ADSORPTION OF CARBON DIOXIDE ONTO HYDROPHOBIC ZEOLITE UNDER HIGH MOISTURE

TAKANORI SUZUKI, AKIYOSHI SAKODA AND MOTOYUKI SUZUKI

Institute of Industrial Science, University of Tokyo, Tokyo 106

JUN IZUMI

Nagasaki R&D Center, Mitsubishi Heavy Industries Ltd., Nagasaki 851-03

Keywords: High Moisture Conditions, Adsorption Equilibrium Coefficient, Effective Diffusion Coefficient, Chromatographic Measurement, Moment Analysis

Introduction

Adsorption processes, especially Pressure Swing Adsorption (PSA), play very important roles for bulk gas separation, gas purification, and other chemical processes. Recently, much more attention has been paid to their application to environmental technologies involving CO₂ recovery from stack gases such as industrial combustion waste gas and bio gas (Kapoor and Yan, 1989 and Pande and Fabiani, 1989).

In the case of CO₂ separation, zeolite adsorbents are generally employed because of their high adsorption capacity at low CO₂ concentration, high selectivity, rapid mass transfer in the particle and other factors. However, water vapor is often contained in the stack gases. Adsorption phenomena under such high moisture conditions are not well known so far in terms of the adsorption equilibrium and rate (Garg and Ausikaitis, 1983 and Suzuki and Doi, 1981).

In this work, the apparent adsorption equilibrium coefficient and the effective diffusion coefficient of CO₂ in zeolite adsorbents at ambient pressure and temperature were chromatographically measured and moment analysis is attempted on the basis of frozen water model. The differences of the adsorption equilibrium and diffusivity in the zeolite particle between the systems with and without coexistent water vapor have become clear.

1. Experimental

1.1 Apparatus and adsorbents

A schematic diagram of an experimental apparatus for column adsorption chromatography is shown in Fig. 1. The adsorption column was 1.0 m in length and 32×10^{-3} m in inner diameter. The volume of pulse-injected gas was 79.5×10^{-6} m³. The effluent peak was detected by a thermal conductivity detector (TCD, Shimadzu Corporation Ltd.) using on He stream as reference and recorded by a pen recorder (Yokogawa Electric Work Ltd.). The components of carrier and

Fig. 1 Schematic diagram of experimental apparatus

pulse gases were set up by controlling the flow rate of each gas, which were measured by a soap bobble flow meter. These gases were humidified by passing through temperature-controlled water and the humidity was measured by a temperature-hygrometer using thermocouples and a polymer film (Chino Corporation Ltd.). The experimental apparatus was placed in a constant temperature room at 298 K.

Adsorbents used were commercial 5A zeolite (Union Showa Corporation Ltd.) and modified Y zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$, Mitsubishi Heavy Industries Ltd.) in the form of cylindrical pellets. The properties of these adsorbents were shown in Table 1. The macropore and micropore volume and radius of both adsorbents were measured by the mercury penetration method (PORESIZER 9310, Micromeritics Ltd.) and the nitrogen adsorption method at liquid nitrogen temperature (BELLSORP 36, Bell Japan, Inc.), respectively.

1.2 Procedure

Chromatographic experiments were carried out as follows. The tracer concentration in the carrier gas was set up to 0 or 20%. The relative humidity in the carrier

* Received on March 7, 1997. Correspondence concerning this article should be addressed to T. Suzuki.

Table 1 Properties of zeolites

	5A zeolite	Y zeolite (SiO ₂ /Al ₂ O ₃ =70)
Packed density [kg/m ³]	0.706 × 10 ³	0.534 × 10 ³
Shape of adsorbent	cylindrical pellet (1.50 × 10 ⁻³ mφ × 4.03 × 10 ⁻³ m)	cylindrical pellet (1.77 × 10 ⁻³ mφ × 4.80 × 10 ⁻³ m)
Particle density, ρ _p [kg/m ³]	1.27 × 10 ³	0.911 × 10 ³
Bed void fraction, ε [-]	0.431	0.443
Particle void fraction, ε _p [-]	0.368	0.518
Macropore void fraction, ε _a [-]	0.329	0.328
Micropore void fraction, ε _i [-]	0.0396	0.00785
Macropore radius, r _a [m]	0.311 × 10 ⁻⁶	0.0301 × 10 ⁻⁶
γ ₁ of Eq.(5) [-]	0.687	0.693
γ ₂ of Eq.(5) [-]	0.5	0.5

gas was set to 0, 50 or 80%. After stabilization of the zeolite bed, a pulse of tracer of 20 or 40%, which was 20% higher than those in the carrier gas, was introduced into the entrance of the column. Then, the pulse responses were measured and analyzed by the moment method analysis.

Adjustment factors such as dead volume of the experimental equipment were measured by Ne pulse responses with a He carrier gas.

2. Method of Moment Analysis

2.1 Assumptions

The assumptions employed in this work are as follows (Suzuki, 1990b):

- 1) The adsorption isotherms are regarded as linear and written by the Henry equation, since perturbation chromatography with a small concentration change was employed in the experiments.
- 2) Adsorbents have bidisperse pore structures, where the macroparticle consists of many microparticles with micropores inside.
- 3) The fluid-to-particle mass transfer, the micropore diffusion, and the adsorption to adsorption sites are fast enough.
- 4) Water vapor concentrations in the gas and adsorbed phases are kept constant, since (i) the adsorption capacity and energy for water vapor is much larger than those for tracer gases such as N₂ and CO₂ and (ii) the relative pressure of tracer N₂ and CO₂ gases are in the order of magnitude of 10⁻⁴, though that of water vapor is 0.5 or 0.8. Then, replacement and competitive adsorption are not taken into account by assuming that the adsorbed water is frozen.
- 5) The temperature in the whole system is constant.

2.2 Basic equations

The basic equations used for moment analysis are the same as those found in the literature (Suzuki and Smith, 1971).

From basic equations, the first absolute moment is given as,

$$\Delta\mu_1 = \mu_1 - (\mu_1)_{\text{inert}} = \frac{1-\varepsilon}{\varepsilon} \rho_p K_a^* \left(\frac{z}{u} \right) \quad (1)$$

where K_a^* , ε and ρ_p are the apparent adsorption equilibrium constant, the bed void fraction and the particle density. u and z are the average velocity in intraparticle space in the bed and the axial desistance in the bed, respectively. And $(\mu_1)_{\text{inert}}$ was introduced to correct the dead volume of the experimental equipment (Suzuki, 1990b).

The second central moment is defined as,

$$\mu_2 = [\delta_d + \delta_e] \left(\frac{2z}{u} \right) + (\mu_2)_{\text{pulse}} \quad (2)$$

where, δ_d and δ_e represent diffusion restrictions in fluid and zeolites, which are simplified by introducing the effective diffusion coefficient, D_e , based on the assumptions made in this work (Chihara, Suzuki and Kawazoe, 1978), as follows.

$$\delta_d = \left\{ 1 + \frac{1-\varepsilon}{\varepsilon} (\varepsilon_a + \rho_p K_a^*) \right\}^2 \left(\frac{E_z}{u^2} \right) \quad (3)$$

$$\delta_e = \frac{1}{\phi} \frac{1-\varepsilon}{\varepsilon} \frac{R^2}{D_e} (\varepsilon_a + \rho_p K_a^*) \quad (4)$$

ε_a is the void fraction of macropore in the particle. ϕ is the correction factor regarding cylindrical and spherical adsorbent shapes (Kawazoe, 1967), and $(\mu_1)_{\text{pulse}}$ is the pulse length correction factor (Suzuki, 1990b).

The axial dispersion coefficient, E_z , is given as a function of the empty bed velocity, u_0 , and the molecular diffusion coefficient, D_m , (Bird *et al.*, 1960) as Eq. (5). By introducing Eq. (5) into Eq. (2), Eq. (2) is rewritten as Eq. (6).

$$E_z = \gamma_1 D_m + 2\gamma_2 R u_0 \quad (5)$$

$$\begin{aligned} \frac{\Delta\mu_2}{(2z/u)} = & \left[\gamma_1 D_m \left\{ 1 + \frac{1-\varepsilon}{\varepsilon} (\varepsilon_a + \rho_p K_a^*) \right\}^2 \right] \left(\frac{1}{u} \right)^2 \\ & + \left[2\varepsilon\gamma_2 R \left\{ 1 + \frac{1-\varepsilon}{\varepsilon} (\varepsilon_a + \rho_p K_a^*) \right\}^2 \right] \left(\frac{1}{u} \right) + \delta_e \end{aligned} \quad (6)$$

Fig. 2-(a) Comparison between apparent adsorption equilibrium constants, K_a^* , of CO_2 measured by volumetric method and chromatographic method (Temperature: 298 K, Adsorbent: 5A and Y zeolite, Tracer gas in carrier gas: 20%)

where, γ_1 and γ_2 are constants defined by the characteristics of the adsorption bed (Ruthven, 1984) such as those listed in Table 1.

2.3 Procedure

The moment analyses of experimental data were carried out as follows.

- 1) The apparent adsorption equilibrium constant, K_a^* , was obtained from the slope of the plot of $\Delta\mu_1$ vs z/u , according to Eq. (2).
- 2) The time constant of the effective diffusion coefficient, R^2/D_e , was derived from the curve fitting to the $\Delta\mu_2'/(2z/u)$ vs. $1/u$ plots on the basis of Eq. (6) calculated using the resultant K_a^* .

3. Results and Discussion

3.1 Effects of moisture on CO_2 adsorption equilibrium relations

Comparison between the apparent adsorption equilibrium constants, K_a^* , for 5A and modified Y zeolites under conditions of no moisture measured by the volumetric method (BELLSORP 36, Bell Japan, Inc.) and the chromatographic method are shown in **Fig. 2-(a)** and **(b)**, respectively. In the cases of both adsorbents, the K_a^* values obtained under these constants measured chromatographically and volumetrically were in fairly good agreement.

The first moment analyses for He- N_2 and He- CO_2 systems with coexistent water vapor were examined and changes in the apparent adsorption equilibrium constant, K_a^* , were shown in **Fig. 3-(a)** and **(b)**. In the case of 5A zeolite, the adsorption constants, K_a^* , for He- N_2 and He- CO_2 with water vapor, were much smaller than those for He- N_2 and He- CO_2 without water vapor. In other words, 5A zeolite had no adsorption capacities for N_2 or CO_2 under high moisture conditions. On the contrary,

Fig. 2-(b) Comparison between apparent adsorption equilibrium constants, K_a^* , of N_2 measured by the volumetric method and chromatographic method (Temperature: 298 K, Adsorbent: 5A and Y zeolite, Tracer gas in carrier gas: 0%)

in the case of modified Y zeolite, K_a^* decreased by only one-third to two-thirds under high moisture conditions.

It is thought that the results reflect the differences in polarity on the adsorbent surface. The adsorption sites of the hydrophilic zeolite, 5A, were considered to be completely occupied by water molecules and no sites remained for N_2 or CO_2 adsorption.

It should be noted that the changes of humidity in the elution gas were not detected in all pulse response experiments.

The frozen water model appears to be reasonable as far as the experimental conditions in this work are concerned.

3.2 Effects of moisture on CO_2 adsorption rate

The adsorption rate to modified Y zeolite only is discussed because 5A zeolite has no adsorption capacities for CO_2 under high moisture conditions as described previously. The D_e/R^2 were obtained from the $\Delta\mu_2'/(2z/u)$ vs. $1/u$ plots in **Fig. 4** for He- N_2 and He- CO_2 systems with and without coexistent water vapor and shown in **Fig. 5**. It was found that the changes of D_e/R^2 were negligibly small regardless of the coexistence of water vapor.

The resultant intraparticle diffusion expressed by D_e/R^2 is considered as follows. The pore diffusion process consists of the macropore and micropore diffusion processes for the adsorbents with bidisperse structure, and Eq. (7) holds (Suzuki 1990b).

$$\delta_e = \delta_a + \delta_i \quad (7)$$

where,

Fig. 3-(a) Dependence of apparent adsorption equilibrium constant, K_a^* , on humidity in carrier gas (Temperature: 298 K, Adsorbent: 5A and Y zeolite, Tracer gas in carrier gas: 20% of CO_2) [$K_a^* \times 10^{-3} \text{ m}^3/\text{kg}$]: 5A zeolite; (0%) 30.2, (50%) 0.07, (80%) 0.05, Y zeolite; (0%) 12.0, (50%) 7.13, (80%) 4.26]

Fig. 3-(b) Dependence of apparent adsorption equilibrium constant, K_a^* , on humidity in carrier gas (Temperature: 298 K, Adsorbent: 5A and Y zeolite, Tracer gas in carrier gas: 0% of N_2) [$K_a^* \times 10^{-3} \text{ m}^3/\text{kg}$]: 5A zeolite; (0%) 7.45, (50%) 0.01, (80%) 0.01, Y zeolite; (0%) 1.11, (50%) 0.74, (80%) 0.61]

$$\delta_a = \frac{1}{\phi} \frac{1-\varepsilon}{\varepsilon} \frac{R^2}{D_a} (\varepsilon_a + \rho_p K_a^*)^2 \quad (8)$$

$$\delta_i = \frac{1-\varepsilon}{\varepsilon} \frac{a^2}{15D_i} \rho_p K_a^* \quad (9)$$

and D_a and D_i are the diffusivity in macropore and micropore, respectively (Suzuki, 1990a). ϕ is the correction factor for cylindrical and spherical adsorbent shapes (Kawazoe, 1967).

The ratio of D_e/R^2 experimentally obtained to

Fig. 4 Plots of $\Delta\mu_2'/(2z/u)$ against $1/u$ for determining D_e/R^2 (Temperature: 298 K, Adsorbent: Y zeolite, Tracer gas in carrier gas: (N_2) 0 %, (CO_2) 20%)

Fig. 5 Changes of D_e/R^2 , and contribution of macropore diffusion of N_2 and CO_2 on Y zeolite with the humidity of carrier gas (Temperature: 298 K, Adsorbent: Y zeolite, Tracer gas in carrier gas: (N_2) 0%, (CO_2) 20%)

D_a/R^2 thus estimated is shown in Fig. 5. It is found that the intraparticle diffusions of N_2 and CO_2 in hydrophobic Y zeolite used in this work are independent of the coexistence of water vapor and controlled by the macropore diffusion.

Conclusion

The effects of high moisture conditions on CO_2 adsorption onto hydrophilic and hydrophobic zeolites were elucidated by chromatographic experiments and moment analysis on the basis of the frozen water model. The adsorption capacity of hydrophobic zeolite is not drastically reduced by the coexistent water vapor,

however the adsorption capacity of hydrophilic zeolite is lost completely. The rate of overall mass transfer in a particle of hydrophobic zeolite is almost constant regardless of the moisture content. The contribution of macropore diffusion in the intraparticle diffusion is dominant either with or without coexistent water vapor. The hydrophobic Y zeolite can be preferably used for adsorption processes in high moisture conditions such as the PSA for CO₂ recovery from stack gas.

Nomenclature

a	= radius of microparticle	[m]
C	= concentration	[%]
D_a	= diffusion coefficient in macropore	[m ² /s]
D_e	= effective diffusion coefficient	[m ² /s]
D_i	= diffusion coefficient in micropore	[m ² /s]
D_m	= molecular diffusion coefficient	[m ² /s]
E_z	= axial dispersion coefficient	[m ² /s]
K_a^*	= apparent adsorption equilibrium constant	[m ³ /kg]
R	= radius of particle	[m]
r_a	= radius of macropore	[m]
u	= average velocity in intraparticle space in the bed	[m/s]
u_0	= empty bed velocity	[m/s]
z	= axial distance in the bed	[m]
δ	= constant defined in Eq. (3), (4), (7), (8) and (9)	[s]
ε	= void fraction in the bed	[-]
ε_a	= void fraction of macropore	[-]
ε_p	= void fraction in the particle	[-]
ϕ	= function (Kawazoe, 1967)	[-]
γ_1	= constant (Ruthven, 1984)	[-]
γ_2	= constant (Ruthven, 1984)	[-]
μ_1	= first absolute moment	[s]
μ_2'	= second central moment	[s ²]
ρ_p	= density of particle	[kg/m ³]

<Subscripts>

a	= macropore
e	= effective
i	= micropore

Literature Cited

- Bird, R. B., W. E. Stewart and E. N. Lightfoot; *Transport Phenomena*, p. 496-513, 563-572, John Wiley and Sons, New York, USA (1960)
- Chihara, K., M. Suzuki and K. Kawazoe; "Adsorption Rate on Molecular Sieving Carbon by Chromatography," *ACH E J.*, **24**, 237-246 (1978)
- Garg, D. R. and J. P. Ausikaitis; "Molecular Sieve Dehydration Cycle for High Water Content Streams - New technology is Extending the Use of Molecular Sieve Adsorptive Dehydration to the Remove of over 20 wt% Water from Organic Admixtures," *Chem. Eng. Prog.*, April, 60-65 (1983)
- Kapoor, A. and R. T. Yang; "Kinetic Separation of Methane-carbon Dioxide Mixture by Adsorption on Molecular Sieve Carbon," *Chem. Eng. Sci.*, **44**, 1723-1733 (1989)
- Kawazoe, K.; "On Intraparticle Diffusion Rate in Adsorption," *KagakuKogaku*, **31**, 354-358 (1967)
- Suzuki, M.; *Adsorption Engineering*, p. 64-70, Kodansha, Tokyo, Japan (1990a)
- Suzuki, M.; *Adsorption Engineering*, p. 125-147, Kodansha, Tokyo, Japan (1990b)
- Suzuki, M. and H. Doi; "Effect of Adsorbed Water on Adsorption of Oxygen and Nitrogen on Molecular Sieving Carbon," *Carbon*, **20**, 441-444 (1982)
- Suzuki, M. and J. M. Smith; "Kinetic Studies by Chromatography," *Chem. Eng. Sci.*, **26**, 221-235 (1971)
- Pande, D. R. and C. Fabiani; "Feasibility Studies on the Use of a Naturally Occurring Molecular Sieve for Methane Enrichment from Biogas," *Gas Sep. Purif.*, **3**, 143-147 (1989)
- Ruthven, D. M.; *Principles of Adsorption and Adsorption Processes*, p. 208-213, John Wiley and Sons, New York, USA (1984)