig. 6.

These values are in good agreement with those determined by McCrea *et al.*,⁹⁾ who carried out the adsorption of SO₂ with copper oxide at 300°C or above. And these values are much greater than the values for other metal oxides (Mn, Fe, Co, Ni, Zn) determined by Koballa and Dudukovic⁷⁾ (Table 2).

From 250°C to 425°C the saturation capacity increased with temperature and then began to decrease above 425°C. This phenomenon may be explained by the fact that catalytic oxidation of SO₂ over CuO would begin above 425°C.³⁾

4.4 Rate equation

The rate equation of the reaction between SO₂ and CuO in excess of O₂ can be expressed as Eq. (15), and the SO₂ breakthrough curve equation for this system can be expressed as Eq. (17) with

$$K_r = 560.96 \exp(-8.314/RT)$$

and

$$K_d = 0.156 \exp(-3.43/RT).$$

K_r may be considered as the overall rate coefficient, and K_d as the consumption rate coefficient of CuO*.

These equations are valid over the range of temperature, 250–450°C and SO₂ initial concentration 3000–10000 ppm under the assumption of gas plug flow.

Table 2. Saturation capacities of other metal oxides adsorbent at 315°C⁽⁷⁾

Adsorbent	Saturation capacity [g-SO ₂ /g adsorbent]
CoO	0.014
Fe ₂ O ₃	0.015
MnO ₂	0.023
NiO	0.011
ZnO	0.0055

By means of the breakthrough curve equation, the influence of space time on breakthrough curve was estimated (Fig. 7). By this estimation, some preliminary predictions can be made for reactor design to regulate the SO₂ concentration of the flue gas. For example, the outlet concentration of SO₂ gas may be zero for 12 minutes from the beginning of operation at 350°C if space velocity is 50 θ , i.e., 18 sec.

Conclusions

SO₂ breakthrough curves obtained from various experiments were fitted well to a kinetic model.

Adsorption rate and saturation capacity increased with temperature between 250°C and 450°C. Saturation capacity, however, appeared to reach a maximum at about 425°C because of the catalytic oxidation of SO₂ above 425°C. Therefore, considering both adsorption rate and saturation capacity, the optimal adsorption temperature to produce the maximum adsorbent capacity is about 425°C for this reaction system.

Estimation of kinetic parameters from the experimental data gave $K_r = 560.96 \exp(-8.314/RT)$ and $K_d = 0.156 \exp(-3.43/RT)$, and the rate and breakthrough curve can be expressed as Eqs. (15) and (17), respectively. These equations are valid for the conditions of temperature, 250–450°C, SO₂ concentration 3000–10000 ppm and O₂ in excess under the assumption of gas plug flow.

Nomenclature

A_r, A_d	= preexponential factors of K_r and K_d , respectively	[l/min]
C_A	= concentration of SO ₂ gas	[g·mol/cm ³]
C_{Ao}	= final concentration	
C_{Ai}	= initial concentration	
CuO*	= active site of copper oxide	
(CuO*)	= concentration of CuO* in the adsorbent	
(CuO*) ₀	= original concentration of CuO*	
E_r, E_d	= activation energies of K_r and K_d , respectively	[kJ/mol]
e_j	= error between f_j and F_j	
F	= volumetric gas flow rate	[cm ³ /min]
F_j	= experimental value of C_{Ao}/C_{Ai} for a time t_j	
f_j	= calculated value of C_{Ao}/C_{Ai} for a time t_j	

Fig. 7. Influence of space time on breakthrough curve, $T = 350^\circ\text{C}$ and $\theta = V/F = 0.36$ s.

K_1, K_2, K_3	= reaction equilibrium constants	
K_r	= overall rate coefficient	[l/min]
K_d	= consumption rate coefficient of CuO*	[l/min]
k_a, k_a'	= adsorption rate coefficients	
k_d, k_d'	= desorption rate coefficients	
k_1, k_2, k_r	= reaction rate coefficients	
l	= active site for oxygen adsorption	
n	= number of experimental points, (F_j, t_j)	
t	= time	[s]
V	= bulk volume of adsorbent in reactor	[cm ³]
τ	= space time	[s]
θ	= V/F	[s]

Literature Cited

- 1) Bienstock, D., J. H. Field and J. G. Myers: *U. S. Bur. Mines, Rept. Invest.*, 5735, 25 (1961).
- 2) Dautzenberg, F. M. and J. E. Nader: *Chem. Eng. Progr.*, **67**, 86 (1971).
- 3) Glass, R. W. and R. A. Ross: *Can. J. Chem.*, **49**, 2832 (1971).
- 4) Ingraham, T. R.: *Trans. Met. Soc. AIME*, **233**, 359 (1965).
- 5) Ingraham, T. R. and P. Marier: *Trans. Met. Soc. AIME*, **233**, 363 (1965).
- 6) Keuster, J. L. and J. H. Mize: "Optimization Techniques with Fortran," McGraw-Hill, New York, N. Y. (1973).
- 7) Koballa, T. E. and M. P. Dudukovic: *AIChE Symp. Ser. No. 165*, Vol. 73, p. 199 (1978).
- 8) Lowell, P. S., K. Schwitzgebel and T. B. Parsons: Paper presented at AIChE 65th National Meeting, May (1969).
- 9) McCrea, D. H., A. J. Forney and J. G. Myers: *J. Air Pollution Control Assoc.*, **20**, 819 (1970).
- 10) Slack, A. V.: *Pollution Control Review No. 4*, Noyes Data Corporation, Park Ridge, New Jersey (1971).
- 11) Smith, J. M.: "Chemical Engineering Kinetics," 2nd ed., pp. 364, 402, McGraw-Hill, N. Y. (1970).
- 12) Stone, F. S., "Advances in Catalysis" ed. by D. D. Eley *et al.*, p. 13, Academic Press, N. Y. (1962).
- 13) Van Heldon, H. J. and J. E. Naber: U. K. Patent 1, 160, 662 (1969).
- 14) Acetis, J. D. and G. Thodos: *Ind. Eng. Chem.*, **52**, 1003 (1960).
- 15) Levenspiel, O.: "Chemical Reaction Engineering," 2nd ed., p. 477, John Wiley and Sons, Inc., N. Y. (1972).
- 16) Yates, J. G. and R. J. Best: *Ind. Eng. Chem., Process Des. Dev.*, **15**, 239 (1976).