Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 691–695

KINETIC MODEL FOR THE REACTION BETWEEN SO_2 AND COAL FLY ASH/CaO/$CaSO_4$ SORBENT

K. T. Lee, S. Bhatia and A. R. Mohamed[*]

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal,
Seberang Perai Selatan, Pulau Pinang, Malaysia

The reaction between SO_2 and sorbent prepared from coal fly ash, CaO and $CaSO_4$ were investigated and modeled. The experiments were conducted using thermogravimetric analysis at isothermal conditions, where the rate measurements were carried out in the temperature range from 60 to 140°C. The kinetics of the sulfation reaction is characterized by a dramatic decrease in the rate of reaction at the initial period of reaction time and the sorbent is left partially converted. Using isoconversional method, the activation energy of the sulfation reaction was found to be independent on the conversion of the sorbent. A one step global model was then proposed and the model based on almost second order (n=2.2) reaction was found to fit the kinetic data. Based on the propose model, the activation energy and frequency factor for the sulfation reaction was found to be 22.9 kJ mol^{-1} and 64.4 min^{-1} respectively. The model was found to give a good prediction of the conversion–time curve for experimental run not used in the development of the model. The value of activation energy obtained using the proposed model was found to be in agreement with the value calculated using the isoconversional method.

Keywords: *isoconversional method, kinetics, sulfation, thermogravimetric analysis*

Introduction

Recent studies have shown that when silica (SiO_2) eluted from coal fly ash is mixed with $Ca(OH)_2$ or CaO in a hydration process, sorbents with high SO_2 capture efficiency can be obtained [1–3]. This is largely due to the pozzolanic reactions between $Ca(OH)_2$/CaO and SiO_2 which produce highly hydrated products that has a much higher surface area as compared to the raw materials. It has also been shown that the addition of calcium sulfate ($CaSO_4$) to the preparation mixture can further promote the formation of the hydrated products [4]. It was believed that the active species in the sorbent that reacts with SO_2 is calcium (Ca) ions. The role of the high surface area hydrated compound is basically to make the Ca ions contain in the sorbent more accessible to SO_2 during the sulfation reaction.

The preparation, characterization and activity study of sorbent made from hydrated coal fly ash has been thoroughly reported in the literature [3–7], however, the kinetic modeling for the sulfation reaction between the sorbent and SO_2 is still scare. The kinetics of the reaction between the hydrated coal fly ash sorbent is complicated as it involves a series of reactions in parallel and many species. The changing product layer diffusivity and the porosity in the sorbent further complicates the kinetics. The aim of this paper is to develop a one step global reaction mathematical model that can describe the sulfation reaction using thermogravimetric analysis (TG). The use of TG to develop kinetic model for various processes has been well reported in [8–10]. From the kinetic data, isoconversional method was initially used to determine the dependency of the activation energy on the conversion of the sorbent [11–13]. Based on the results, a mathematical model was then proposed to calculate the kinetic parameters of the sulfation reaction. The validity of the model was verified by comparing simulated with experimental results.

Experimental

The sorbent were prepared from calcium oxide (CaO), coal fly ash and calcium sulfate ($CaSO_4$). The details of the sorbent preparation method is reported elsewhere [14]. The chemical composition of the stock sorbent was analyzed using Rigaku X-ray Spectrometer RIX 3000 to determine the weight percentage of Ca in the sorbent. A Perkin Elmer TGA7 thermogravimetric analyzer was used to study the sulfation reaction between the sorbent and SO_2. Since the sulfation reaction is a gas–solid reaction, it is very important to work with minimal sorbent weight in order to minimize the effects of interparticle heat and mass transfer resistance. On the other hand, since the sorbent consists of a

---

[*] Author for correspondence: chrahman@eng.usm.my

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

mixture of reacted and unreacted raw materials, the amount of sorbent used must be big enough to represent the bulk sorbent. Therefore, in the preliminary experimentation, experiments were carried out using different amount of sorbent (5, 10, 15, 20 and 25 mg) in order to determine the right amount of sorbent to be used. Based on the preliminary experimental results, it was decided to use 10 mg of sorbent in the experimentation. The details and results of the preliminary experiments are presented elsewhere [14].

The experiments of the sulfation reaction was carried out by placing approximately 10 mg of sorbent in the sample pan. Before each run, the temperature of the sorbent was increased to the reacting temperature under N_2 flow to ensure that no reaction takes place and any adsorbed species on the sorbent were desorbed. When the reaction temperature was achieved, a feed gas consisting 4000 ppm SO_2 and balance N_2 are fed to the sorbent from the top at a flow rate of 150 mL s^{-1}. The experiment was carried out under isothermal conditions at 60 to 140°C. The sorbent mass was measured continuously by a microbalance as a function of time. Reaction was carried at that temperature until no more mass changes were recorded at that point which the reaction is assumed to have been completed. A base run was performed to take into account the mass changes in the sorbent due to loss of water and desorption of adsorbed gases. In the base run, the temperature of the sorbent in the TG was increased to the reacting temperature under inert N_2 flow. The sorbent was held at that temperature and under N_2 gas flow until no more mass loss was recorded. The mass difference between the experimental run where SO_2/N_2 were used and the base run would indicate the mass changes due to the sorption of SO_2 in the solid sorbent. For every experiment, including the base run, was repeated three to six times to increase the precision of the mass measurements. The relative error for the data obtained between the repetitions was less than 5%. This procedure also diminished the impact of the variation in composition or shape of the sorbents in each run. For clarity, only the averages are presented in this paper.

Theory

The mass gain in each of the experimental run may be correlated to the conversion by the use of fractional conversion, X [15]. Note that this is a gas–solid reaction that produces solid as the product. The fractional conversion, X, is defined as mmol of SO_2 adsorb on the sorbent divided by the mmol of Ca contain in the sorbent [16, 17] as given in Eq. (1):

$$X = \frac{m_t - mb_t}{m_0} \frac{M_{Ca}}{M_{SO_2}} \tag{1}$$

where m_0 is the initial mass of Ca in the sorbent, m_t is the mass of the sorbent when expose to SO_2/N_2 gas at time t, mb_t is the mass of the sorbent during base run at time t, M_{Ca} is the molecular mass of Ca and M_{SO_2} is the molecular mass of SO_2. Theoretically the fractional conversion should increase from 0 and reaches 1 when the sorbent is fully converted.

Before proposing a mathematical model for the sulfation reaction, the dependency of activation energy on the conversion of the sorbent was checked using isoconversional method [11–13, 18]. The differential method for evaluating the activation energy using isoconversional method is shown in Eq. (2):

$$\ln \frac{dX}{dt} = \ln Af(X) - \frac{E}{RT} \tag{2}$$

where A is the frequency or pre-exponential factor, $f(X)$ is the conversion dependent term, E is the activation energy, R is the universal gas constant and T is the absolute reaction temperature. For a constant value of X, a plot of $\ln dX/dt$ *vs.* $1/T$ should yield a straight line whose slop allows an evaluation of the activation energy, assuming that the activation energy is independent on the conversion [18]. Once the dependency of the activation energy on the conversion is determined, the conversion dependent term, then $f(X)$ of the sulfation reaction can be determined.

In order to determine the conversion dependent term, $f(X)$ of the sulfation reaction, a rate of reaction per unit time, r, is expressed as in Eq. (3):

$$r = \frac{dX}{dt} = k(T) f(X) \tag{3}$$

where $k(T)$ is the temperature dependent term, usually taken as the global reaction rate constant, k, which is assumed to obey the Arrhenius equation given by Eq. (4):

$$k(T) = k = A \exp\left(-\frac{E}{RT}\right) \tag{4}$$

Assuming that a simple n^{th} order kinetic relationship holds for the conversion dependent term, $f(X)$, such that, $f(X)=(1-X)^n$, Eq. (3) can be rewritten as in Eq. (5):

$$r = \frac{dX}{dt} = k(1-X)^n \tag{5}$$

In order to determine the value of k, integral method is used to solve Eq. (5). Rearranging and integrating Eq. (5), Eq. (6) is obtained as:

$$\frac{1-(1-X)^{1-n}}{1-n} = kt \text{ (for n}\neq 1) \tag{6}$$

Thus, a plot of $[1-(1-X)^{1-n}]/(1-n)$ *vs.* t (for $n\neq 1$) should result in a straight line of slope k for the proper value of n. The criterion used to determine acceptance value of n is when the plot $[1-(1-X)^{1-n}]/(1-n)$ *vs.* t (for $n\neq 1$) give the best straight line for all reaction temperature studied. The best straight line is defined as the line that gives the highest correlation coefficient (R^2) for all the data point obtained from the conversion–time curve for each and every reaction temperature studied.

In order to obtain the activation energy and frequency factor of the sulfation reaction, Eq. (4) will be utilized. By determining the value of global reaction rate constant at different temperatures, a plot of global reaction rate constant, ln$k$, *vs*. reciprocal of reaction temperature, $1/T$, can be obtained. The plot should again result in a straight line of slope $-E/R$ and intercept equivalent to ln$A$.

Results and discussion

Conversion vs. time curve

Figure 1 shows the conversion *vs*. time data for the sorbent at different reaction temperature ranging from 60 to 140°C. The sulfation reaction is characterized by a dramatic decrease in the rate of the reaction at the initial period and then the sorbent is left partially converted. This reaction behavior is similar to those reported in the literature [19]. It was observed that the initial rate of the sulfation reaction increases with increasing reaction temperature. The highest initial rate of reaction was obtained at a reaction temperature of 140°C. The increase in the initial rate of reaction is a direct consequence of higher reaction rate constant at higher reaction temperature, which obeys the Arrhenius law. On the other hand, the drop of sulfation reaction rate with time could be possibility due to two reasons. The first reason could be due to the availability of less active species (Ca) in the sorbent as the reaction proceeds longer and the second reason could be due to the plugging of the pores of the sorbent. This sulfation reaction is a solid–gas reaction that produces solid product that has a higher molar volume compared to the reactant [20]. Thus when the reaction occurs at the pore mouth, expansion of the product layer could cause plugging of the pore and thus preventing SO_2 from further diffuse into the inner pore of the sorbent to react with the active species. This also explains why the sorbent is left partially converted. When all the pore mouth of the sorbent is block by the products of the sulfation reaction, the Ca contain in the inner pore of the sorbent can no longer react with SO_2 and thus leaves the sorbent partially converted.

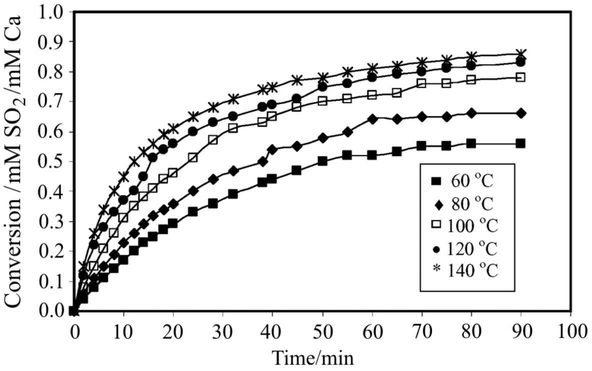

Fig. 1 Conversion as a function of time at different reaction temperature

Dependency of activation energy on conversion

The dependency of activation energy on conversion was checked using isoconversional method. Figure 2 shows the plot of lndX/dt *vs*. $1/T$ at a constant value of X=0.3. The slope of the plot, which is equivalent to $-(E/R)$ allows the evaluation of activation energy, E. The value of E at X=0.1, 0.3 and 0.5 is shown in Table 1. The results indicated that the activation energy is constant irrespective of the conversion with a mean value of 22.7 kJ mol^{-1}.

Global reaction rate constant

Using trial and error, beginning with the value of n=1.1, the plot of $[1-(1-X)^{1-n}]/(1-n)$ *vs.* t at various reaction temperature was plotted. The value of n was varied from 1.1 to 100. In order to reduce the time re-

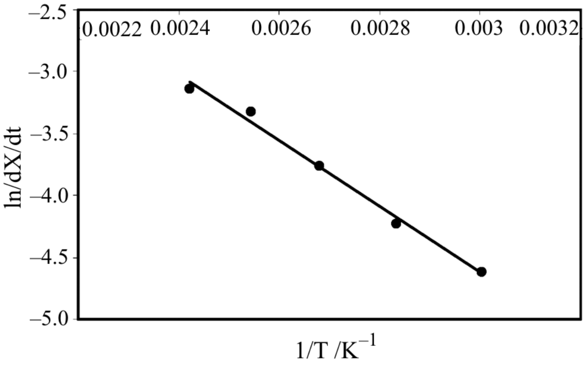

Fig. 2 Plot of lndX/dt *vs*. $1/T$ at a constant value of X=0.3

Table 1 Activation energy at various conversion value determined using isoconversional method

Conversion, X	E/kJ mol^{-1}
0.1	22.8
0.3	22.1
0.5	23.1
Average	22.7

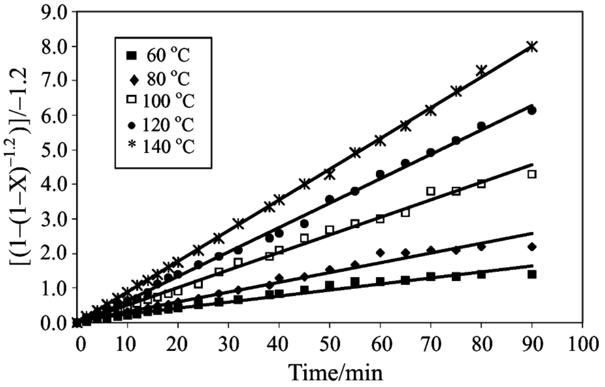

Fig. 3 $[1-(1-X)^{1-2.2}]/1-2.2$ *vs.* t plot at different reaction T

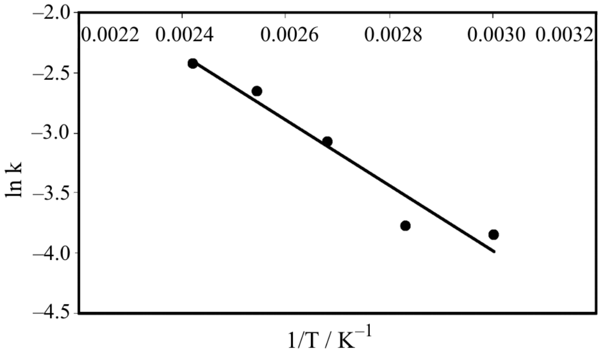

Fig. 4 Arrhenius plot of rate constant *vs.* reciprocal of reaction T

quire to attempt this procedure, a program written in Matlab was developed. It was found that the value of n=2.2 fitted the selection criteria for n. The plot for $[1-(1-X)^{1-2.2}]/(1-2.2)$ *vs.* t is given in Fig. 3. The global reaction rate constant, which is equivalent to the slope of the $[1-(1-X)^{1-2.2}]/(1-2.2)$ *vs.* t plot is summarized in Table 2. The correlation coefficient for the various straight line obtained in the $[1-(1-X)^{1-2.2}]/(1-2.2)$ *vs.* t plot is also given in Table 2. From Table 2, it is clear that the global reaction rate constant increases with reaction temperature. The increase in global reaction rate constant will result in higher rate of sulfation reaction at higher reaction temperature. The high value of correlation coefficient (above 0.96) for all the straight line drawn in the $[1-(1-X)^{1-2.2}]/(1-2.2)$ *vs.* t plot shows that the underlying assumption used in this analysis are satisfied.

Activation energy and frequency factor

Based on the data obtained in Table 2, a plot of ln$k$ *vs.* $1/T$ as shown in Fig. 4 was obtained. The plot was found to yield a straight line indicating that the global reaction rate constant does obey the Arrhenius Law as in Eq. (4). Thus the slope of the plot would be equivalent to $-E/R$ and intercept equivalent to ln$A$ respectively. The value of activation energy and frequency factor for the sulfation reaction was found to be 22.9 kJ mol^{-1} and 64.4 min^{-1} respectively. The good agreement between the activation energy obtained by means of isoconversional method (22.7 kJ mol^{-1}) and the proposed kinetic model again indicated that the underlying assumptions made in this work are satisfied. The activation energy of the sulfation reaction using the sorbent synthesized from coal fly ash was found to be way much lower than the sulfation reaction when CaO (41.8 kJ mol^{-1}) and $Ca(OH)_2$ (133.9 kJ mol^{-1}) is used as the sorbent [21]. This result shows that the reaction between SO_2 and the sorbent synthesized from coal fly ash/CaO/$CaSO_4$ is easier to occur as compared to using CaO or $Ca(OH)_2$ alone as the sorbent. With the kinetic parameters obtained, a mathematical model was proposed for the sulfation reaction:

$$r=\frac{\mathrm{d}X}{\mathrm{d}t}=64.4\exp\left(-\frac{22.9}{RT}\right)(1-X)^{2.2} \qquad (7)$$

In order to verify the model developed, the model was used to predict the conversion–time curve at a reaction temperature of 90°C. Figure 5 shows the comparison between the experimental conversion–time curve and simulated conversion–time curve predicted using the model developed. It was found that the model predicted the conversion–time curve very well with error less than 5%, indicating that the model is highly reliable in predicting the kinetics of the sulfation reaction.

Table 2 Global reaction rate constant and correlation coefficient extracted from the $[1-(1-X)^{1-2.2}]/(1-2.2)$ *vs.* t plot

Reaction temperature/K	Global reaction rate constant, k/min^{-1}	Correlation coefficient, R^2
333 (60°C)	0.0188	0.965
353 (80°C)	0.0289	0.979
373 (100°C)	0.0506	0.994
393 (120°C)	0.0692	0.997
413 (140°C)	0.0887	0.999

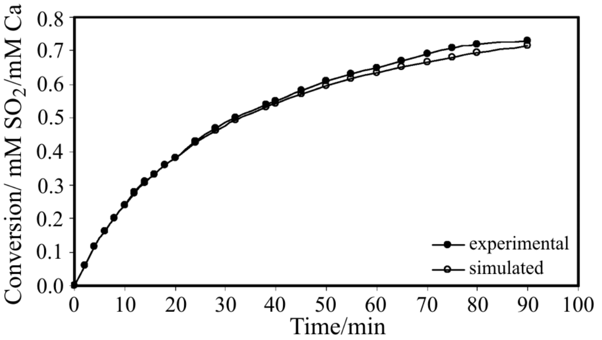

Fig. 5 Comparison between experimental and simulated conversion *vs.* time curve at a reaction temperature of 90°C

Conclusions

The kinetics of the reaction between sorbent synthesized from coal fly ash/CaO/$CaSO_4$ with SO_2 at the lower temperature range has been reported. Using isoconversional method, the activation energy of the sulfation reaction was found to be independent of the conversion. A kinetic model based on a one step model was then proposed for the sulfation reaction and was found to fit the kinetic data very well.

Acknowledgement

The authors would like to thank JSPS-VCC (Program on Environmental Science, Engineering and Ethics) and Ministry of Science, Technology and Environment Malaysia (Project No. 08-02-05-2040EA001) for the funding on this project.

References

1 B. L. Lin, S. M. Shih and C. F. Liu, Ind. Eng. Chem. Res., 42 (2003) 1350.
2 M. J. Renedo and J. Fernandez, Ind. Eng. Chem. Res., 41 (2002) 2412.
3 J. Fernandez, M. J. Renedo, A. Pesquera and J. A. Irabien, Powder Technol., 119 (2001) 201.
4 T. Ishizuka, T. Yamamoto, T. Murayama, T. Tanaka and H. Hattori, Energy Fuels, 15 (2001) 438.
5 T. Ishizuka, H. Tsuchiai, T. Murayama, T. Tanaka and H. Hattori, Ind. Eng. Chem. Res., 39 (2000) 1390.
6 N. Karatepe, A. E. Mericboyu and S. Kucukbayrak, Environ. Technol., 20 (1999) 377.
7 M. J. Renedo, J. Fernandez, A. Garea, A. Ayerbe and J. A. Irabien, Ind. Eng. Chem. Res., 38 (1999) 1384.
8 K. Chrissafis, K. G. Efthimiadis, E. K. Polychroniadis and S. C. Chadjivasiliou, J. Therm. Anal. Cal., 74 (2003) 761.
9 K. Chrissafis, J. Therm. Anal. Cal., 73 (2003) 745.
10 J. J. Sunol, J. Saurina, R. Berlanga, D. Herreros, P. Pages and F. Carrasco, J. Therm. Anal. Cal., 55 (1999) 57.
11 P. Simon, J. Therm. Anal. Cal., 76 (2004) 123.
12 F. Rodante, G. Catalani and S. Vecchio, J. Therm. Anal. Cal., 68 (2002) 689.
13 P. Budrugeac, D. Homentcovschi and E. Segal, J. Therm. Anal. Cal., 63 (2001) 465.
14 K. T. Lee, Ph.D. Thesis, School of Chemical Engineering, Universiti Sains Malaysia, Penang, Malaysia 2004.
15 M. E. Brown, Handbook of Thermal Analysis and Calorimetry, Vol. 1. Elsevier, Amsterdam 1998.
16 J. R. Garea, R. Viguri and A. Irabien, Chem. Eng. Sci., 52 (1997) 715.
17 A. Garea, J. L. Herrera, J. A. Marques and A. Irabien, Chem. Eng. Sci., 56 (2001) 1387.
18 P. Budrugeac, D. Homentcovschi and E. Segal, J. Therm. Anal. Cal., 63 (2001) 457.
19 F. L. Chiung, S. M. Shin and B. L. Ren, Chem. Eng. Sci., 57 (2002) 93.
20 N. Karatepe, A. E. Mericboyu, R. Yavuz and S. Kucukbayrak, Thermochim. Acta, 335 (1999) 127.
21 D. P. Trempel and G. T. Rochelle, Philadelphia AIChE Meeting SO_x Emission Control Technology and Strategies 1989.

Received: May 5, 2004
In revised form: October 17, 2004