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Modified shrinking unreacted-core model for the reaction between sulfur dioxide and coal fly ash/CaO/$CaSO_4$ sorbent

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ABSTRACT

The kinetics for non-catalytic solid gas reaction between SO_2 and sorbent prepared from coal fly ash, CaO and $CaSO_4$ in a fixed-bed reactor at low temperature were modeled and simulated. A modified shrinking unreacted-core model (SCM) with chemical reaction coupled with diffusion as the rate limiting step were developed to predict the breakthrough curves of the desulfurization reaction. The kinetic parameters of the mathematical model were obtained from a series of experimental desulfurization reactions conducted under isothermal conditions at various operating parameters; SO_2 initial concentration ($500\,\text{ppm} \le C_{SO} \le 2000\,\text{ppm}$), NO initial concentration ($250\,\text{ppm} \le C_{NO} \le 750\,\text{ppm}$), reaction temperature ($60\,^{\circ}\text{C} \le T \le 90\,^{\circ}\text{C}$) and relative humidity ($50\% \le \text{RH} \le 80\%$). MATLAB software was used to solve the partial differential equations using finite difference method. The SCM model was found to give a good description of the experimental data with error less than 5%. The validated model was then used to simulate the desulfurization reaction under a wide range of operating conditions. It was found that higher initial concentration of SO_2 reduces the desulfurization activity. In contrast, the presence of higher concentration of NO, reaction temperature and relative humidity in the system enhanced the desulfurization activity of the sorbent.

1. Introduction

Lately, the negative impact of sulfur dioxide (SO_2) released from power plants to the environment has led to national and international legislation to limit the emissions of SO_2. Since the requirement to limit sulfur emissions are being implemented in more and more countries throughout the world, many coal-fired plants are currently under pressure to install flue gas desulfurization (FGD) unit. The commercial technology currently available for FGD is using the wet-process method with lime stone derivatives as the absorbent. However, this technology requires high investment cost that might not be economically viable for small scale power plants. Recently, it was reported that sorbent prepared from various siliceous material such as coal fly ash, rice husk ash and oil palm ash can be used to remove SO_2 from flue gases using the dry-process. This dry-process is significantly cheaper and simpler than the current wet-process, making it a viable option for small scale power plants. The preparation, characterization and activity study of sorbent made from various siliceous material had been thoroughly reported in the literature [1–4], however, reports on kinetic modeling of the sulfation reaction between the sorbent and SO_2 has not been conclusive.

In a study by Liu and Shih [5], modified surface coverage model was proposed for the desulfurization reaction between $Ca(OH)_2$/fly ash sorbent and SO_2. The reaction between the dry sorbents with SO_2 was studied under the conditions similar to those in the bag filters in the spray-drying flue gas desulfurization system. The hypothesis of this model was that the sorbent was made up of plate grains and that the reaction rate was controlled by chemical reaction on the surface of the grain. The reacting surface area of the grain decreases as the reaction progresses further. Based on the proposed model, the reaction reached an ultimate conversion when the entire reacting surface was covered by the product. Besides that, it was assumed that the change of sorbent surface coverage with reaction time depends on the reaction rate, the dispersion of Ca and the way by which the product deposits on the surface. In another study, Bausach et al. [6] investigated the kinetics of the non-catalytic solid gas desulfurization reaction between $Ca(OH)_2$ and SO_2 at low temperature. In their study, they reported a modified deactivation model (DM) to improve the fitting of the desulfurization experimental data. The deactivation model assumed that the reaction between the gas molecules and the solid sorbent depends mainly on the concentration of the gas on the solid surface, which was referred to as active surface and the ratio of active surface of

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un-reacted solid to the initial solid surface. As the reaction progressed, the solid activity reduces as solid product deposited on the surface reducing the un-reacted surface area. Han et al. [7] proposed a modified grain reaction model for the sulfation kinetics between solid sorbents and SO_2. The sulfation process and kinetics were analyzed using thermogravimetric method using three types of shells and two types of limestone. The microstructure and pore structure of the limestone and shell during the sulfation reaction were investigated using scanning electron microscope and porosimeter, respectively. It was concluded that the rate of the sulfation reaction is principally controlled by particle pore diffusion and product layer diffusion.

Based on the previous study, it can be concluded that the non-catalytic reaction between SO_2 and solid sorbent is either reaction or diffusion rate limiting. In our previous study, a global reaction rate was proposed for the desulfurization reaction with the aim to incorporate both the reaction and diffusion controlling step [8]. However, this method of global process modeling provides little valuable information on the actual physical and chemical process that is occurring during the desulfurization reaction. Therefore, the aim of this study is to develop an alternative model that can describe the desulfurization reaction in the fixed-bed reactor more accurately. The model will be useful for prediction of reactor performance for the desulfurization reaction under different mode of operation and also as a tool for design and optimization of the flue gas desulfurization processes.

2. Experimental

2.1. Sorbent preparation

Sorbents used in this study were prepared from coal fly ash, CaO and $CaSO_4$. The coal fly ash was supplied by Kapar Power Plant, Malaysia of Tenaga Nasional Berhad with the following composition: SiO_2, 60%; Al_2O_3, 20%; Fe_2O_3, 4.7%; CaO, 3.0%; K_2O, 1.1%; MgO, 1.0%; C, 7.5%; others, 2.4% and ignition loss, 0.3%. The $CaSO_4$ used was reagent grade, calcium sulfate hemihydrate while the CaO used was of laboratory grade. Both of these chemicals were supplied from BDH Laboratory Supplies, England. The sorbents were prepared using water hydration method. 5 g of CaO was added into 100 ml of water at 70 °C. After that, 13.7 g of coal fly ash and 7.4 g of $CaSO_4$ were added simultaneously into the slurry. The slurry was then heated under reflux at 98 °C for 10 h of hydration time. Upon completion of the hydration period, the slurry was then filtered and dried using a vacuum pump. The sorbent in powder form was then palletized and subsequently crushed and sieved into the required particle size range of 200–250 μm. The preparation parameters of the sorbent such as the amount of each starting materials were selected according to an optimization study reported elsewhere [9]. The resulting sorbent had a specific BET surface area of 64.5 m^2/g (Autosorb 1C Quantachrome).

2.2. Desulfurization activity study

The desulfurization activity of the sorbent was carried out in a fixed-bed stainless steel adsorber (2.2 cm in length (L) and transversal bed section of 0.5 cm^2 (A)) under isothermal conditions. 0.7 g of sorbent was packed in the center of the adsorber supported by 0.05 g of borosilicate glass wool. The reaction bed porosity, ε, is taken as the average value reported in the literature, 0.6. The fixed-bed adsorber was heated up to desired temperature by a furnace heater and the bed temperature is continuously measured and monitored by a thermocouple. A stream of gaseous mixture containing SO_2 (500–2000 ppm where 1 ppm = 2.62 mg/m^3), O_2 (5.2%), CO_2 (13%), NO (250–750 ppm) and balance N_2 were passed through the sorbent. Prior to that, the N_2 gas stream was humidified using a humidification system where the gas was saturated with water vapor. This was carried out by passing the N_2 gas through two 250 ml conical flask immersed in a water bath at constant temperature. The total flow rate of the gas stream was controlled at 150 ml/min using a series of mass flow controllers. The concentration of SO_2 in the flue gas was measured using a Portable Flue Gas Analyzer IMR2800P before and after the sorption process. The concentration of SO_2 was recorded continuously every 1 min until 60 min. The schematic diagram of the experimental set-up used in this activity study is shown in Fig. 1. Every experimental run was repeated two to three times to increase the precision of the results. The relative error for the data obtained between the repetitions was less than 10%. 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. The desulfurization activity of the sorbent reported in this work is presented as the breakthrough curves of the desulfurization reaction (SO_2 concentration at time t/initial SO_2 concentration vs. time (C/C_0) vs. t) or is reported as the duration of time the sorbent can maintain 80% removal of SO_2 from the initial feed gas [2].

2.3. Experimental data

The proposed model for the desulfurization reaction of the $CaO/CaSO_4$/coal fly ash sorbent is based on experimental data obtained from a fixed-bed reactor operated under various operating conditions; initial concentration of SO_2 ($500\,\text{ppm} \leq C_{SO} \leq 2000\,\text{ppm}$), initial concentration of NO ($250\,\text{ppm} \leq C_{NO} \leq 750\,\text{ppm}$), reaction temperature ($60\,^\circ\text{C} \leq T \leq 80\,^\circ\text{C}$) and relative humidity ($50\% \leq \text{RH} \leq 70\%$). A series of experiments have been performed in order to study the influences of these four variables on the desulfurization reaction and is presented in Figs. 2–5.

2.4. Software

The partial differential equations employed in this work were solved using finite difference method implemented in MATLAB v7.0 and run under the Microsoft Windows NT environment.

3. Model development

3.1. Gas phase

The gas phase composition in the fixed-bed reactor is represented using Eq. (1):

$$\frac{n}{L_o A_s}\frac{\partial Y}{\partial z} + \varepsilon \rho C_{SO}\frac{\partial Y}{\partial t} + \frac{S_e w}{V_R} r_s = 0 \tag{1}$$

where n it the initial molar flow rate of SO_2 (mol/s), L_o is the total fixed-bed length (m), A_s is the transversal bed section (m^2), Y is the dimensionless SO_2 concentration (dimensionless), z is the dimensionless length position (dimensionless), ε is the reaction bed porosity (dimensionless), ρ is the gas molar density (mol/m^3), C_{SO} is the initial SO_2 concentration (mol/m^3), t is the reaction time (s), S_e is the specific surface area of sorbent (m^2/g), w is the sorbent weight in bed (g), V_R is the volume of reaction bed (m^3), and r_s is the reaction rate ($mol/m^2 s$). However, for most non-catalytic solid gas reaction, the concentration of SO_2 in the gas phase does not change rapidly with time at a given point [10]. Thus, the time derivative