

## Cesium Carbonate에 의한 이산화탄소의 흡착 해석

박상욱\*, 최병식, 천미선, 이재욱<sup>1</sup>  
 부산대학교 화학공학과  
<sup>1</sup>서강대학교 화학공학과  
 (swpark@pusan.ac.kr\*)

### Sorption Analysis of Carbon Dioxide onto Cesium Carbonate

Sang-Wook Park\*, Mi-Sun Chun, Byoung-Sik Choi, Jae-Wook Lee<sup>1</sup>  
 Division of Chemical Engineering, Pusan National University  
<sup>1</sup>Department of Chemical Engineering, Sogang University  
 (swpark@pusan.ac.kr\*)

#### INTRODUCTION

In mass transfer processes that accompany chemical reactions, the diffusion may have an effect on the reaction kinetics. The simplest and the most commonly used models for non-catalytic heterogeneous gas-solid reactions are the shrinking-core model and the homogeneous model with negligible pore diffusion limitations. Also, the deactivation model has been used to obtain the reaction kinetics using an analysis of reactivity of the solid reactant, which may be decreased by the changing the reaction circumstances. We believe that it is worthwhile to investigate the reaction kinetics of gas-solid heterogeneous reaction, such as the CO<sub>2</sub>-carbonate reaction, from a comparison among these models.

In our previous work (1), we studied the sorption kinetics of the gas-solid reaction between CO<sub>2</sub>, H<sub>2</sub>O, and Na<sub>2</sub>CO<sub>3</sub> using breakthrough data of CO<sub>2</sub> in series. In this study, Cs<sub>2</sub>CO<sub>3</sub> was used as a sorbent of CO<sub>2</sub> to analyze the sorption kinetic using breakthrough data of CO<sub>2</sub> in a fixed bed, comparing the shrinking-core model, the homogeneous model and the deactivation model even though the carbonation mechanism of Rb<sub>2</sub>CO<sub>3</sub> by CO<sub>2</sub> and moisture is very complicated.

#### THEORY

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 area, and activity per unit area of solid reactant with respect to the extent of the reaction. All of these changes cause a decrease of activity of the solid reactant with time. In the deactivation model, the effects of all of these factors on the diminishing rate of CO<sub>2</sub> capture were combined in a deactivation rate term.

With assumptions of a pseudo-steady state and a constant concentration of water vapor, the isothermal species conservation equation for the reactant gas CO<sub>2</sub> in the fixed bed is

$$-Q_g \frac{dC_A}{dw} - k_0 C_A \alpha = 0 \quad (1)$$

where  $k_0 = kC_w$ ,  $\alpha$  and  $Q_g$  are reaction activity of absorbent and volumetric flow rate of gaseous mixture, respectively.

In writing this equation, axial dispersion in the fixed bed and any mass transfer resistances were assumed to be negligible. According to the proposed deactivation model, the rate of change of  $\alpha$  is expressed as

$$-\frac{d\alpha}{dt} = k_d C_A^n \alpha^m \quad (2)$$

where  $k_d$  is the deactivation rate constant. The zeroth solution of the deactivation models is obtained by taking  $n=0$ ,  $m=1$ , and the initial activity of the solid as unity.

$$a = \exp\left[-\frac{k_o w}{Q_g} \exp(-k_d t)\right] \quad (3)$$

This solution is equivalent to the breakthrough equation proposed by Suyadal and coworkers [2] and assumes a fluid phase concentration that is independent of deactivation processes along the reactor. More realistically, one would expect the deactivation rate to be concentration-dependent and, accordingly, axial-position-dependent in the fixed bed.

To obtain the analytical solution of Eq. (1) and (2) by taking  $n=m=1$ , an iterative procedure was applied. The procedure used here is similar to the procedure proposed by Dogu [3] for the approximate solution of nonlinear equations. In this procedure, the zeroth solution [Eq.(3)] is substituted into Eq. (2), and the first correction for the activity is obtained by the integration of this equation. Then, the corrected activity expression is substituted into Eq. (1), and integration of this equation gives the first corrected solution for the breakthrough curve.

$$a = \exp\left[\frac{\left[1 - \exp\left(\frac{k_o w_f}{Q_g} (1 - \exp(-k_d t))\right)\right]}{1 - \exp(-k_d t)}\right] \exp(-k_d t) \quad (4)$$

This iterative procedure can be repeated for further improvement of the solution. In this procedure, higher-order terms in the series solutions of the integrals are neglected. The breakthrough curve for the deactivation model with two parameters ( $k_o$  and  $k_d$ ) is calculated from the concentration profiles by Eq. (4).

## **EXPERIMENTAL**

Sorption experiments were carried out in the presence of carbon dioxide and moisture with cesium carbonate sorbent in a fixed bed pyrex glass reactor. Water vapor was fed to the reactor through a line heated using a micro syringe. The flow rates of gas mixture of carbon dioxide and nitrogen were within the range of 6-20 cm<sup>3</sup>/min (measured at 25°C); the composition of CO<sub>2</sub> in the gas mixture was 12 % in most of the experiments. The flow rate of water was in the range 0.6-3 cm<sup>3</sup>/h. The amount of sorbent was in the range 0.5-2 g. Experiments were repeated over a temperature range between 50 and 80°C. A gas chromatograph (detector: thermal conductivity detector; column: Haysep D (10 feet by 1/8 inch of stainless steel); detector temperature: 190°C; feed temperature: 160°C; flow rate of He: 25.7 cm<sup>3</sup>/min; retention times of N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O: 0.9, 1.323, 20.6 min, respectively) connected to the exit stream of the reactor allowed for on-line analysis of CO<sub>2</sub>, N<sub>2</sub>, and water. The experimental procedure used to obtain the breakthrough data of CO<sub>2</sub> duplicated in detail the reported approach [1].

## **RESULTS AND DISCUSSION**

The measured values of breakthrough curves of CO<sub>2</sub> were plotted against the reaction time, with

parameters of the flow rate of the gaseous mixtures of CO<sub>2</sub> and N<sub>2</sub> and water indicated as various symbols in Fig. 1. As shown in Fig. 1, a shift of the breakthrough curves to shorter times was observed at greater flow rate of the gaseous mixture with a decrease in sorption capacity. This result means that the reaction conversion decreases as the space time of the gaseous mixtures in the fixed bed, i.e., the reaction time, decreases. Analysis of the experimental breakthrough data using a nonlinear least-squares technique gave a very good agreement with Eq. (4). The calculated curves using Eq. (4) are shown in Fig. 1 as solid lines with regression coefficient greater than 0.996.

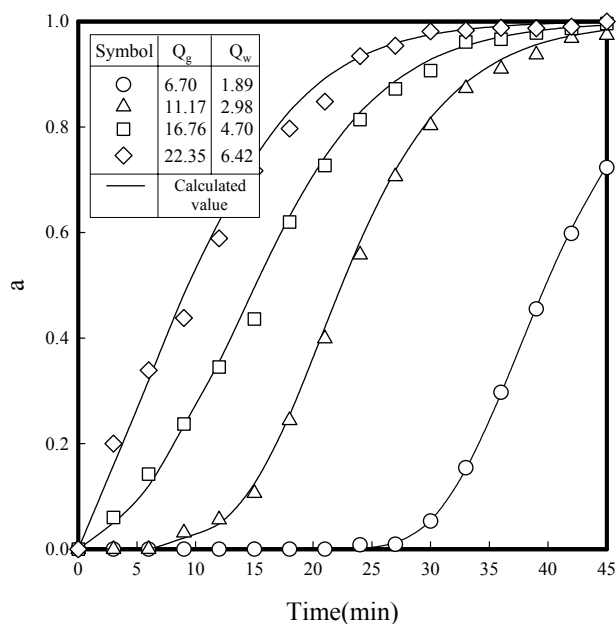


Fig. 1. Effect of the flow rate of mixture of N<sub>2</sub> and CO<sub>2</sub> on the breakthrough curve of CO<sub>2</sub> at 60°C and W<sub>0</sub> = 1.5 g.

To obtain the dependence of reaction parameters on the sorption temperature (T), the breakthrough curves of CO<sub>2</sub> were measured in the temperature range between 50 and 80°C at flow rate and concentration of CO<sub>2</sub> in gaseous mixture of CO<sub>2</sub> and N<sub>2</sub> of 10 cm<sup>3</sup>/min and 0.12 mole fraction, respectively, a flow rate of water of 2.98 cm<sup>3</sup>/h, 1.5 g of sorbent. The values of k<sub>0</sub> and k<sub>d</sub> were evaluated from the analysis of the experimental breakthrough data using a nonlinear least-squares technique using the same procedure mentioned above; k was obtained using k<sub>0</sub> and the initial concentration of moisture. The Arrhenius plots are shown in Fig. 7 and 8, respectively. As shown in Fig. 7 and 8, the plots satisfy linear relationship. Using the values of the slopes and intercepts of these straight lines of the Arrhenius plots, the following empirical equations were obtained.

$$k = 2.184 \times 10^5 \exp\left(-\frac{0.159}{RT}\right) \quad (5)$$

$$k_d = 1.189 \times 10^{10} \exp\left(-\frac{0.682}{RT}\right) \quad (6)$$

## CONCLUSIONS

The breakthrough data of CO<sub>2</sub> were measured in a fixed bed to observe the reaction kinetics of CO<sub>2</sub> sorption among cesium carbonate, carbon dioxide, and moisture under the experimental conditions of a flow rate of the gaseous mixture of 6-20 cm<sup>3</sup>/min, a flow rate of water of 0.6-3 cm<sup>3</sup>/h, a potassium

carbonate mass of 0.5-2 g, and a reaction temperature of 50-80°C. A good agreement of the deactivation model was obtained with the experimental breakthrough data in the heterogeneous solid-gas reaction system, with respect to changes in the pore structure and the reactivity of the solid reactant. The sorption rate constant and the deactivation rate constant were evaluated through analysis of the experimental breakthrough data using a nonlinear least squares technique and were described in the Arrhenius form.

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