

## NONISOTHERMAL ADSORPTION IN A SINGLE SPHERICAL PELLET HAVING BIDISPERSED PORE STRUCTURES

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**Abstract**—ZSM-5 and Y-zeolite as adsorbents for the adsorption of ethanol vapor were used to investigate the nonisothermal adsorption. Diffusivity and equilibrium constant in the pellet having both micro- and macropores were represented as a function of temperature to establish a nonisothermal model. More rapid adsorption rate was found in the early stage of adsorption in nonisothermal model than that in isothermal model. But the time taken to reach the equilibrium state from the start of adsorption was nearly the same for both models. As diffusivity in macropore became larger than that in micropore, the adsorption had a more rapid rate and a higher maximum temperature rise. The lower value of equilibrium constant showed a more rapid adsorption rate, but a lower maximum temperature rise. The maximum temperature rise of pellet up to 20°C above the ambient temperature was found. When the adsorption rate curves from the experimental data are compared with those from the modeling, a deviation was obtained at a high uptake ratio while a good fitting was found in the early stage of adsorption.

### INTRODUCTION

When heat generation of adsorption is high, large temperature rise within the adsorbent can result in the change of mass transfer rate. This can cause a large different value of diffusion coefficient compared with the value obtained from isothermal adsorption rate measurements [1]. The modeling and experiments of nonisothermal adsorption kinetics have received little attention. This is probably due to the difficulties in experiment as well as in mathematical modeling. Particularly experimental verification of any nonisothermal model is extremely difficult because temperature within the adsorbent pellets must be measured simultaneously with adsorbate loading.

Pelletizing fine powders, the resulting large particles generally have relatively large pores (macropores) between the crystals and small pores (micropores) in the crystals. Since the macropore diffusivity is generally quite different in magnitude from the micropore diffusivity, both of micro and macropore diffusions must be considered [2].

Nonisothermal adsorption in a single pellet or powders has recently attracted the attention of several different researchers. The significance of thermal effects on the mass transfer have been demonstrated experimen-

tally by Eagan, Kindl and Anderson [3]. They concluded that when the maximum temperature occurs late during adsorption process, the rate curve is drastically different from that expected for isothermal adsorption. An approximate analysis based on a linear driving force of the mass transfer rate was carried out by Chihara, et al [4]. But they used a constant diffusivity and single pore structure in their model. A more detailed theoretical analysis was presented by Brunovska, et al [5]. They solved numerically the simultaneous equations of diffusion and heat conduction for an adsorption subjected to a step change of adsorbate concentration at the external surface of single spherical particle with a finite thermal conductivity. But they also used constant diffusivity. Kmietek, et al [6] made a nonisothermal and single pore model which account for the temperature effect on the diffusivity.

In this paper, a mathematical model incorporating temperature effects on diffusivity and adsorption equilibrium constant is developed to analyze nonisothermal adsorption in a pellet with a bidispersed pore structure. Calculated results of such a model was shown and compared with experimental data.

### THEORY

A mathematical attempt was made to describe the

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thermal effects on adsorption in a single sphere of zeolite with bidispersed pore structures under the following assumptions.

1) The spherical pellet is made of small spherical particles of uniform size which have micropores.

2) The pellet is initially at equilibrium with the surrounding fluid. At time zero, a step change of adsorbate concentration is applied to the surrounding of the pellet. The adsorbate diffuses into the pellet and then into the small particles whose micropore structure is uniform and is considered as cages.

3) Both micropore and macropore diffusions are the controlling steps of mass transfer mechanism and characterized by Fick's law.

4) The macropore diffusion coefficient  $D_a$  is a function of temperature which is the Arrhenius form. But typical reported micropore diffusion coefficients in zeolites range downwards from about  $10^{-11}$  cm<sup>2</sup>/s. The diffusion in this region corresponds to the restricted or configurational diffusion. In the configurational diffusion region, the increase in diffusivity with change in zeolite generally parallels the increase in pore size, as determined by adsorption measurements with differentsized molecules [7]. And so, temperature effect on the micropore diffusivity is negligible relative to that on the macropore diffusivity.

5) The temperature is uniform throughout the spherical pellet. In zeolite pellet, thermal conduction through an individual particle and heat transfer between the particles within the pellet is much rapid than the heat transfer between the pellet surface and surrounding fluid film [8], so that the only significant heat transfer resistance is at the external surface of the pellet. In practice, Lavsky and et al [9] showed experimentally that the maximum temperature difference between the pellet and its surrounding was 20-25°C and the maximum difference in the pellet of diameter 1.0 cm was about 5°C in 5A zeolite-heptane system.

6) Diffusion coefficient, heat capacity and heat of adsorption are independent of concentration and temperature.

From the above assumptions the mass balances in both macropore and micropores are given by the following equations;

material balance in macropore;

$$\epsilon_p \frac{\partial C_a}{\partial t} = D_{ao} \exp(-E/RT) \frac{\epsilon_p}{r_a^2} \frac{\partial}{\partial r_a} \left( r_a^2 \frac{\partial C_a}{\partial r_a} \right) - \frac{3(1-\epsilon_p)}{R_i} D_i \left( \frac{\partial C_i}{\partial r_i} \right)_{r_i=R_i} \quad (1)$$

material balance in micropore;

$$D_i \left( \frac{\partial^2 C_i}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial C_i}{\partial r_i} \right) = \frac{\partial C_i}{\partial t} \quad (2)$$

and the energy balance gives;

$$(-\Delta H) \frac{d(M_t)}{dt} = M_o C_p \frac{dT}{dt} + hA(T - T_o) \quad (3)$$

Equations (1), (2) and (3) should be solved with the following initial and boundary conditions:

$$\begin{aligned} C_a(o, r_a) &= C_{ao} & C_i(o, r_i) &= C_{io} \\ M_t(o, r) &= 0 & T(o, r_a) &= T_o \end{aligned} \quad (4a)$$

$$\begin{aligned} C_a(t, R_a) &= C_{a\infty} & C_{ao} &= C_{io} \\ \frac{\partial C_a(t, o)}{\partial r_a} &= \frac{\partial C_i(t, o)}{\partial r_i} = 0 \end{aligned} \quad (4b)$$

$$C_i(t, R_i) = KC_a(t, r_a) \quad (4c)$$

where the linear adsorption isotherm coefficient (equilibrium constant)  $K$  is dependent on temperature in the following form;

$$K = K_o \exp(-\Delta H/RT) \quad (5)$$

If one defines the following dimensionless variables,

$$\begin{aligned} \tau &= \frac{D_{ao}}{r_a^2} t & \gamma &= \frac{3(1-\epsilon_p)}{\epsilon_p} \\ \eta_a &= \frac{r_a}{R_a} & \eta_i &= \frac{r_i}{R_i} \\ \theta_i &= \frac{C_i - C_{io}}{C_{a\infty} - C_{io}} & \theta_a &= \frac{C_a - C_{ao}}{C_{a\infty} - C_{ao}} \\ \epsilon &= \frac{T - T_o}{T_o} \end{aligned} \quad (6)$$

and the parameters

$$\begin{aligned} \beta &= \frac{D_i/R_i^2}{D_{ao}/R_a^2} = \frac{D_i R_a^2}{D_{ao} R_i^2} \\ \alpha_1 &= \frac{(-\Delta H) M_o}{C_p T_o M_o} & \alpha_2 &= \frac{hA}{M_o C_p} \left( \frac{D_{ao}}{R_a^2} \right) \end{aligned} \quad (7)$$

equations (1), (2) and (3) are changed in the form below

$$\begin{aligned} \frac{\partial \theta_a}{\partial \tau} &= \exp\left(-\frac{E}{RT_o} \left(\frac{1}{1+\epsilon}\right)\right) \left( \frac{\partial^2 \theta_a}{\partial \eta_a^2} + \frac{2}{\eta_a} \frac{\partial \theta_a}{\partial \eta_a} \right) \\ &\quad - \gamma \beta \left( \frac{\partial \theta_i}{\partial \eta_i} \right)_{\eta_i=1} \end{aligned} \quad (8)$$

$$\frac{1}{\beta} \frac{\partial \theta_i}{\partial \tau} = \frac{\partial^2 \theta_i}{\partial \eta_i^2} + \frac{2}{\eta_i} \frac{\partial \theta_i}{\partial \eta_i} \quad (9)$$

$$\frac{\partial \epsilon}{\partial \tau} = \alpha_1 \frac{\partial}{\partial \tau} \left( \frac{M_t}{M_o} \right) - \alpha_2 \epsilon \quad (10)$$

and equations (4) and (5) become

$$\begin{aligned} \theta_i(o, \eta_i) &= \theta_a(o, \eta_a) = 0 \\ \epsilon(o) &= 0, \quad \frac{M_t(o)}{M_o} = 0 \\ \theta_a(\tau, 1) &= 1 \end{aligned} \quad (11a)$$

$$\frac{\partial \theta_a}{\partial \tau_i}(\tau, 0) = \frac{\partial \theta_i}{\partial \tau_a}(\tau, 0) = 0 \quad (11b)$$

$$\theta_i(\tau, 1) = K \theta_a(\tau, \eta_a) \quad (11c)$$

$$K = K_0 \exp\left(-\frac{\Delta H}{RT_0} \left(\frac{1}{1+\varepsilon}\right)\right) \quad (12)$$

The fractional uptake expression based on the equilibrium adsorption is the ratio  $M_t/M_\infty$  where  $M_t$  and  $M_\infty$  are the net change of solute quantity in the pellet at a certain time and an infinite time, respectively. This is done by using the following relationship:

$$M_t = \int_0^t \varepsilon_a D_a 4\pi R_a^2 \left(\frac{\partial C_a}{\partial r_a}\right)_{r_a=R_a} dt \quad (13a)$$

at a certain time

$$M_\infty = \int_0^\infty \varepsilon_a D_a 4\pi R_a^2 \left(\frac{\partial C_a}{\partial r_a}\right)_{r_a=R_a} dt \quad (13b)$$

at an infinite time

As a result, the fractional uptake can be given in the

$$\frac{M_t}{M_\infty} = \frac{\int_0^t \left(\frac{\partial \theta_a}{\partial \eta_a}\right)_{\eta_a=1} d\tau}{\int_0^\infty \left(\frac{\partial \theta_a}{\partial \eta_a}\right)_{\eta_a=1} d\tau} \quad (14)$$

form by using dimensionless variables.

## EXPERIMENTS

ZSM-5 was received from Mobil Oil Company with  $\text{NH}_4$ —form powder. It was converted to H-form by degassing under the condition of  $550^\circ\text{C}$  for 6 hours. The size of ZSM-5 crystals used was under  $24\text{ }\mu\text{m}$ . Zeolite Y was received from Strem Chemical Inc. with Na-form powder and its average crystal size was  $0.76\text{ }\mu\text{m}$ . The pellets were made from the powders by pelletizing under the pressure of  $703\text{ kg/cm}^2$ . The pellets were rounded to a sphere of diameter 6 mm. In the center of a spherical pellet a deep and narrow round hole was made by inserting with a Chromel-Alumel thermocouple wire (30 AWG; 0.25 mm dia.). Ethanol absolute was used as an adsorbate. A Cahn 2000 electrobalance was used to measure the weight change of the pellet as a function of time during the adsorption of ethanol. One pellet was put on the pan of electrobalance for the measurement of weight and another pellet was located just under the former for the measurement of temperature. A schematic diagram of the system was shown in Fig. 1.

An adsorbent in either powder or pellet form in the balance chamber was activated for 4 hours under the vacuum  $10^{-3} - 10^{-4}\text{ mmHg}$  at a temperature of  $400^\circ\text{C}$ . After the completion of activation, it was allowed to cool to the surrounding temperature. And then the balance chamber was filled with Helium gas to atmospheric

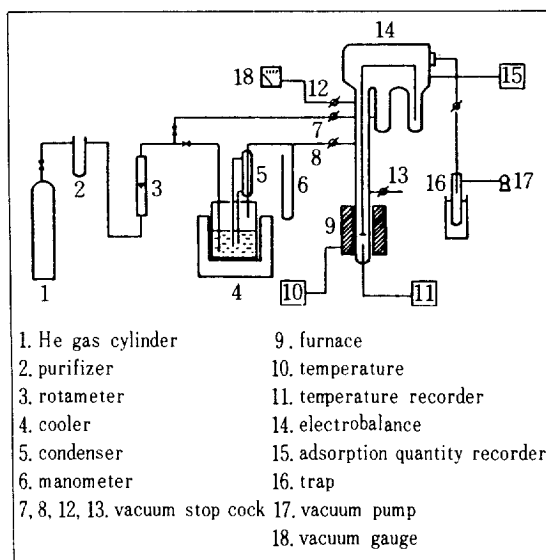


Fig. 1. Experimental apparatus.

pressure. After equilibration, the Helium gas carrying ethanol vapor was passed around the sample pellet. The weight change of adsorbent was continuously recorded as a function of time. The pellet was reactivated after each experimental run.

## RESULTS AND DISCUSSION

Computer simulation corresponding to the non-isothermal model was carried out to determine if the nonisothermal effect would be significant.

The solution of equations (8) to (12) was obtained by Crank-Nicholson finite difference method [10, 11] and equation (14) was integrated by the Simpson's rule. Equation (9) has analytic solution [12] and it was incorporated in equation (8) during the calculation. The parameter  $\beta$  represents to the relative importance of the diffusional resistance in micropores to that in macropores. Large  $\beta$  means that diffusional resistance in the micropores is lower and mass transfer is more controlled by macropore diffusion.

During the adsorption process, the temperature of the pellet increases because of adsorption heat. This heat generation affects the diffusivity and the equilibrium constant. These variables are represented by usual Arrhenius' temperature relations, in which the values of the variables increase as temperature increases. The adsorption rate curves of a nonisothermal model are shown in Fig. 2. One can see in Fig. 2 that the adsorption rate increases as the value of  $\beta$  is increased, that is, as micropore resistance decreases. And the shapes of adsorption rate curves become more similar to those of

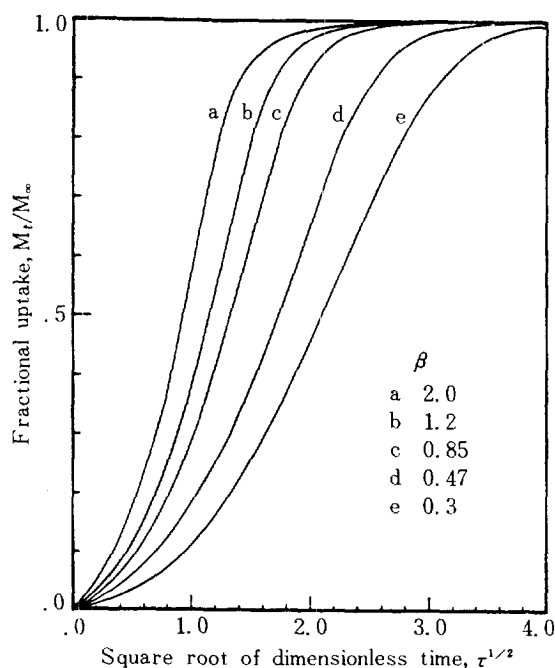


Fig. 2. Rates of adsorption with varying values of  $\beta$ .

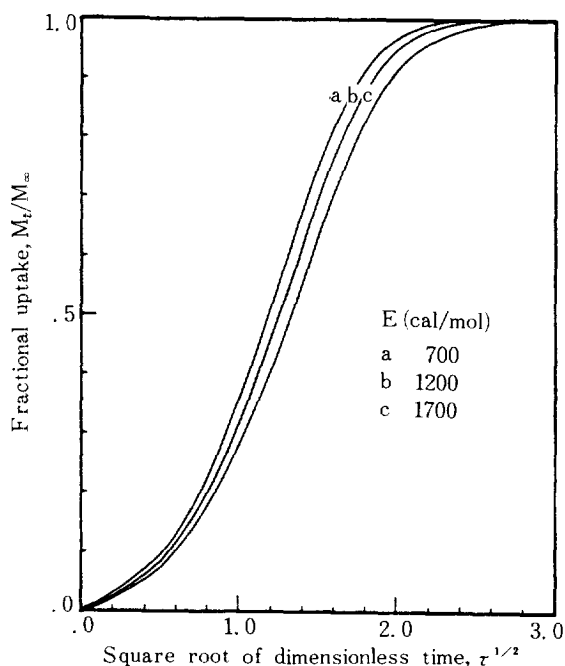


Fig. 4. Effect of activation energy on adsorption rate.

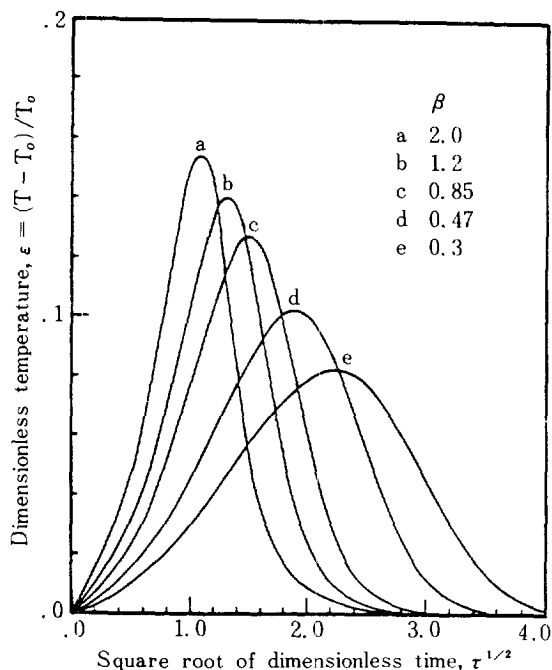


Fig. 3. Temperature profiles with varying values of  $\beta$ .

Ma's [6] model, as the value of  $\beta$  increases. The Ma's model used a nonisothermal and macropore diffusion control model in which only the diffusivity was con-

sidered to be affected by temperature.

The temperature changes during adsorption are represented in Fig. 3. As macropore diffusion becomes more controlling step, the peak of temperature becomes higher with  $\alpha_2$  fixed because of rapid adsorption rate. In Fig. 4, the adsorption reaches the final equilibrium more rapidly as the activation energy becomes lower since the lower activation energy of diffusion makes diffusion more easy.

In Fig. 5, the maximum temperature occurs earlier as  $E$  becomes lower. Small values of  $K$  correspond to the case where the solute concentration at the crystal surface is small and thus the solute can be easily transported into the crystal. If adsorption heat,  $\Delta H$ , is constant, the value of  $K$  can be determined from the values of proportional constant  $K_0$  and temperature. Thus small value of  $K_0$  means the easiness of solute transfer into the crystal and the rapid equilibration as shown in Fig. 6. As shown in Fig. 7 the peak of temperature for low value of  $K_0$  is less than that for large value of  $K_0$  because  $K$  value becomes smaller.

The parameter  $\alpha_2$  represents the relative rate of heat transfer to mass transfer. When  $\alpha_2$  approaches zero at constant value of  $\alpha_1$ , the system becomes adiabatic and the temperature rise has maximum value when equilibrium is reached. A large  $\alpha_2$ , alternatively, means faster heat transfer to the ambient than the heat transfer within the sphere. Therefore, temperature rise becomes

smaller when  $\alpha$  becomes larger, as shown in Fig. 8.

Parameter  $\alpha_1$  represents the ratio of the total heat generated during adsorption to the heat capacity of the

zeolite. A lower value of  $\alpha_1$  gives a smaller temperature rise.

In isothermal model, there is no temperature rise

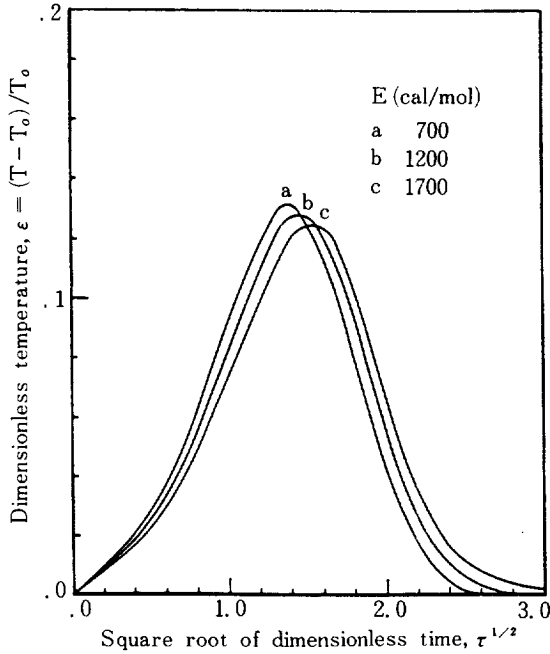


Fig. 5. Effect of activation energy on temperature profile.

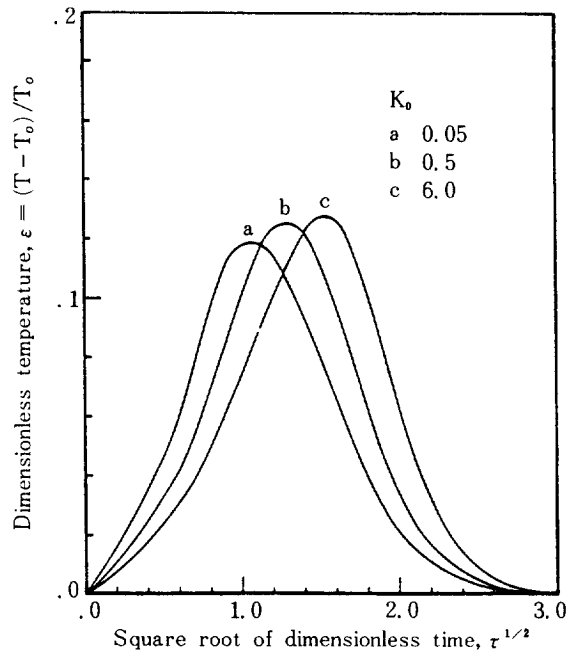


Fig. 7. Effect of proportional coefficient of equilibrium constant on adsorption rate.

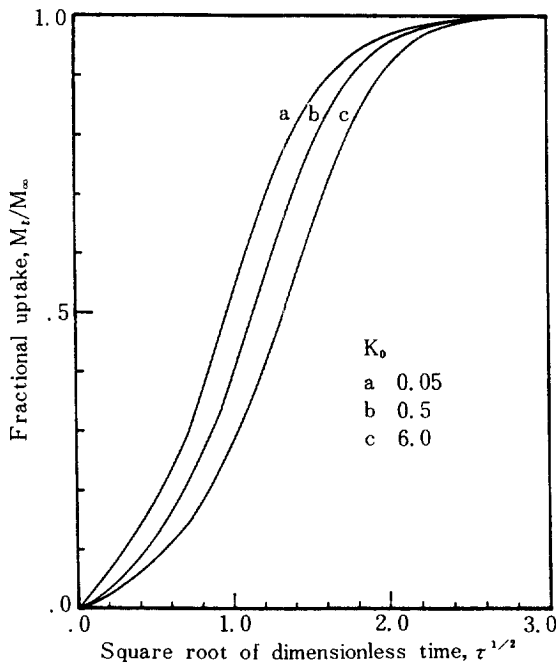


Fig. 6. Effect of proportional coefficient of equilibrium constant on adsorption rate.

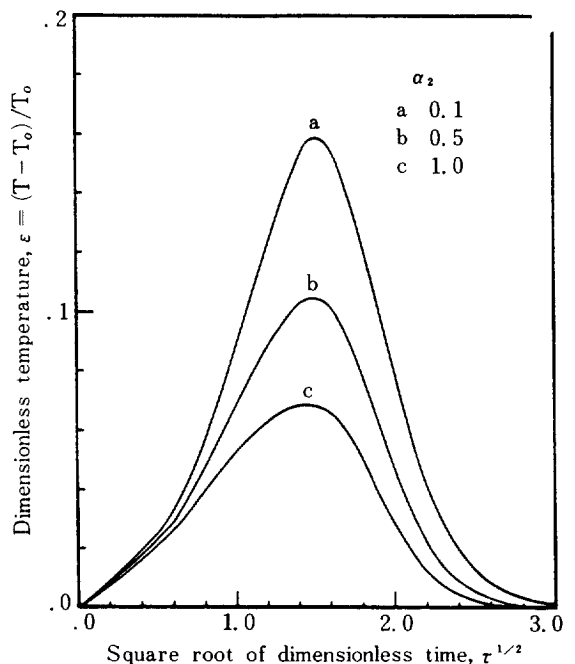


Fig. 8. Effect of parameter  $\alpha_2$  on temperature profile.

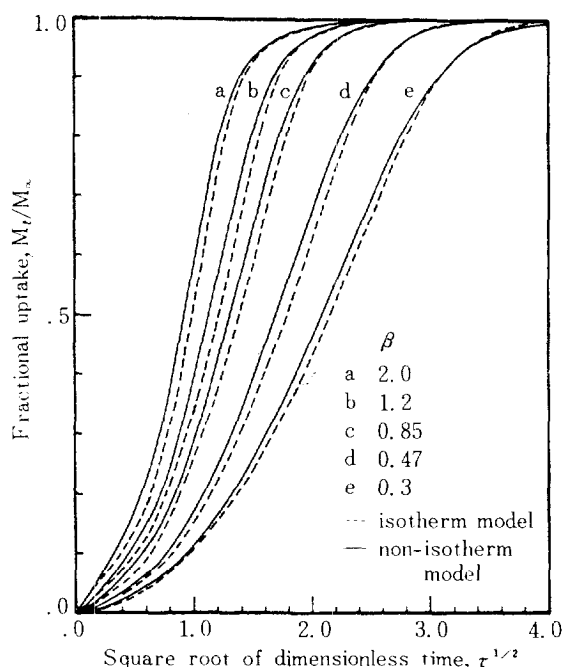


Fig. 9. Comparison of isothermal and nonisothermal adsorption rates with varying values of  $\beta$ .

through the spherical pellet. Consequently the variables of equilibrium constant,  $K$ , remain constant during adsorption.

Nonisothermal and isothermal adsorption rate curves are compared in Fig. 9. The values of parameters for nonisothermal rate curve (solid line) are the same as those in Fig. 2, and isothermal rate curve (dashed line) is drawn by using the same values of variables and parameters except the constant diffusivity and equilibrium constant. The adsorption rates of nonisothermal model are more rapid than those of isothermal model. These phenomena may be explained by the fact that diffusivity increases and equilibrium constant decreases (that is, diffusional resistance decreases) with the temperature rise. The explanation of the latter case is that, for small values of  $K$ , the solute concentration at the crystal surface is small and thus can easily be transported into the crystal. Approaching the final equilibrium state, nonisothermal adsorption rate

curves reach equilibrium more slowly than isothermal rate curves, because equilibrium constant and diffusivity approach to their initial values with decreasing temperature. As the results, the curves of both models reach the equilibrium state nearly at the same time.

#### Comparison of modeling with experimental data

To obtain the best fitting of the data with the theoretical curves, all variables and parameters should be varied. However, it is very difficult practically because all parameter values can not be varied at the same time. Hence, it may be reasonable to vary most sensitive parameters,  $\beta$  and  $\alpha_2$ , to fit the adsorption rate and temperature history curves respectively while remaining variables are kept constant. The chosen values of parameters for the calculation of adsorption curves are listed in Table 1. Here, the value of  $C_p$  was obtained from the experiment using Thermal Analysis Instrument. And the value of  $\Delta H$  was obtained from the plots of  $\log p$  vs.  $1/T$  curves by the equation of Clausius-Clapeyron. Average diameter of powder  $R_p$  was measured by virtue of X-ray diffraction photographs. The value of  $\alpha_1$  can be fixed by the predetermined values through the equation (7). Remained variables  $E, D_{ac}, K_0$  were determined from the data fittings with model equations. Also from the curve fitting, the values of parameters  $\beta$  and  $\alpha_2$  can be determined. These values listed in Table 2.

Adsorption rate and temperature curves are shown for the case of ZSM-5 in Fig. 10 and 11, and for zeolite Y in Fig. 12 and 13. It can be seen in Fig. 10 that agreement between the experiment and the model is good. At higher values of uptake ratio, however, a deviation is found. It can be expected that, as uptake ratio becomes higher, the diffusion is more affected by adsorbed material.

Consequently the assumptions of a linear isotherm and a concentration independent diffusivity are doubtful. Some investigators [13] reported an increase in dif-

Table 2. The list of values from the curve fittings.

Zeolite	$E$ (kcal/mol)	$D_0$ (cm <sup>2</sup> /sec)	$K_0$	$\beta$	$D$ (cm <sup>2</sup> /sec)	$\alpha_1$
Y	1.5	0.025	4.54	1.0	$6.25 \times 10^{-12}$	0.2
ZSM-5	1.5	0.025	4.54	1.6	$1.0 \times 10^{-11}$	0.5

Table 1. The list of the values of each variables and constants.

Zeolite	$R_a$ (cm)	$R_t$ ( $\mu$ m)	$\Delta H$ (kcal/mol)	$C_p$ (cal/g $^\circ$ K)	$M_0$ (mg)	$M_\infty$ (mg)	$\alpha_1$	$T_0$ (K)
Y	0.6	24	6.0	0.25	51.5	8.8	0.296	301
ZSM-5	0.6	0.76	6.0	0.25	50.0	5.7	0.202	301

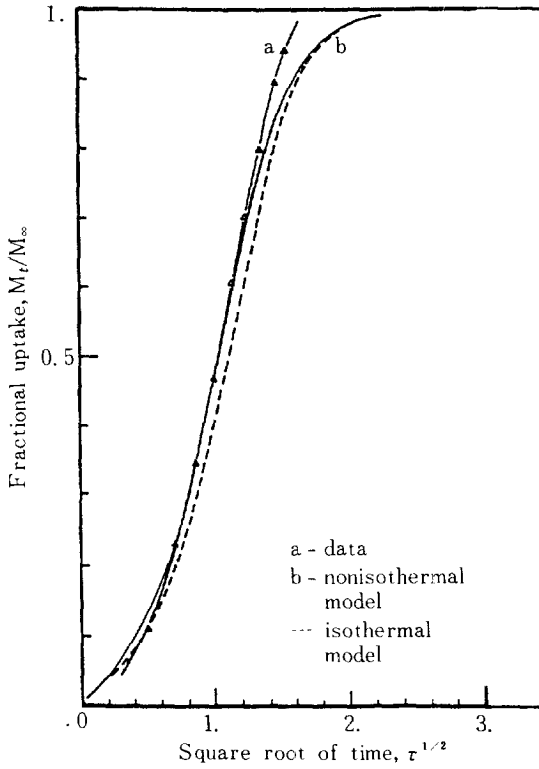


Fig. 10. Comparison of sorption rate of experiment with those of models in case of ZSM-5.

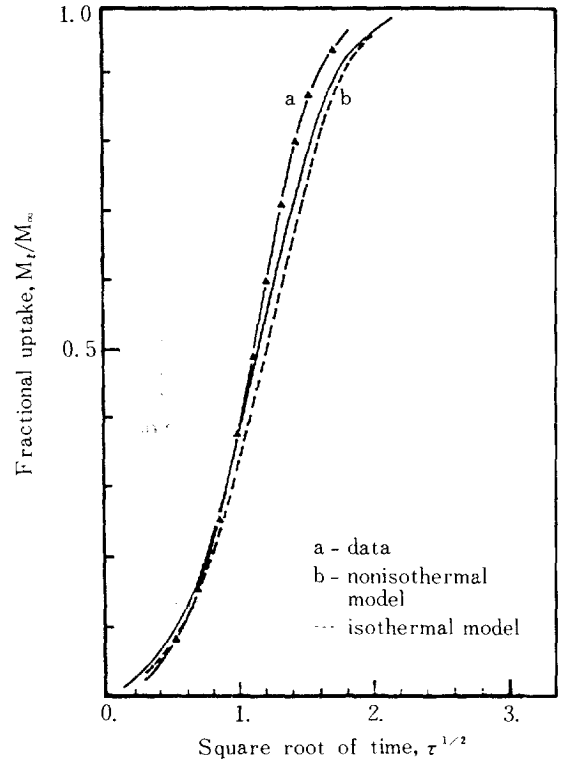


Fig. 12. Comparison of sorption rate of experiment with those of model in case of Y zeolite.

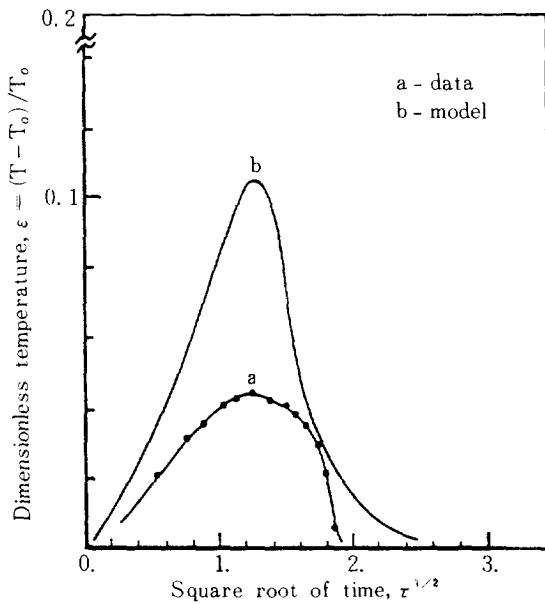


Fig. 11. Comparison of temperature profile of experiment with that of model in case of ZSM-5.

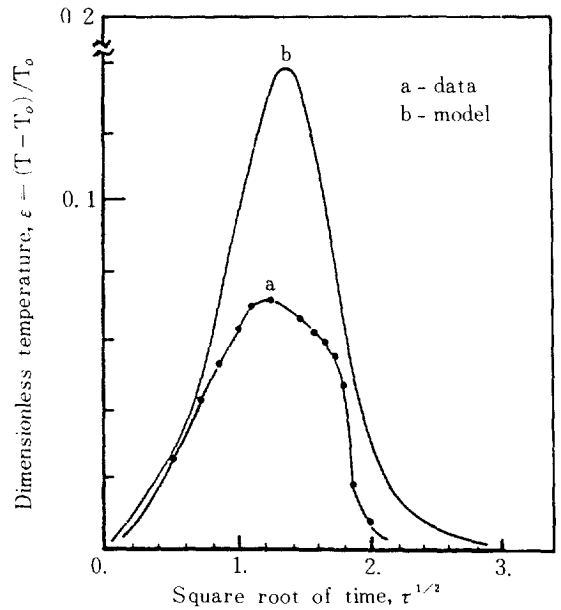


Fig. 13. Comparison of temperature profile of experiment with that of model in case of Y zeolite.

fusivity with increasing adsorbate concentration. Bratton and Rudloff reported on no change in diffusivity with concentration variation [14]. Barthomeuf [15] reported a decrease in diffusivity. If diffusivity is represented by a function of adsorbate concentration and if nonlinear isotherm, a better fitting can be expected at higher value of uptake ratio. Almost the phenomena is shown for zeolite Y in Fig. 12.

In Fig. 11 and 13, the temperature fittings are shown in cases of ZSM-5 and Y spheres respectively. The maximum temperature differences between data and model are large. Those differences seem to be originated from the difficulty in measuring the pellet temperature.

### CONCLUSION

During adsorption, the temperature of an adsorbent pellet increased because of the heat of adsorption and then it decreased as approaching the equilibrium state. Nonisothermal model showed more rapid adsorption rate than isothermal model in early stage of adsorption. As temperature becomes lower and returned to its original value at the later stage of adsorption, nonisothermal model showed slower adsorption rate than isothermal model. As the result, the time taken to reach the equilibrium state from the start of adsorption was nearly the same for both models.

As the value of  $\beta$  was being larger, that is, diffusivity in micropore became larger than that in macropore, the adsorption rate became more rapid and the maximum temperature rise became higher during adsorption.

The lower value of equilibrium constant showed a more rapid adsorption rate, but a lower maximum temperature rise.

When the adsorption rate curves from the experimental data were compared with those from the modeling, a deviation was found at a high uptake ratio while a good fitting was shown in early stage of adsorption. It might be due to the assumptions of linear isotherm and/or concentration independent diffusivity.

### NOMENCLATURE

A	: Surface area for heat transfer (cm <sup>2</sup> )
C	: Concentration of sorbate (mole/cm <sup>3</sup> )
C <sub>p</sub>	: Heat capacity of zeolite (cal/mol °C)
D	: Diffusion coefficient (cm <sup>2</sup> /sec)
D <sub>0</sub>	: Pre-exponential of diffusivity
E	: Diffusional activation energy (cal/mol)
ΔH	: Heat of adsorption (cal/mol)
h	: Heat transfer coefficient
K	: Equilibrium constant
M	: Net change in solute in the solid (mg)
r	: Radial distance (cm)
R	: Particle radius (cm)

t : Time (sec)

T : Temperature (°K)

### Subscripts

o : Initial value

∞ : Value at an infinite time

a : Macropore

i : Micropore

t : Value at time t

### Greek Letters

$\alpha_1$  : Dimensionless parameter defined in equation (7)

$\alpha_2$  : Dimensionless parameter defined in equation (7)

$\beta$  : Defined in equation (7)

$\gamma$  : Dimensionless constant defined in equation (7)

$\epsilon_p$  : Macropore void fraction

$\eta$  : Dimensionless distance defined in equation (6)

$\tau$  : Dimensionless time defined in equation (6)

$\theta$  : Dimensionless concentration

$\epsilon$  : Dimensionless temperature defined in equation (7)

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