Kinetics of DeSOx Reaction on Copper and Cerium-based Sorbent-Catalysts

HUI WANG, GUO JIE LIU, YAO WANG, WEI QING LI, LI ZHOU, SEN SHI AND JIAN SUN*

*School of Chemical and Environmental Engineering, Shanghai University,
Shanghai 201800, China.*

Summary: Kinetics of SO_2 removal using a copper-based sorbent $CuO/\gamma-Al_2O_3$ and a cerium modified copper sorbent $CuO-CeO_2/\gamma-Al_2O_3$ were measured on a TGA and their kinetics behaviors were simulated with a proposed empirical rate model (ERM). The purpose of cerium addition to the copper sorbent was to study the difference of sorbent's kinetics. The cerium modified copper sorbent showed a higher reaction rate on initial sulfation than the regular copper sorbent. Both sorbents however had similar calculated activation energy. The proposed ERM model appeared to describe the SO_2 removal kinetics well in the temperature range 250-400 °C.
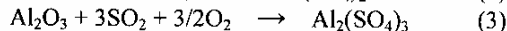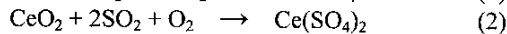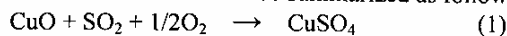
Introduction

Air pollution rooting in SO_x emission from the combustion of fossil fuels is a worldwide environmental problem. Among a wide selection of SO_2 control techniques, dry sorption process has been developed as an effective means for SO_2 removal. Many metal oxides supported on alumina ($\gamma-Al_2O_3$) were studied for the process, in which CuO has been considered as a good regenerable sorbent because it can simultaneously remove SO_2 and NO_x [1-4]. As a catalyst additive, CeO_2 has a high oxygen storage capacity and its oxidation states can change between Ce^{4+} and Ce^{3+} with reaction condition. It is widely used as a promoter in the catalyst design to enhance the metal dispersion and stabilization of the support against sintering [5]. Rodas-Grapain [6] used a $CuO-CeO_2$ sorbent-catalyst for the deSOx reaction and found that interaction of the copper with cerium oxide can improve its SO_2 adsorption capacity.

There are not many kinetic studies dealing with SO_2 removal by CuO and very few by $CuO-CeO_2$ in the literature. The objective of this investigation is to study the difference of intrinsic kinetics of SO_2 removal on the CuO and $CuO-CeO_2$ sorbent-catalysts prepared in this study and to develop a corresponding empirical rate model (ERM). Isothermal thermogravimetry was applied to determine the reaction activation energy and rate constants. As a method of model validation, the ERM model was applied to model experimental data from the literature and compared with other kinetics models.

Results and Discussions

Chemical reactions that occur in the sulfation of sorbents can be summarized as follows:

$$CuO + SO_2 + 1/2O_2 \rightarrow CuSO_4 \qquad (1)$$
$$CeO_2 + 2SO_2 + O_2 \rightarrow Ce(SO_4)_2 \qquad (2)$$
$$Al_2O_3 + 3SO_2 + 3/2O_2 \rightarrow Al_2(SO_4)_3 \qquad (3)$$

SO_2 removal by metal oxides is a catalyzed gas-solid reaction. Oxidative adsorption of SO_2 usually forms two types of sulfates: surface and bulk-like species [7], which are linked to active sites. Majority of the bulk-like sulfation usually does not occur until temperature reaches 450 °C [8]. Lin [9] reported that sulfation on the $\gamma-Al_2O_3$ support could be negligible when the reaction temperature was below 450 °C. Centi [7] reported that the SO_2 adsorption by alumina was much lower than that observed for $CuO/\gamma-Al_2O_3$. In this study, the temperature range was 300-400 °C and therefore reaction was primarily surface-sulfation. The SO_2 and O_2 concentrations were assumed to be constant during reaction due to their oversupplying amount in comparison with relatively small batch of sorbents (about 20 mg for each run) during the TGA runs of sulfation. The copper and cerium oxides conversion, defined as $X = \Delta m / \Delta m_{max}$, is calculated as a function of time t. Δm, expressed as $\Delta m = m_0 - m_t$, is recorded from TGA, where m_0 is the mass (sorbent excluding support) at the start of sulfation and m_t is the mass at time t. Δm_{max} is the max mass of the weight gain calculated according to reactions (1) and (2) based on the sorbent composition.

*To whom all correspondence should be addressed.

The rate of SO_2 reaction is presumably proportional to the gas concentration and density of the active sites on solid. Therefore, the sulfation rate r can be expressed as:

$$r = k_1 C S^n \qquad (4)$$

where r, the intrinsic gas-solid reaction rate, is a function of temperature and reactant concentrations; k_1 is the rate constant; C is the SO_2 concentration in the simulated flue gas; S is the number of copper and cerium active sites on the solid surface; and n is the assumed reaction order with respect to the active sites. Since the active sites are proportional to the solid density, the rate can also be described in an empirical manner

$$r = -d\rho/dt = k_1 C (k_2 \rho)^n \qquad (5)$$

where ρ, the solid bulk density, represents the changing amount of active oxides in the sorbents; and k_2 is a constant to linearly correlate S with ρ.

Combining $k = k_1 k_2^n$ and the Eq. 5 becomes:

$$r = -d\rho/dt = kC\rho^n \qquad (6)$$

Our rate equation can be rewritten after inserting the solid conversion $X = (\rho_0 - \rho)/\rho_0$

$$dX/dt = -kC\rho_0^{(n-1)}(1-X)^n \qquad (7)$$

where ρ_0 is the initial solid bulk density.

Integration of Eq. 7 gives expressions for X as a function of time

$$X = 1 - \exp(-kCt) \quad n=1 \quad (8.a)$$

$$X = kC\rho_0 t/(1+kC\rho_0 t) \quad n=2 \quad (8.b)$$

$$X = 1 - [1+(n-1)kCt/\rho_0^{(1-n)}]^{1/(1-n)} \quad n \neq 1,2 \quad (8.c)$$

Eqs. (8.a) and (8.b) were used to model the experimental data of SO_2 removal over samples FCu and FCuCe in this study. Modeling results in Fig. 1 show that the better fit for FCu was obtained with Eq. (8.a) and n = 1, and the better fit for FCuCe was obtained with Eq. (8.b) and n = 2. The ERM model appears to be able to describe the kinetics behaviors for both sample sorbents. According to Eq. 6, the change of n results in a different behavior in reaction rate change over time. This means that FCuCe has a
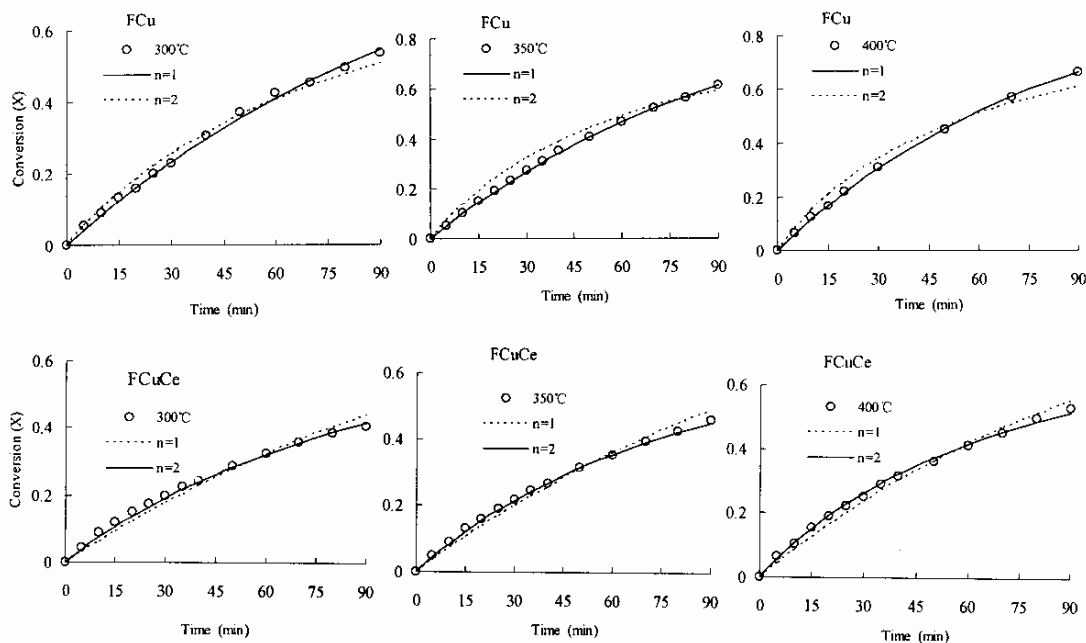

Fig. 1: Experimental and modeled conversion versus time for the CuO/γ-Al$_2$O$_3$ and CuO-CeO$_2$/γ-Al$_2$O$_3$ sorbents at 300 400°C in 0.1vol. % SO$_2$/air (symbols: circles stand for experiment data and lines for modeling)

higher initial reaction rate for SO_2 removal than FCu at the same reaction conditions, although the difference is small (Fig. 1). More work is underway to study the kinetics behavior with sorbent going through regeneration cycles.

As a routine in kinetics study, activation energy of sulfation was calculated in this study (Fig. 2). Slopes in the Arrhenius plots represent the activation energy (Ea) divided by the universal constant of gases (R). Ea was calculated as 10.3 kJ/mol and 10.6 kJ/mol at 300-400℃ for FCu and FCuCe, respectively. Table-1 presents the comparison of activation energy of sulfation between the copper or ceria oxide sorbents made from this study and literature. Activation energy for the sorbents in our study is lower. This could be attributed to the process of sorbent preparation and the existence of water vapor in the simulated flue gas. Water vapor can promote recrystallization of formed sulfates and create more porous structure for the sorbent [10]. In addition, there is no significant difference in the activation energy between samples FCu and FCuCe in our study, although the activation energy for CeO_2 is higher than CuO (Table-1). It implies that the addittition of CeO_2 has little effect on changing the kinetics nature of CuO sulfation.

As a part of model validation, the proposed ERM was used to model the sulfation data reproduced from the literature. Fig. 3 plots the modeling results for the sulfation of CuO sorbents at 0.15 % SO_2 at 400℃ from Jia [13] and 0.2 % SO_2 at

Table-1: Comparison of activation energy of copper or cerium oxides sorbent for sulfation.

Sorbent	Ea (kJ/mol)	T (℃)	References
CuO/γ-Al₂O₃	47.4	200-450	Ourania [10]
CuO/γ-Al₂O₃	20.1	350-450	Yeh [11]
CuO/γ-Al₂O₃	19.98	300-500	Yu [12]
CuO/γ-Al₂O₃	10.3	300-400	This study
CeO₂/γ-Al₂O₃	12.54	250-450	Yu [4]
CeO₂/γ-Al₂O₃	12.73	300-400	This study
CuO-CeO₂/γ-Al₂O₃	10.6	300-400	This study

350℃ from Yu [4], respectively. Results show that the model predictions are in good agreement with the data in the literature.

The ERM was also compared with other models from the literature for validation. The surface reaction model (SRM) by Centi [2,7] and its modified versions have been widely used to describe the sulfation kinetics of $CuO/\gamma-Al_2O_3$ or other CuO-types of sorbents for SO_2 removal. Frequently being studied for the surface reaction over CuO, it assumes that chemisorbed SO_2 on the copper species forms chemisorbed SO_3 on the sorbent surface [7]. Fig. 4 plots the comparison of SRM and ERM for a $CuO/\gamma-Al_2O_3$ sorbent at 250 ℃ and 350 ℃ respectively. The ERM model gives good prediction for both sulfation at 250℃ and 350℃. Bulk density of the sorbent made in this study was used for modeling the data reproduced from the literature. It presumably did not influence the result since it is a constant and the only changing variable in the ERM is the rate constant.
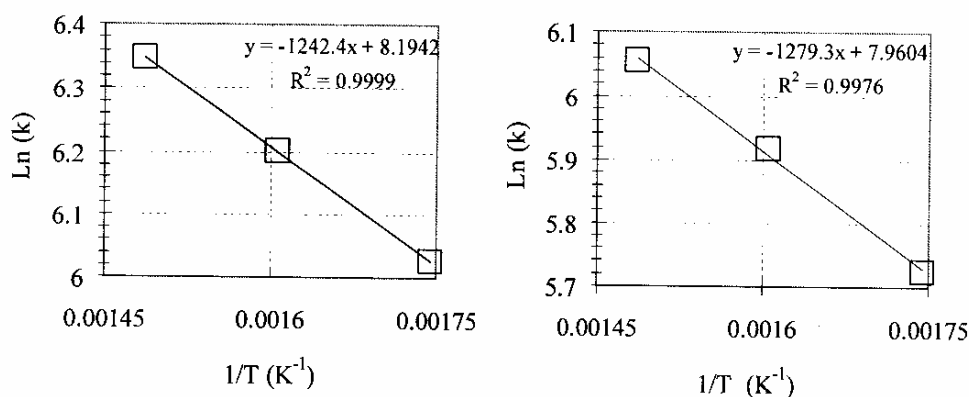

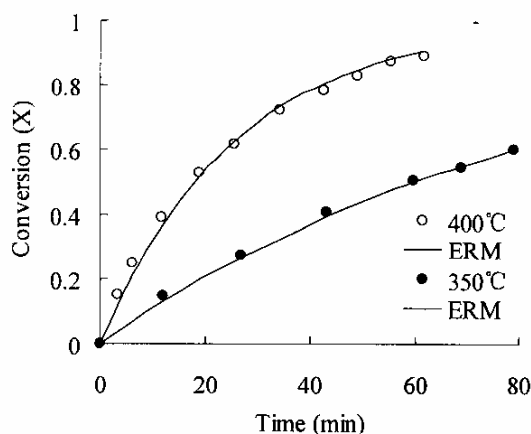Fig. 2:   Plots of the kinetic constants of SO_2 removal reaction at 300-400℃.

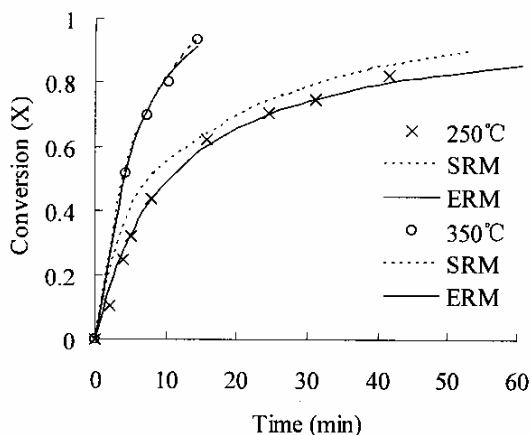Fig. 3: TGA experiment of CuO/γ-Al₂O₃ conversion over time reproduced from Jia [13] and Yu [4] and the ERM prediction.

Fig. 4: Comparison of the SRM and ERM models. Experimental and SRM data were reproduced from Centi [7]. Symbols o: experiments at 250°C and × at 350°C; Lines: models. Reaction conditions: 4.8wt%CuO with 0.8vol.% SO₂.

Experimental

Commercially available Cu(NO₃)₂·3H₂O and Ce(NO₃)₃·6H₂O (AR, Sinopharm Chemical Reagent (SCR) Co., Ltd, Shanghai) were used to prepare CuO and CuO-CeO₂ sorbents by wet impregnation followed by calcinations. γ-Al₂O₃ (SCR, Shanghai, 80-100 mesh and BET surface area of 252 m²/g) were used as the sorbent support.

After impregnation of sorbent support with nitrate solution, sorbent sample was kept under a static condition for 1 h at room temperature. Sample was heated at 50 °C for 1 h with stirring and excessive water after impregnation was evaporated. Samples were then dried in a DHG-9053 oven (Shanghai Yi-heng Technology Co., Ltd.) at 110 °C for 6 h. Finally, sample was calcined in an SXL-1208 muffle furnace (Shanghai Jing-hong Laboratory Instrument Co., Ltd) in nitrogen at 500 °C for 5 h to convert nitrate to metal oxide.

Two fresh samples were prepared and termed as FCu and FCuCe in this study, containing 8 wt.% Cu and 8 % Cu - 4 % Ce, respectively.

Kinetics measurements were carried out isothermally in an HCT-1 thermo-gravimetric analyzer (Beijing Heng-jiu Scientific Apparatus Factory) using a simulated flue gas containing 0.1vol.% SO₂ / air at 300-400°C. After sample was heated to the reaction temperature under flowing N₂, the simulated gas was introduced to start the kinetics measurement. To minimize the effect of intra-particle mass transfer, sorbent samples were crushed after preparation and samples (20-30 μm) were used in the experiment. To eliminate the external or bulk mass-transfer resistance in sulfation reaction, the effect of gas flow rate on the SO₂ removal kinetics was tested. Results showed that external mass-transfer was negligible when the flow rate of flue gas was 50 mL/min or higher. Therefore, particle with the size range of 20-30μm and gas flow rate of 50 mL/min were used in this study.

Conclusion

CuO and CuO-CeO₂ sorbents on γ-Al₂O₃ support were prepared and their intrinsic kinetics for SO₂ removal from simulated flue gas was investigated. Their activation energy was calculated as 10.3 kJ/mol and 10.6 kJ/mol, respectively. The proposed kinetics model fitted the TGA experimental data from this study well and it was also applicable to select SO₂ removal TGA data from the literature. More work is underway to study the intrinsic kinetics behavior of sorbents after going through vigorous regeneration cycles.

Acknowledgement

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