



Experimental Study and Kinetic Analysis of CuO/ γ -Al₂O₃ Absorbed SO₂

www.ericjournal.ait.ac.th

Zhongqing Yang^{*1}, Jianghao Xie^{*}, Li Zhang^{*}, Mingnv Guo^{*#} and Jingyu Ran^{*}

Abstract – This study reports the results of an empirical evaluation of the effects of the Cu loading, concentration of SO₂, and temperature on the reaction of CuO/ γ -Al₂O₃ and SO₂. In this experiment, the kinetic characteristics of the sulfation reaction of CuO/ γ -Al₂O₃ particles are studied using the equivalent particle model. The result shows that surface reaction control zone and the diffusion control zone exist in this reaction, the demarcation point between the two zones is in the vicinity of 500°C. With increasing temperature, the conversion ratio of CuO/ γ -Al₂O₃ absorbed SO₂ gradually increases, but at 500°C, the enhancement of the conversion ratio slows down. And where the first stage of the reaction between CuO/ γ -Al₂O₃ and SO₂ is mainly controlled by surface chemical reaction with an activation energy (*E_a*) of 5.8 kJ/mol, and the latter stage is diffusion controlled with an *E_a* of 11.6 kJ/mol.

Keywords – CuO/ γ -Al₂O₃, diffusion, kinetics, SO₂, sulfation reaction.

1. INTRODUCTION

Cu-loaded catalysts have many merits, like good catalytic activity and low price, and are thus widely used in the catalytic combustion of low concentration methane [1]-[2]. Low concentration methane, present in coal bed methane (CBM) [3], contains impurities such as SO₂. Despite the low concentration, SO₂ seriously affects the catalyst activity. Therefore, it is necessary to clarify the mechanism by which SO₂ influences the catalyst activity and the reaction kinetic characteristics of the interaction of SO₂ with the Cu-based catalyst. Roy *et al.* [4] reported deactivation of platinum, the most active precious metal catalyst, in the presence of sulfur. Niu *et al.* [5] reveals that the addition of copper and tin to the PdO catalyst promotes catalytic ability and sulfur resistance, and among the prepared catalysts, the CuO/SnO₂/PdO catalyst exhibit the highest activity and excellent resistance to sulfur compounds, and the incorporation of copper and tin promotes catalytic activity and sulfur resistance of the PdO catalyst. Yang *et al.* [6] proposed a specific process for the reaction between CuO and SO₂, and concluded that the existence of SO₂ in the feed gas leads to the phenomenon of sulfur poisoning [7]-[8] of the CuO/ γ -Al₂O₃ catalyst, which in turn leads to a decline in the catalyst activity. Malyi *et al.* [9] evaluated the mechanism of surface sulfur poisoning of two potential Cu-based catalysts based on density functional theory [10], and predicted the formation of Cu-S on the surface of the Cu-based

catalysts. Ordóñez *et al.* [11]-[12] empirically evaluated the catalyst conversion and concluded that deactivation is caused by the reaction of SO₂ with the metal, which alters the structure of the material or forms metal sulfates. Cimino *et al.* [13]-[14] found that in catalytic reactions, sulfur and its compounds could also be adsorbed on the surface of metal atoms, as well as become bonded to other oxygen atoms and form stable and attached sulfates. Electrons from these sulfates occupy the metal's outer orbital. Consequently, the bonds of molecular oxygen could not be broken on the metal surface, resulting in formation of surface oxygen. This surface oxygen is available for oxidation of methane and dehydrogenation, causing the catalytic surface of the metal to lose the capacity to absorb and release oxygen; this eventually results in a loss of catalytic activity.

Most of the studies presented in the literature deal with the causes of catalyst poisoning by SO₂. However, the role of the operating conditions in influencing the sulfur absorption reaction and the kinetic characteristics need to be further explored. Therefore, this study is devoted to evaluating the characteristics of the reaction between CuO/ γ -Al₂O₃ and SO₂ and investigating the law of reactivity governing the reaction of SO₂ absorption by CuO/ γ -Al₂O₃ and the factors governing the changes in the physical and chemical characteristics of CuO/ γ -Al₂O₃, as well as determining the kinetic parameters for the reaction.

2. EXPERIMENTAL SET-UP

The γ -Al₂O₃ particles (9-16 mesh) as the carrier and Cu(NO₃)₂·6H₂O (Aldrich 99.99%) as the solution were used for preparing the CuO/ γ -Al₂O₃ catalyst with incipient wetness impregnation at room temperature. After 10 hours for impregnation, the catalyst was dried in an oven at 110°C for 12 hours, and then calcined in a muffle furnace at 600°C for 4 hours. CuO/ γ -Al₂O₃, selected as the catalyst in this experiment, had the following characteristics: 5~10wt% loading of Cu, 1-2 mm CuO/ γ -Al₂O₃ particle diameter, 168.06 m²/g specific surface area. The reaction of CuO/ γ -Al₂O₃ with

^{*}Key Laboratory of Low-grade Energy Utilization Technologies and Systems (Chongqing University), Ministry of Education of China, Shapingba District, Chongqing, 400030, China.

[#]College of Mechanical and Power Engineering, Chongqing University of Science and Technology, Shapingba District, Chongqing 401331, China

¹ Corresponding author;
Tel.: +86 23 6510 3115; Fax: +86 23 6511 1832
E-mail: zqyang@cqu.edu.cn.

SO₂ was carried out in a micro fixed bed reactor; a schematic of the experimental system is shown in Figure 1. The reaction tube in the micro fixed bed reactor was a ceramic tube of 1200 mm length and 10 mm inner diameter that was placed in a horizontal tube furnace for heating. Gas cylinders provided air and SO₂ (pure SO₂);

the volume concentration of SO₂ was 0.01-0.02 vol %; the reaction temperature was 300-600°C. The detailed preparation and characterization of the catalyst, experimental system, and detailed evaluation of the catalyst activation process are documented in a previous publication [6], [15].

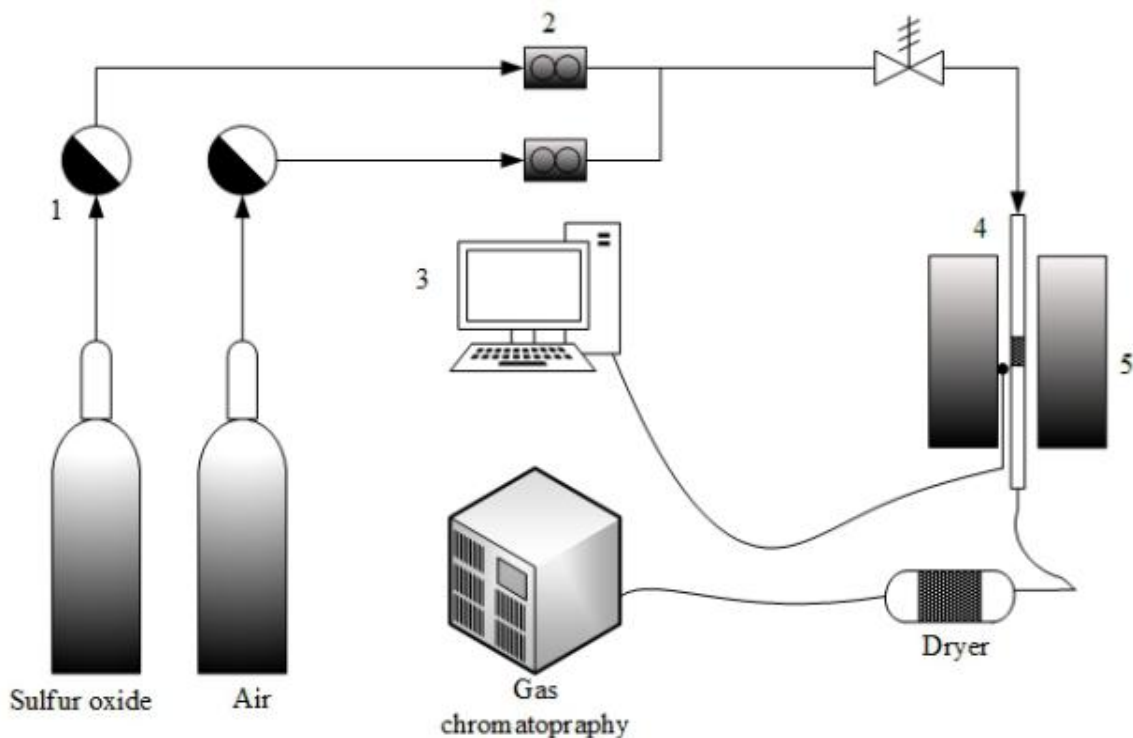
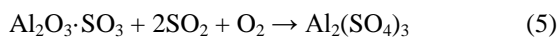
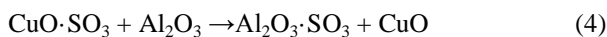
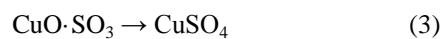


Fig.1. Schematic of the reactor system (1: control valve; 2: flow meter; 3: data acquisition and control system; 4: fixed bed reactor; 5: electric heater).

The following global mechanism of SO₂ deactivation of CuO/ γ -Al₂O₃ is proposed:



Therefore, the conversion ratio (X) of the CuO/ γ -Al₂O₃ catalyst sulfide reaction is defined as follows:

$$X = \frac{W - W_0}{W_{\text{smax}} - W_0} \quad (6)$$

W : the weight of the catalyst at a given time, W_0 : the original weight of the catalyst, W_{smax} : the theoretical weight of the catalyst after completion of the sulfide reaction.

Methane conversion is defined as the follows:

$$\eta = \frac{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}}{[\text{CH}_4]_{\text{in}}} \times 100\% \quad (7)$$

where η is methane conversion, and $[\text{CH}_4]_{\text{in}}$ and $[\text{CH}_4]_{\text{out}}$ are the volume concentration of methane in the feed gases and products, respectively.

3. RESULTS AND DISCUSSION

3.1 Effect of Cu Loading

As shown in Figure 2, the conversion ratio for SO₂ absorption by CuO/ γ -Al₂O₃ increased gradually as the loading of Cu increased from 5% to 10%. However, when the loading of Cu was higher than 10% up to 15%, the conversion ratio declined. This may be interpreted that as the loading of metal increases, the active components of the CuO crystal particles become more, and new holes will be formed in the γ -Al₂O₃ carriers, which results in an increase in the total holes of the catalyst; this leads to an increase in the oxygen storage capacity, and the conversion ratio will naturally improve. When the metal loading reached a critical point, the ratio of SO₂ absorption by CuO/ γ -Al₂O₃ would slow down. This case can be interpreted that when the loading of Cu is less, the active component could be equally distributed on the surface of the γ -Al₂O₃ carrier. When the Cu loading reached a certain extent, the active component accumulated on the surface of γ -Al₂O₃; however, the superficial area would not increase linearly with the metal loading, which may influence SO₂ absorption by CuO/ γ -Al₂O₃. This conforms to the monolayer dispersion theory [16].

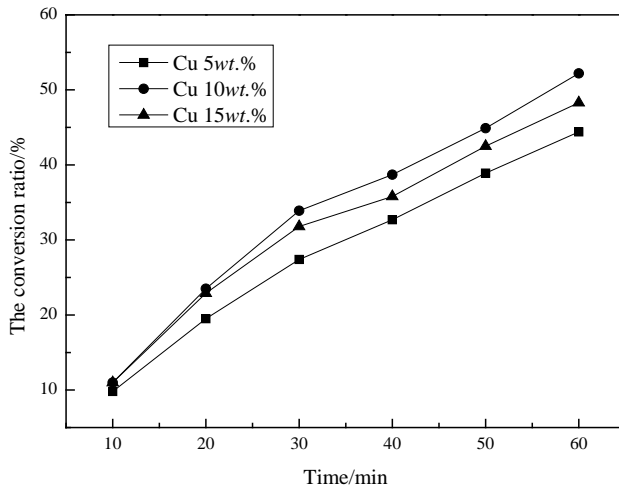


Fig. 2. Influence of Cu loading in CuO/ γ -Al₂O₃ on SO₂ absorption (400°C reaction temperature, 0.01-0.02 vol. % volume concentration of SO₂).

3.2 Effect of SO₂ Concentration

From Figure 3, it can be seen that the conversion ratio for SO₂ absorption by CuO/ γ -Al₂O₃ is low in the absence of O₂, and the sulfation reaction of CuO is strongly suppressed. However, in the absence of O₂, the concentration of SO₂ has a significant influence of the conversion ratio, the higher the concentration of SO₂, the faster CuO/ γ -Al₂O₃ reacted with SO₂, thus, the higher the conversion ratio. Thus, it is evident that oxygen plays a key role; when sufficient oxygen is available, the concentration of SO₂ affects the conversion ratio for SO₂ absorption by CuO/ γ -Al₂O₃; the higher the concentration of SO₂, the greater the amount of SO₂ absorbed. This is because as time progresses, the amount of SO₂ in contact with CuO on the carrier increases, thus the conversion ratio becomes higher.

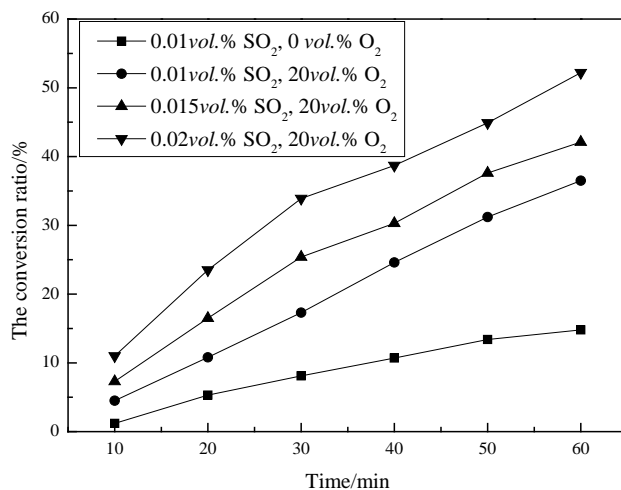


Fig. 3. Influence of SO₂ concentration on conversion (400°C reaction temperature, 200 ml/min gas volume flow, 10wt % loading of Cu).

3.3 Effect of Reaction Temperature

From Figure 4, it can be seen that as the temperature increased, the conversion ratio for SO₂ absorption by CuO/ γ -Al₂O₃ gradually increased. When the temperature was raised from 300°C to 500°C, the conversion ratio

increased significantly. However, with continued increase of the temperature, the trend towards enhancement of the conversion ratio slowed, where the overall trend is towards a slow increase after an initial rapid increase. Based on these findings [17], the main active component in CuO/ γ -Al₂O₃ is highly dispersed-state CuO. Fang *et al.* [17] claim that highly dispersed-state CuO could be simultaneously distributed in CuO/ γ -Al₂O₃ in octahedral and tetrahedral coordination environments, with higher activity in the octahedral coordination environment. As the reaction temperature gradually increased, the population of species in the octahedral environment will increase, while the number of tetrahedral coordination sites will be reduced, increasing the activity of CuO. However, if the temperature is too high, the CuAl₂O₄ phase of the spinel class will be generated, which reestablishes a stable structure with a tetrahedral environment, resulting in decreased activity of CuO.

4. KINETIC ANALYSIS OF THE SULFATION REACTION OF CUO/ γ -AL₂O₃

The sulfation reaction of CuO/ γ -Al₂O₃ is a typical non-catalytic gas-solid reaction [18]. In the initial stage, SO₂ gas is distributed on the surface of the CuO/ γ -Al₂O₃ particles and the reaction ratio is controlled by the chemical reaction. After some time, the number of active sites located on the surface would be reduced, leading to diffusion controlled reaction. Therefore, the surface reaction control zone and the diffusion control zone exist in this reaction. However, during the sulfation reaction, the control zone would change. In the initial stage, the product layer is very thin, SO₂ gas easily goes through the product layer and makes contact with the unreacted solid. This process is of low resistance and is mainly controlled by chemical reaction. As the product layer thickens, the diffusion resistance increases, resulting in diffusion controlled reaction. The equivalent grain mode [19]-[20] is mainly applied to porous particles; here, the pores in the Cu-based catalyst are well developed. Therefore, the experimental data are treated with the equivalent particle model in this paper. The equivalent particle model is expressed as follows:

The surface reaction control zone [21] is described by:

$$t = AG_{fp}(X) \quad (8)$$

Where n is the reaction order. Many research findings revealed that the reaction between the metal oxide and SO₂ is a first order reaction, thus $n = 1$. $G_{fp}(X)$ is a function of the conversion ratio of CuO/ γ -Al₂O₃, the expression is:

$$G_{fp}(X) = 1 - (1 - X)^{1/3} \quad (9)$$

$$\frac{1}{A} = \frac{K_s \times C_A^n}{\rho_{im} \times R_0} \quad (10)$$

The relationship between the ratio constant K_s and the temperature T conforms to the Arrhenius equation:

$$K_s = K_{s0} \exp(-E_a / R_g T) \quad (11)$$

Taking the log of Equation 10 and Equation 11 together gives:

$$\ln \frac{1}{A} = \ln \frac{K_{s0} \times C_{A0}}{\rho_{fm} \times R_0} - E_a / R_g T \quad (12)$$

The diffusion control zone is described by:

$$t = B_1 + B_2 P_{fp}(X) \quad (13)$$

where B_1 is the correction factor, $P_{fp}(X)$ is a function of the conversion ratio of $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$; the expression for $P_{fp}(X)$ is:

$$P_{fp}(X) = 1 - 3(1 - X)^{2/3} + 2(1 - X) \quad (14)$$

$$B_1 = \frac{\rho_{fm} \times D}{C_{A0}^n (1 - \xi)} \quad (15)$$

$$B_2 = \frac{\rho_{fm} \times R_0^2 (1 - \xi)}{6D_{ep} C_{A0}^n} \quad (16)$$

The relationship between the ratio constant K_s and the temperature T conforms to the Arrhenius equation:

$$D_{ep} = D_{ep0} \exp(-E_p / R_g T) \quad (17)$$

Taking the log of Equation 10 and Equation 11 together gives:

$$\ln \frac{1}{B_2} = \ln \frac{6D_{ep0} C_{A0}}{\rho_{fm} \times R_0^2 (1 - \xi)} - E_p / R_g T \quad (18)$$

The conversion ratio for the $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst with variation of the reaction temperature of SO_2 absorption by $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ (300°C, 400°C, 500°C, 600°C) is shown in Figure 4. Based on the results of Figure 4 and Equation 9, $G_{fp}(X)$ - t can be determined, as shown in Figure 5.

Figure 5 shows a deviation in the curves that occurred after 30 minutes. This is attributed to a change in the control zone from the surface reaction controlled zone to the diffusion controlled zone around 30 minutes. Using Equation 9 to match the line with the results obtained before 30 min in Figure 4 gives rise to Figure 6, from which the slope was calculated for different temperatures. Using Equation 14 for linear fitting, we get Figure 7, after which we calculated the related kinetic parameters for the surface chemical reaction controlled zone, as shown in Table 1.

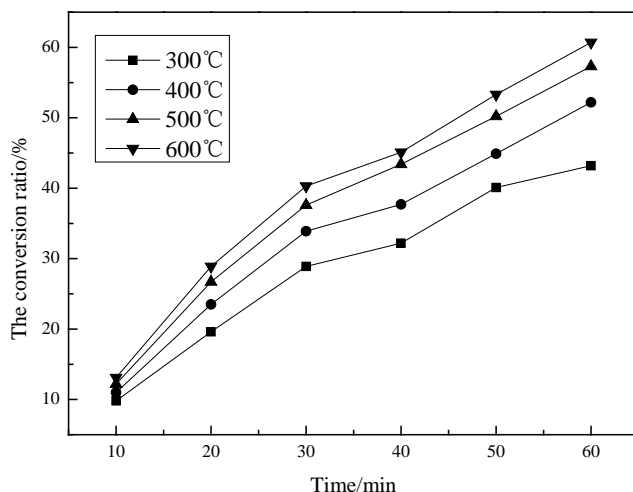


Fig. 4. Influence of reaction temperature (200 ml/min gas volume flow, 10wt% loading of Cu, 0.02% volume concentration of SO_2).

Table 1. Kinetics parameters for $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ in the surface reaction controlled zone.

Temperature (°C)	300	400	500	600
A(min)	270.270	222.222	192.307	178.571
R^2	0.9999	0.9946	0.9976	0.9967
K_s (mol/cm ² ·min)	2.688×10^{-2}	3.267×10^{-2}	3.775×10^{-2}	4.219×10^{-2}
K_{s0} (mol/cm ² ·min)		2.005×10^{-3}		
E_a (kJ/mol)		5.843		
R^2		0.9859		

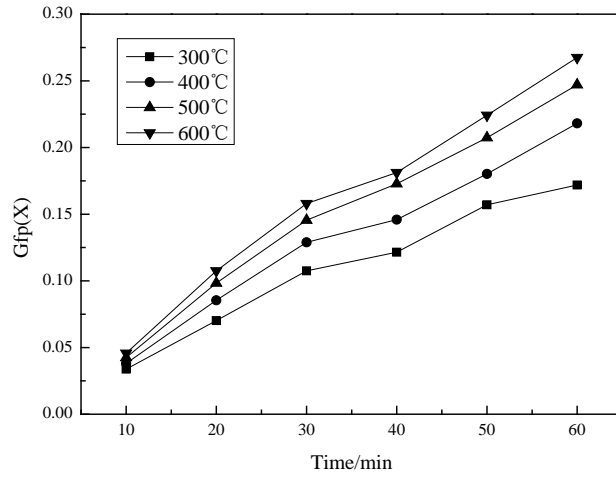


Fig. 5. $G_{fp}(X)$ - t diagram for SO_2 absorption by $CuO/\gamma-Al_2O_3$.

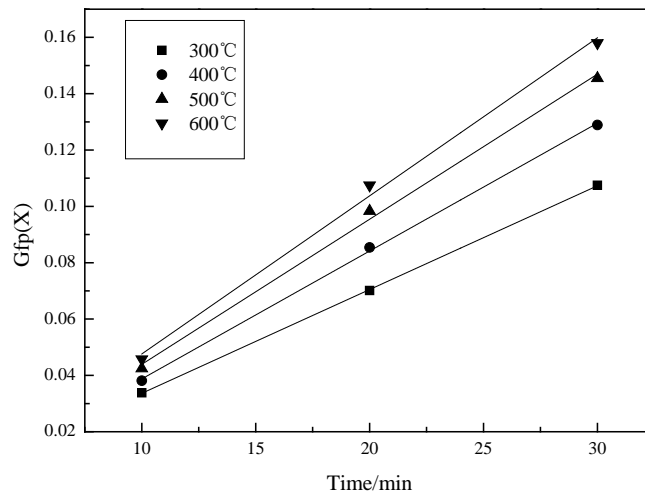


Fig. 6. Fitting diagram for $G_{fp}(X)$ - X (pre-30 min).

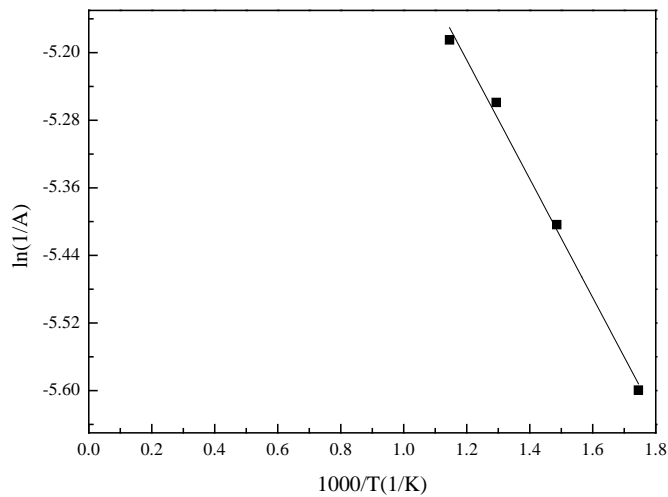


Fig. 7. Relationship between $\ln(1/A)$ and $1/T$.

Using Equation 14 to match the line with the post-30 min results in Figure 4 produces Figure 6, from which the slope is determined for different temperatures. Using Equation 18 for linear fitting gives Figure 9, from

which we calculated the related kinetic parameters for the surface chemical reaction controlled zone, as shown in Table 2.

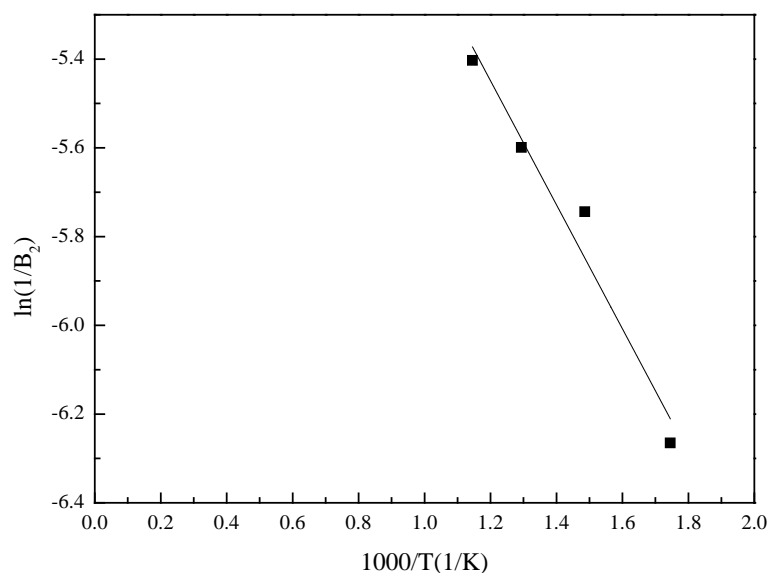


Fig. 8. Fitting diagram for $P_{fp}(X)$ -t (post-30 min).

Table 2. Kinetics parameters for $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ in the diffusion controlled zone.

Temperature ($^{\circ}\text{C}$)	300	400	500	600
B_1 (min)	17.157	22.593	18.810	20.933
B_2 (min)	526.315	312.500	270.270	222.222
R^2	0.96	0.9946	0.9941	0.9982
D_{ep} ($\text{mol}/\text{cm}^2 \cdot \text{min}$)	1.524×10^{-4}	1.254×10^{-4}	1.607×10^{-4}	1.920×10^{-4}
D_{ep0} ($\text{mol}/\text{cm}^2 \cdot \text{min}$)		1.589×10^{-4}		
E_a (KJ/mol)		11.617		
R^2		0.963		

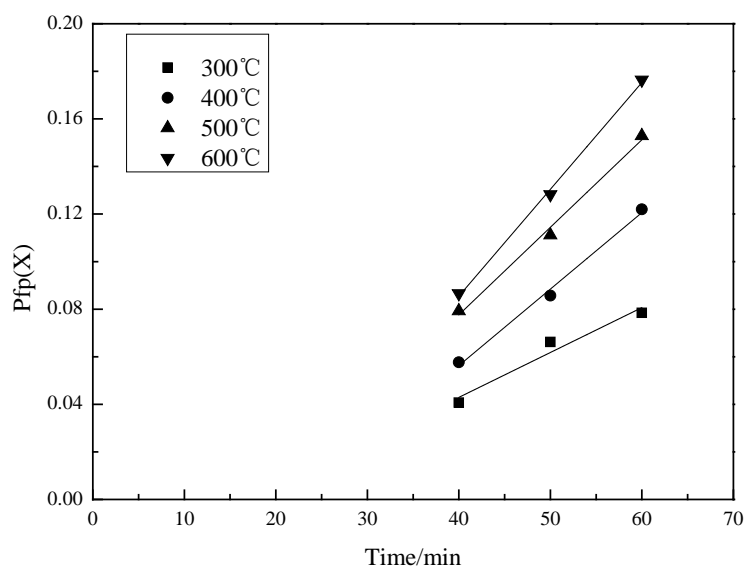


Fig. 9. Relationship between $\ln(1/B_2)$ and $1/T$.

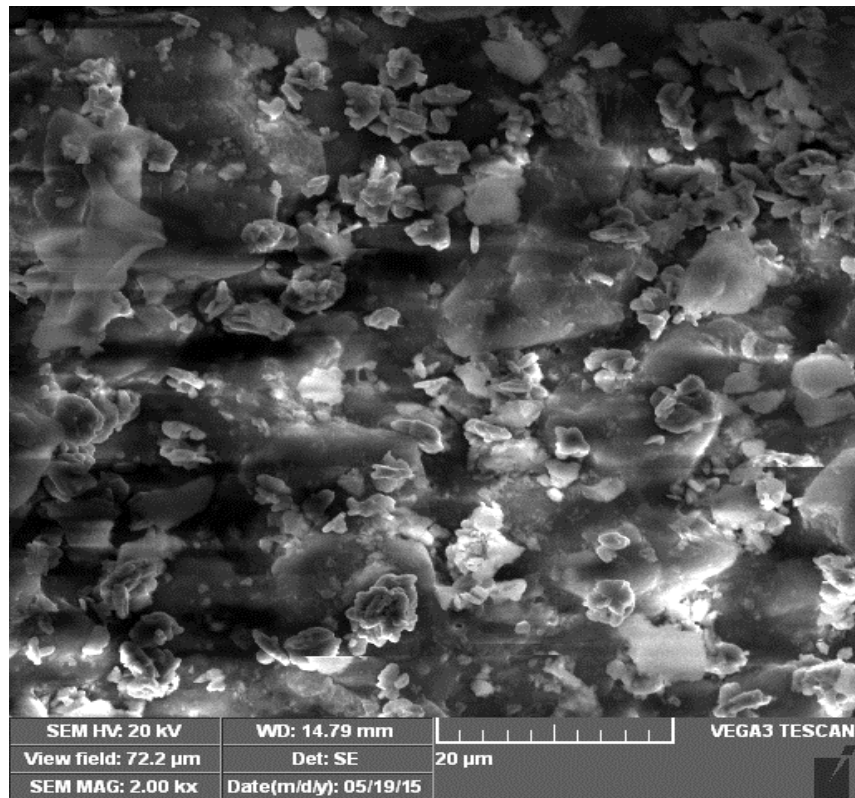


Fig.10. SEM image of fresh CuO/ γ -Al₂O₃.

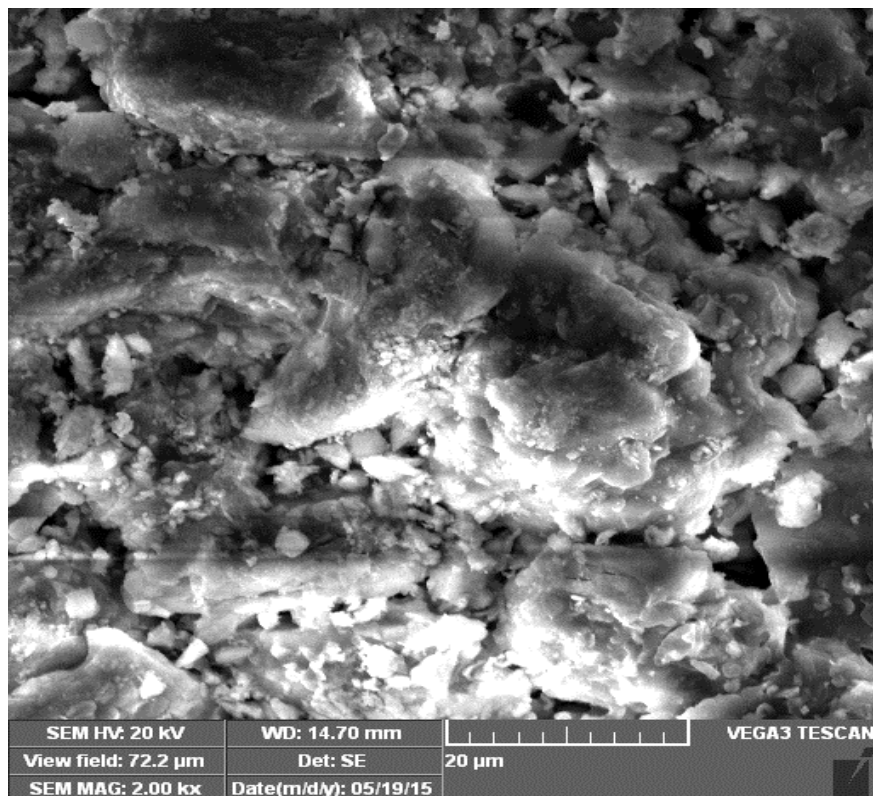


Fig. 11. SEM image of reacted CuO/ γ -Al₂O₃.

Figure 10 and Figure 11 show the microstructure image before and after the reaction between CuO/ γ -Al₂O₃ and SO₂. Comparison of image Figure 10 and Figure 11 shows that there are uniformly sized particles on the surface of the catalyst after the reaction, some of

which aggregated into larger particle clusters. This phenomenon is more obvious when the gas stream containing SO₂ is piped into the CuO/ γ -Al₂O₃ catalyst. This may be because the reaction gas stream containing SO₂ reacts with the metal on the surface of the catalyst,

thereby generating a metal sulfate, corresponding to the larger particle clusters in the image. Before reaction with SO₂, the CuO active components are uniformly distributed in the γ -Al₂O₃ carrier. After CuO/ γ -Al₂O₃ absorbs SO₂, CuO/ γ -Al₂O₃ assembles with the reaction product. Furthermore, agglomeration occurs, thereby hindering reaction of CuO/ γ -Al₂O₃ with SO₂ and reducing the activity of CuO.

5. CONCLUSION

Herein, we specifically evaluated the characteristics of the reaction between CuO/ γ -Al₂O₃ and SO₂ based on empirical assessment of the factors influencing the reaction between CuO/ γ -Al₂O₃ and SO₂. These factors include the loading of Cu, concentration of SO₂, and temperature, as well as evaluation of the kinetic characteristics of the sulfation reaction of CuO/ γ -Al₂O₃ particles using the effective particle model. The conclusions are as follows:

1. When the metal loading reaches a critical point, the ratio of increase of SO₂ absorption by CuO/ γ -Al₂O₃ will slow down. Under aerobic conditions, the concentration of SO₂ has a significant impact on the conversion ratio of SO₂ absorbed by CuO/ γ -Al₂O₃; the higher the concentration of SO₂, the faster CuO/ γ -Al₂O₃ reacts with SO₂, and the higher the conversion ratio. With increasing temperature, the conversion ratio of CuO/ γ -Al₂O₃ absorbed SO₂ gradually increases, but at 500°C, the enhancement of the conversion ratio slows down.
2. Using the effective particle model to study the kinetic characteristics of CuO/ γ -Al₂O₃, we found that in the initial stage, the reaction between CuO/ γ -Al₂O₃ and SO₂ is mainly controlled by surface chemical reaction with an activation energy of 5.8 kJ/mol; in the latter stage, the reaction is diffusion controlled with an activation energy of 11.6 kJ/mol.

ACKNOWLEDGEMENT

The authors would like to thank the financial support from Natural Science Foundation of China with Project no. 51206200, and the Fundamental Research Funds for the Central Universities with Project no. CDJZR12140031, and visiting Scholar Foundation of Key Laboratory of Low-grade Energy Utilization Technologies and System, MOE of China in Chongqing University (LLEUTS-201301).

REFERENCES

- [1] Nagini Y.S., Sarada N., Murali Krishna M.V.S., Murthy P.V.K., 2012. Comparative Studies on Emissions of Four Stroke Copper Coated Spark Ignition Engine with Catalytic Converter with Different Catalysts with Gasohol. *International Energy Journal* 13(4): 161-168.
- [2] Wu T., Cai W., Zhang P., Song X., Gao L., 2013. Cu-Ni@SiO₂ alloy nanocomposites for methane dry reforming catalysis. *RSC Advances* 3(46): 23976-23979.
- [3] Lin B., Dai H., Wang C., Li Q., Wang K., Zheng Y., 2014. Combustion characteristics of low concentration coal mine methane in divergent porous media burner. *International Journal of Mining Science and Technology* 24(5): 671-676.
- [4] Roy S. and A.K. Saroha. 2014. Ceria promoted γ -Al₂O₃ supported platinum catalyst for catalytic wet air oxidation of oxalic acid: kinetics and catalyst deactivation. *RSC Advances* 4(100): 56838-56847.
- [5] Niu Q., Li B., Xu X.L., Wang X.J., Yang Q., Jiang Y.Y., Chen Y.W., Zhu S.M. and Shen S.B., 2014. Activity and sulfur resistance of CuO/SnO₂/PdO catalysts supported on γ -Al₂O₃ for the catalytic combustion of benzene. *RSC Advances* 4(93): 51280-51285.
- [6] Yang Z.Q., Liu J.J., Zhang L. and Zheng S.W., 2014. Catalytic combustion of low-concentration coal bed methane over CuO/ γ -Al₂O₃ catalyst: effect of SO₂. *RSC Advances* 4: 39394-39399.
- [7] Stanley J.N., Benndorf P., Heinroth F., Masters A.F. and Maschmeyer T., 2014. Probing structure-functionality relationships of catalytic bimetallic Pt-Ru nanoparticles associated with improved sulfur resistance. *RSC Advances*. 4(53): 28062-28071.
- [8] Arjmand M., Azad A., Leion H., Lyngfelt A. and Mattisson T., 2011. Prospects of Al₂O₃ and MgAl₂O₄-supported CuO oxygen carriers in chemical-looping combustion (CLC) and chemical. *Energy Fuels* 25(11): 5493-5502.
- [9] Malvi O.I., Bai K. and Kulish V.V., 2012. Density functional theory study of sulfur tolerance of copper: New copper-sulfur phase diagram. *Chemical Physics Letters* 533(23): 20-24.
- [10] Sun S., Li C., Zhang D. and Wang Y., 2015. Density functional theory study of the adsorption and dissociation of O₂ on CuO (1 1 1) surface. *Applied Surface Science* 333(1): 229-234.
- [11] Ordóñez S., Paredes J. and Díez F., 2008. Sulphur poisoning of transition metal oxides used as catalysts for methane combustion. *Applied Catalysis A: General* 341: 174-180.
- [12] López E., Ordóñez S. and Díez, F.V., 2006. Deactivation of a Pd/Al₂O₃ catalyst used in hydrodechlorination reactions: Influence of the nature of organochlorinated compound and hydrogen chloride. *Applied Catalysis B: Environmental* 62(1): 57-65.
- [13] Cimino S., Torbatib R., Lisia L. and Russo G., 2009. Sulphur inhibition on the catalytic partial oxidation of methane over Rh-based monolith catalysts. *Applied Catalysis A: General* 360(1): 43-49.
- [14] Kyllhammar L., Carlsson P. and Skoglundh M., 2011. Sulfur promoted low-temperature oxidation of methane over ceria supported platinum catalysts. *Journal of Catalysis* 284(1): 50-59.
- [15] Zhang L., Liu J.J. and Yang Z.Q., 2014. Effects of sulfur poisoning on combustion characteristics of low concentration methane with SO₂ over Cu/ γ -Al₂O₃ catalysts. *Journal of Fuel Chemistry and*

- Technology* 42(5): 635-640 (in Chinese).
- [16] Xie Y. and Y. Tang. 1990. Spontaneous monolayer dispersion of oxides and salts onto surfaces of supports: Applications to heterogenous catalysis. *Advanced Catalysis* 37: 1-43.
- [17] Fang S., Lin P. and Fu Y., 1994. A Study of the Dispersed States of Copper Species on CuO/ γ -Al₂O₃ Catalysts. *Journal of Molecular Catalysis (China)* 8(2): 86-90.
- [18] Adlooa H., Safaeib Z., Esfahanyb M.N. and Ehsani M.R., 2015. Development of pore network method in simulation of non-catalytic gas-solid reactions- Study of sulfur dioxide chemisorption on copper oxide sorbents. *Chemical Engineering Journal* 262: 295-312.
- [19] Szekely J., Lin C.I. and Sohn H.Y.A., 1973. structural model for gas-solid reactions with a moving boundary. *Chemical Engineering Science* 28(11): 1975-1989.
- [20] Franco A.A., 2013. Multiscale modelling and numerical simulation of rechargeable lithium ion batteries: concepts, methods and challenges. *RSC Advances* 3(32): 13027-13058.
- [21] Wang F., Zhang D., Zhao H., Wu T. and Gao, J., 2010. Research into the kinetics of COS elimination from syngas at moderate temperatures. *Fuel* 89: 888-893.

