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Fitting of Breakthrough Curve by Deactivation Kinetic Model for Adsorption of H_2S from Syngas with Zn-Contaminated Soil

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A deactivation kinetic model was used to predict the breakthrough curve for the adsorption of H_2S from syngas with Zn-contaminated soil. The H_2S adsorption experiments were carried out in a fixed-bed reactor at high temperature. Results indicated that the deactivation kinetic model can be well fitted the breakthrough curve within the experimental ranges. The breakthrough curves were accurately predicted and provided useful information for the time to reload the solid materials in the reaction. The activation energy of the reaction of Zn-contaminated soil and H_2S was experimentally calculated about 126.4 and 42.2 kJ/mol, respectively for deactivation kinetic model I ($m = 0$, $n = 1$) and model II ($m = 1$, $n = 1$). Both of two types of deactivation kinetic models can fit the experimental results. The order of H_2S adsorption in the deactivation model was probably ranged from zero to one.

Keywords: Deactivation kinetic model, Breakthrough curve, Zn-contaminated soil, Activated energy.

INTRODUCTION

The Zn-based sorbent has been recognized as one of favorable materials for high temperature adsorption of H_2S from synags[1-3]. In spite of excellent thermodynamic property with H_2S at high temperature, the preparation and fabrication of Zn-based sorbent is a major reason leading to additional cost for overall operation in pilot-scale plants. Therefore, the Zn-contaminated soil was used to adsorb H_2S from syngas at high temperature and a series of experimental results were completely investigated in previous report[4]. Although many results and operating parameters were experimentally obtained, discussion of kinetic analysis for adsorption reaction at high temperature is relatively lack. Most of the kinetic analysis is built on the basis of the shrinking core model[5,6]. Prior to fitting the shrinking core model, the experimental work has to be operated with a thermogravimetric analysis. Although the shrinking core model is appropriate to fit the kinetic results, a corrosion effect should be considered when the TGA is used to carry out.

During the adsorption reaction of H_2S at high temperature, a dense sulfide layer is expected to be formed on the reactive oxide. Diffusion resistance through this layer causes a significant decrease in the reactivity of the metal oxide[7,8]. In addition, significant changes in pore structure, active surface area and active site distribution during the sulfurization of the metal oxide will cause a significant deactivation of the solid. Deactivation models proposed in the literature for gas-solid reactions with significant changes of activity of the solid due to textural changes, as well as product layer diffusion resistance during reaction, were reported to be quite successful in predicting conversion time data[9-13]. The main objective of this study is to evaluate the feasibility of the deactivation kinetic model and obtain a series of parameters to predict the breakthrough curve at various operating temperature.

EXPERIMENTAL

The tested soils were collected from one of the severely contaminated sites polluted by zinc metal and was recognized by the Environmental Protection Administration of Taiwan. Contaminated soils were sampled at a depth of 0-15 cm from a site. Unwanted materials, such as leaves, tree root and small gravel were removed from soil sample and then dried at room temperature for a week. The collected soils were ground with an agate mortar and sieved to pass through a 2-mm sieve. The content of total zinc and iron are 9,890 and 106,734 mg/Kg according to the ICP analysis. The physical and chemical properties were analyzed and reported in the previous research[14].

The experiment of this study was carried out using a fixed-bed reactor near atmospheric pressure. The experimental system consisted of three parts: (i) a coal gasified gas simulation system; (ii) a desulfurization reactor system; and (iii) an exiting gas analyzing system. The composition of the simulation coal gas involved was 1 vol % H_2S, 15 vol % H_2 and balanced N_2. To avoid the formation of by-products during the kinetic experiments, only H_2 and H_2S were considered in this study. Gases were supplied from gas cylinders and flow rates were monitored through mass flow controllers. All mass flow controllers were monitored accurately by an IR soap bubble meter and the concentration of all species calculated at the condition of STP. Prior to entering the reactor the gases were conducted in a mixing pipe to confirm that the mixture gas was turbulent flow. The reactor consisted of a quartz tube, 1.6 cm i.d., 2 cm o.d. and 150 cm long, located inside an electric furnace. Quartz fibers were set in the reactor in order to support the soil samples. Weight hourly space velocity (WHSV) was controlled at 4,000 mL/h/g to avoid severe pressure drops and channeling flow effect and provided enough retention time. Two K-type thermocouples were inserted exactly into the reactor near the positions on the top and bottom of the sorbent packing to measure and control the inlet and outlet temperatures. Before sorption proceeding, a pure nitrogen gas (purity 99.99 %) was fed into the reactor for 0.5 h at 773 K in order to remove adsorbed water and impure materials, which coated on the surface of the sorbent. In addition, blank breakthrough experiments were also executed under the same conditions and verified that no reaction was taking place anywhere between H_2S and the lines/reactor. The inlet and outlet concentration of H_2S was analyzed by an on-line gas chromatograph (Shimadzu, GC-14B) equipped with a flame photometry detector (FPD) and fitted with a GS-Q capillary column. A six-port sampling with 0.5 mL sampling loop was used to sample the inlet and outlet concentration of H_2S. The removal experiment was terminated when the outlet H_2S concentration from the reactor approached the inlet concentration of H_2S. In this study, the breakthrough time was defined as the time from the beginning of the sorption to the point outlet H_2S concentration reached 100 ppm.

Deactivation model for kinetic study: The formation of a dense product layer over the solid reactant creates an additional diffusion resistance and is expected to cause a drop in the reaction rate. One would also expect it to cause significant changes in the pore structure, active surface areas and activity per unit area of solid reactant with reaction extent. All of these changes cause a decrease in the activity of the solid reactant with time. As reported in the previous literatures, the deactivation model works well for gas-solid reactions[15-17]. In this model, the effects of the factors on the diminishing rate of sulfur fixation were combined in a deactivation rate term. To simulate the removal of H_2S by sorbents, the following assumptions were made:

(i) The sulfidation is operated under isothermal conditions.

(ii) The external mass-transfer limitations are neglected.

(iii) The pseudo-steady state is assumed.

(iv) The deactivation of the sorbent is first-order with respect to the solid active sites, while zero-order for the concentration of H_2S and can be described as follows:

$$-\frac{da}{dt} = k_d C^m a^n \Rightarrow a = a_0 \exp\left(-k_d t\right) \quad (m = 0, n = 1) \tag{1}$$

With the pseudo-steady state assumption, the isothermal species conservation equation for the reactant gas H_2S is expressed as follows:

$$-Q_0 \frac{dC}{dW} - k_0 C\ a = 0 \tag{2}$$

Integrating eqn. 2, the following equation can be obtained

$$\int_{C_0}^{C} \frac{dC}{C} = -\left(\frac{k_0 a}{Q_0}\right) \int_0^W dW \Rightarrow \ln\left(\frac{C}{C_0}\right) = -\left(\frac{k_0 a}{Q_0}\right) W \tag{3}$$

Combining with eqn. 1 and 3, 4 can be obtained

$$C = C_0 \exp\left[-\frac{k_0 W}{Q_0} \exp\left(-k_d t\right)\right] \tag{4}$$

Arranging eqn 4, the following can be obtained:

$$\ln\left[\ln(\frac{C_0}{C})\right] = \ln\left(\frac{k_0 W}{Q_0}\right) - k_d t \tag{5}$$

Thus, if $\ln[\ln C_o/C]$ is plotted *versus* time, a straight line should be obtained with a slope equal to -kd and intercept giving $\ln[k_o W/Q_o]$, from which ko can be obtained.

To obtain analytical solutions of eqn. 1 and 2 by taking n = m = 1, an iterative procedure was applied. In this procedure, the eqn. 4 is substituted into eqn. 1 and the first correction for the activity is obtained by the integration of this equation. The following approximate expression was then derived (deactivation model type II, n = m = 1).

$$\frac{C}{C_0} = \exp\left\{\frac{\left[1 - \exp\left(k_0 W/Q(1 - \exp(-k_d t))\right)\right]}{(1 - \exp(-k_d t))} \exp(-k_d t)\right\} \tag{6}$$

Nomenclature

α : Activity of the solid reactant
Q_o : Gas flow rate (m^3/min)
C : Outlet concentration of H_2S (kmol/m)
C_o : Inlet concentration of H_2S (kmol/m)
k_d : Deactivation rate constant (1/min)
k_o : Initial sorption rate constant (m^3/ kg/min)
t : Time (min)
W : Active species mass (kg)

RESULTS AND DISCUSSION

Prior to investigating the feasibility of the deactivation kinetic model for the reaction of Zn-contaminated soil and H_2S, the effects of external and internal mass transfer resistances have to be considered in order to understand their influence. The performance of particle size and WHSV are the major indicators for determination of internal and external mass transfer in kinetic study. As shown in Fig. 1(a), the sulfur adsorption capacity decreased with increasing particle size. Small particle size enhanced the sulfur adsorption capacity compared to larger ones, implying that the internal mass transfer resistance should be considered if the particle size ranges from 20 to 100 meshes. On the other hand, the sulfur adsorption capacity maintained constantly while the particle size ranged from 100 to 160 meshes, indicating that the internal mass transfer resistance could be ignored within this range. To obtain an authentic experimental data, particle size samples ranged between 110-150 mesh were collected to carry out the deactivation kinetic model. For the external mass transfer

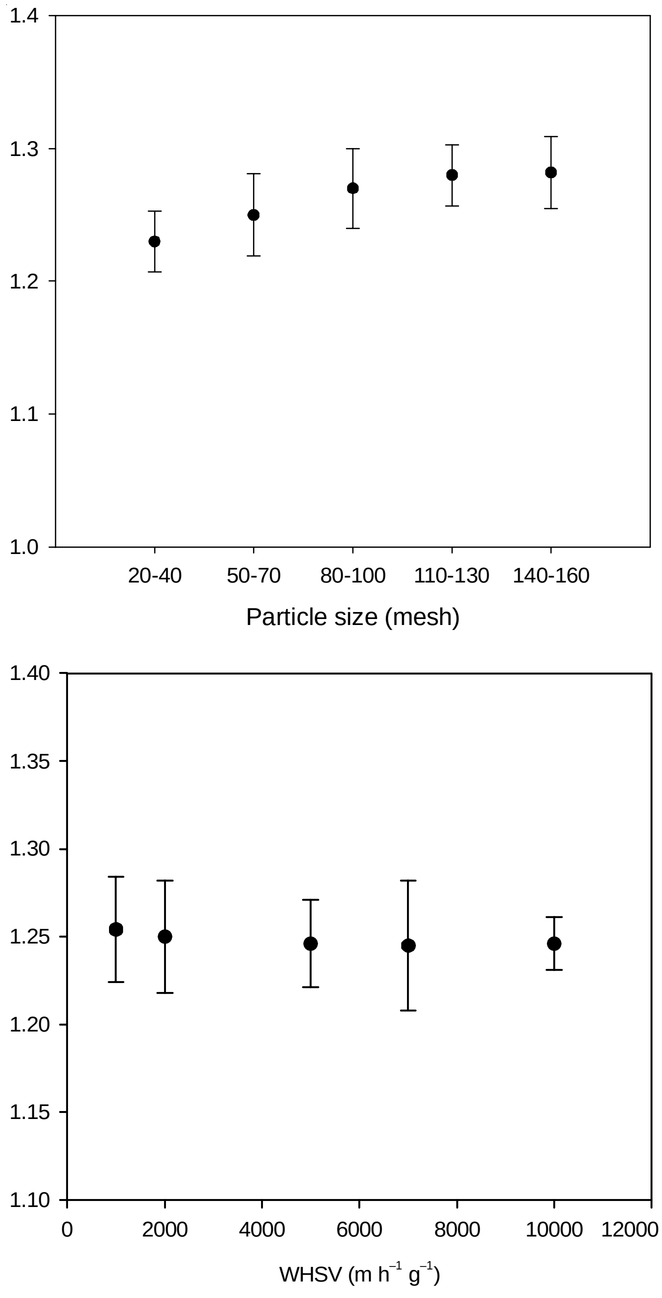

Fig. 1. Effect of the mass transfer resistance experiments (a) particle size (b) WHSV. Inlet H_2S: 1 %, H_2: 15 % and balanced N_2

experiments as shown in Fig. 1(b), no huge change was found within the ranges of 2,000-10,000 mL/h/g. To minimize the external mass transfer resistance the kinetic study was conducted at a WHSV of 4,000 mL/h/g.

Deactivation kinetic type I model (m = 0, n = 1): The temperature dependence of the H_2S breakthrough curves for the Zn-contaminated soil is presented in Fig. 2. According to the breakthrough curves, the relationship of time and ln (ln C_o/C) could be easily obtained at various temperatures, as shown in Fig. 3. The R^2 values for all cases were better than 0.98. The initial reaction rate constants, k_o, were calculated from intercept in Fig. 3. Meanwhile, a straight line was attained by plotting ln k_o *versus* T^{-1} *via* its intercept and slope, the values of frequency factor and the apparent activation energy were calculated from Arrhenius relationship. The frequency factor and activation energy were 2.31×10^{17} and 126.4 kJ/mol, respectively.

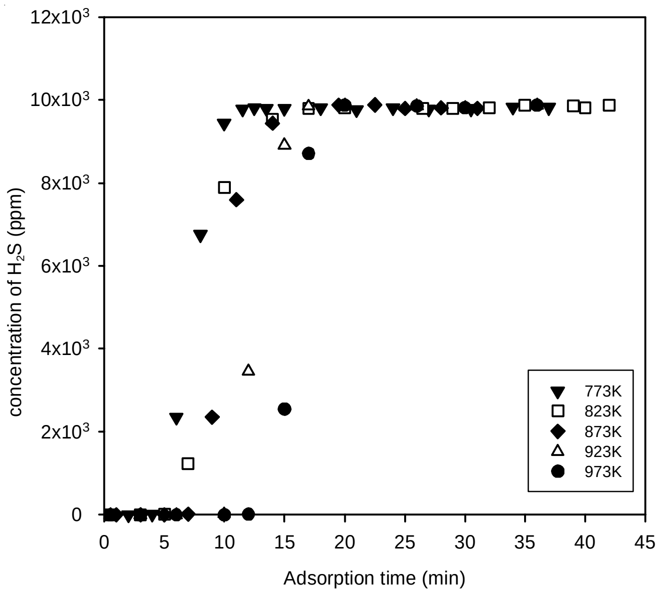

Fig. 2. Breakthrough curves of the adsorption reaction between Zn-contaminated soil and H_2S. Inlet H_2S: 1 %, H_2: 15 % and balanced N_2, WHSV: 4,000 mL/h/g with a flow of 100 mL/min

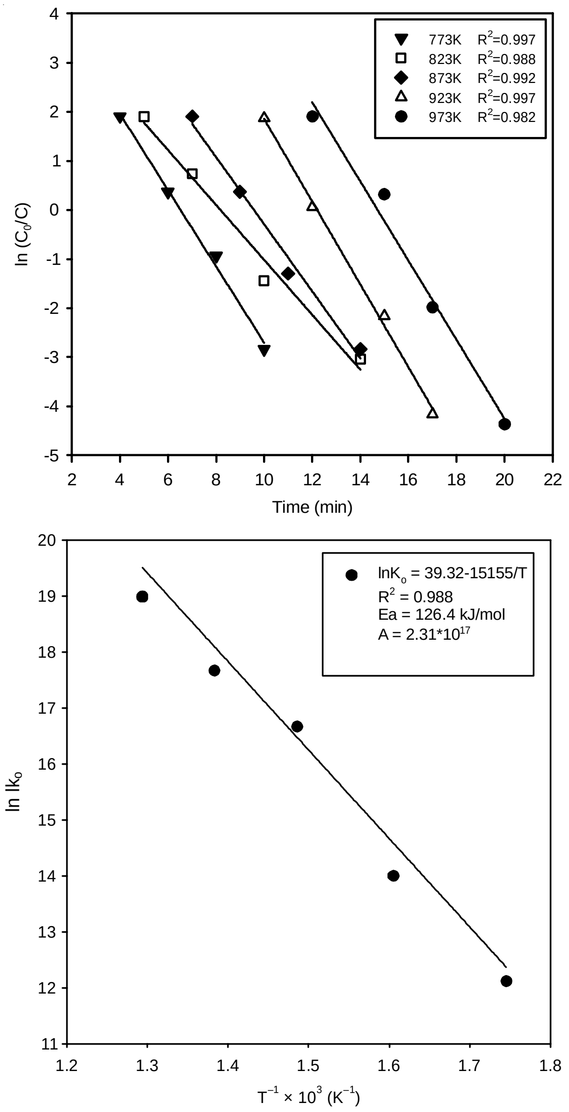

Fig. 3. Relationship of the time and ln(lnC_0/C) at various temperatures by a deactivation model (m = 0, n = 1) and Arrhenius equation fitting result

Deactivation kinetic type II model (m = 1, n = 1): Unlike type I model, the relationship between k_o and C_o is a complex and nonlinear equation. To obtain parameters in eqn. 6, the regression fitting was performed using equation 6 in the Sigma Plot software. Fig. 4 shows the regression results for the experimental data by the deactivation type II model. The R^2 values for all cases were better than 0.99. Likewise, the activation energy could be obtained from Arrhenius relationship. The frequency factor and activation energy were 2.49×10^7 and 42.2 kJ/mol, respectively.

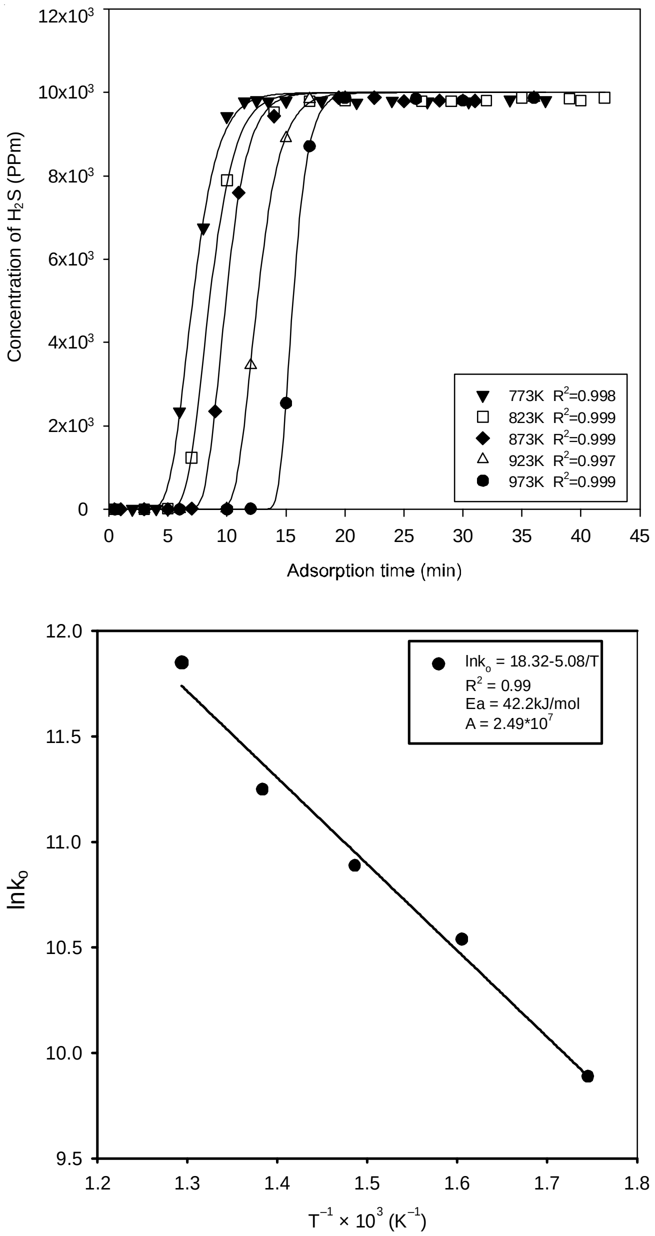

Fig. 4. Regression fittings of the experimental data by a deactivation model (m = n = 1) under various temperatures and Arrhenius equation fitting result. Inlet H_2S: 1 %, H_2: 15 % and balanced N_2, WHSV: 4,000 mL/h/g with a flow of 100 mL/min

To further establish the fitness of the deactivation type I and II models, three sets of adsorption reaction were performed at 723, 853 and 1023 K as well as simulated the model to predict their breakthrough behaviours in Fig. 5. As can be seen, the R^2 values were higher than 0.99, indicating the deactivation kinetic type I and type II models could accurately predict the breakthrough behaviours for the adsorption reaction of Zn-contaminated soil and H_2S. In particular, the breakthrough times were accurately predicted, which provided useful information for the time to change loading materials in actual operating condition.

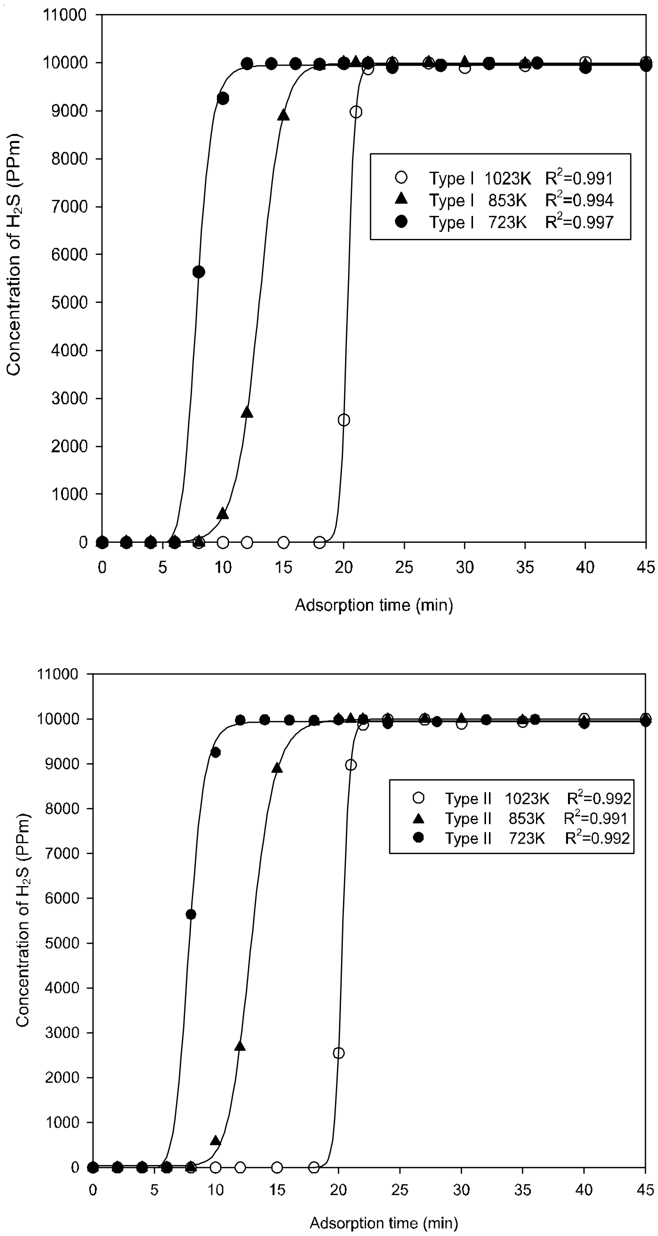

Fig. 5. Regression fittings of the experimental with results predicted by deactivation type I and type II model under various temperatures. Inlet H_2S: 1 %, H_2: 15 % and balanced N_2, WHSV: 4,000 mL/h/g with a flow of 100 mL/min

The difference between the type I and type II was the order of outlet concentration of H_2S (represent by C in the deactivation kinetic model, kmol/m^3). Although there was a significant change in activation energy for both two models, their activation energies appeared to be acceptable because they ranged among the previous report[18]. In addition, the fitting results also presented well predictions for both two models. It was speculated that the actual order of C may be ranged between zero to one, which resulted in the nearly perfective fitting results for both models.

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