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Isobaric Thermogravimetry of the Gas Encapsulation with Molecular Sieves A

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The isobaric gas sorption with (Na,Ca)-A and (K,Ca)-A zeolites was measured gravimetrically in temperature ranges of −160—−40 °C for O_2 and N_2, and of room temperature—200 °C for n-C_4H_{10}. The sorption hysteresis, *i.e.*, the gas encapsulation was observed. The maximum point, in the temperature rising branch of the isobar, was located at about −90 °C for N_2 and in the range 120—170 °C for n-C_4H_{10}, and shifted to the lower temperature side with the increasing content of calcium for n-C_4H_{10}. The observed results are explained in terms of an incomplete blocking action of cations on window sites. This incompleteness was amplified by bivalent cations introduced onto other sites than the window sites, and the sieving character of the ion-exchanged zeolite was delicately modified.

The unit cell of zeolite A is a cube with a side-length of about 1.2 nm, at the center of which there exists a nearly spherical cavity accommodating sorbed molecules. This cavity is surrounded by six 8-membered oxygen rings, which costitute windows to the cavity. In commercial molecular sieves 3A and 4A, all of these windows are blocked by K^+ and Na^+, respectively.[1] The molecular sieving characters of these zeolites are primarily determined by the size of the aperture of the *partially-blocked* windows. The effective size of the aperture, however, depends upon temperature. At higher temperatures, a situation is realized that larger molecules, which are not sorbed at lower temperatures, are able to be sorbed. If the temperature is lowered after such molecules being sorbed at higher temperatures, the windows are closed and the sorbed molecules are encapsulated.[2]

Usually the encapsulation process requires high temperature and pressure, in order to ensure a reasonable rate and amount of sorption. However, the encapsulation may be realized at not so much high temperatures and pressures as usual, if the rate of sorption is increased by some means. This is a problem of the present work.

Experimental

The block diagram of measuring system used is shown in Fig. 1(a). A Cahn RG-type electro-balance was used which was drastically improved in the authors' laboratory to be bakable at 180 °C.[3] The pressure of adsorbed gas was measured with a MKS Baratron type-210 diaphragm gauge, and controlled within ±0.5% of the preset value with a Granville-Phillips type-216 automatic pressure controller by adding some manual operations. A main pumping system consisted of a sorption-pump and an ion-spattering pump of a capacity of 50 $l\,s^{-1}$. Apart from gas handling system, the apparatus was free from grease or oil, and a back-ground pressure of 10^{-5} Pa was easily attained in a few hours by a mild baking-out.

The leg of the balance and cryostat are shown in Fig. 1(b). Radiation heating from the upper part of the apparatus and disturbance due to convection were reduced by a copper shield, S, which acted at the same time as a gasket for conflat flange. A sheath IC junction, J, was fixed on the lowest conflat flange by copper wire.

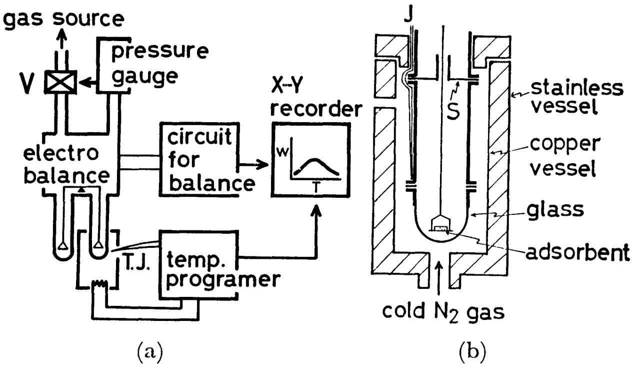


Fig. 1. Apparatus for isobaric thermogravimetry of gas sorption.
(a) Main system: V, Granville-Phillips type-216 automatic pressure controller, (b) details of the leg of balance-chasis for sorbent: thick line, made of stainless steel; thin line, made of glass.

The temperature of the sample was rised or lowered at approximately constant rates, in a similar manner to the usual thermo-gravimetry. Low temperatures were realized by cooling with cold nitrogen gas supplied from a liquid nitrogen reservoir by electric heating, and controlled within ±0.5 °C of a preset value. Before the sorbate gas was introduced, 10 Pa of He gas was introduced to facilitate the rapid temperature equilibration.

Powdery zeolites of given composition were prepared by a method described in the preceding papers.[4,5] These zeolites were pressed in a form of disc, 13 mm in diameter and about 500 mg in weight. Prior to sorption experiments, zeolite samples were carefully dehydrated, at 390—400 °C for about 100 h, the residual pressure being 10^{-5} Pa or so. This dehydration condition was far better than that in conventional sorption experiments. Sorbate gases, N_2, O_2, and n-C_4H_{10} (supplied from Takachiho Chemical Co.), had nominal purities better than 99.9, 99.8, and 99.7%, respectively, according to mass-spectroscopic analyses and were used after further drying with 13 X zeolite.

Results

(Na, Ca)-A Zeolites. The sorption isobar was measured for n-C_4H_{10} and N_2 with $(Na_{12-2x}Ca_x)$-A zeolite, in which $x=1.93$. According to the preceding paper,[5] this zeolite is classified as 4A in their molecular sieving characters. The temperature was rised or lowered at a constant rate from −155 to −50 °C for N_2 at a constant pressure of 9.3×10^3 Pa,

while for n-C_4H_{10} from room temperature to 200 °C at 8.3×10^3 Pa. The temperature was not rised above 200 °C for fear of cracking and polymerization of n-C_4H_{10}. The form of sorption isobar depended upon the rate of temperature rise. Representative curves for $(Na_{12\text{-}2x}Ca_x)$–A are shown in Fig. 2, which shows that the rate of sorption is so low that equilibrium is not attained at 200 °C.

The effect of the composition to the form of the isobar was studied, results being shown in Fig. 3. The peak, in the temperature rising branch, shift to the lower temperature side with the increasing content of calcium. The shift was remarkable for n-C_4H_{10}, but not so for N_2.

(K,Ca)–A Zeolites. The molecular sieving action of $(K_{12\text{-}2x}Ca_x)$–A zeolite drastically changes in the neighbourhood of $x=4$.[4] This tendency was further studied in detail by the present method. Sorption isobars for O_2 and N_2 are shown in Fig. 4. Large amounts of N_2 and O_2 were sorbed, virtually without an activation energy, into $(K_{3.58}Ca_{4.21})$–A at −196 °C, so that this zeolite may be classified as 5A. On the other hand, $(K_{4.30}Ca_{3.85})$–A sorbed very small amounts of these gases, being classified as 3A. A diagram in the lower part of Fig. 4 shows that a small amount of sorption took place even at −196 °C without any activation energy, and that some of windows were in the state of "open" against to O_2 and N_2. In the terminology of percolation theory, however, the percolatable fraction of cell is less than 0.03.

As for n-C_4H_{10}, quite different features were observed as shown in Fig. 5; namely, the peak appeared in the isobar with $(K_{4.30}Ca_{3.85})$–A. This means that n-C_4H_{10} was allowed to pass through the window blocked by K^+ at temperatures higher than 100 °C.

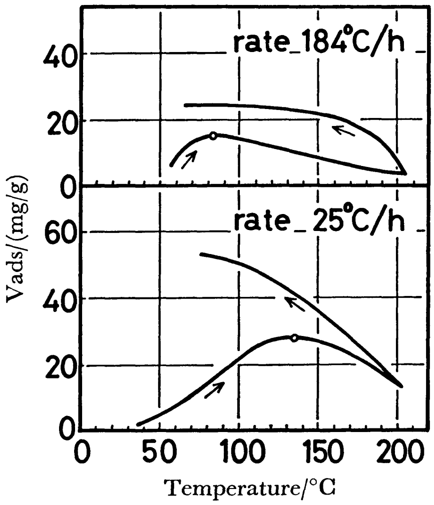


Fig. 2. Sorption isobar and the rate of temperature change.
Zeolite: $(Na_{8.14}Ca_{1.93})$–A, gas: n-C_4H_{10} at constant pressure of 8.3×10^3 Pa (=62 Torr), ○: maximum point in the temperature rising branch.

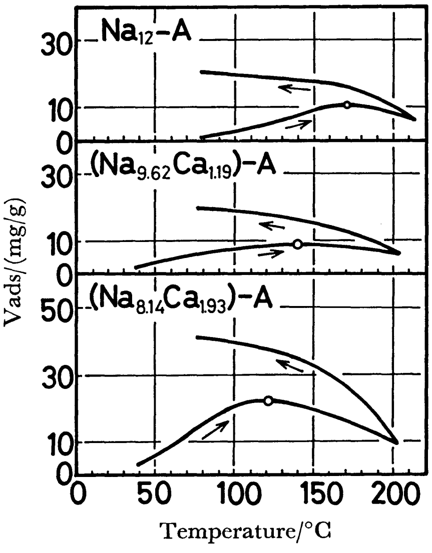


Fig. 3. Effect of the zeolite composition to the sorption isobar of n-C_4H_{10}.
Pressure: 8.3×10^3 Pa (=62 Torr), rate of temperature change: 68 °C h^{-1}, ○: maximum point in the temperature rising branch.

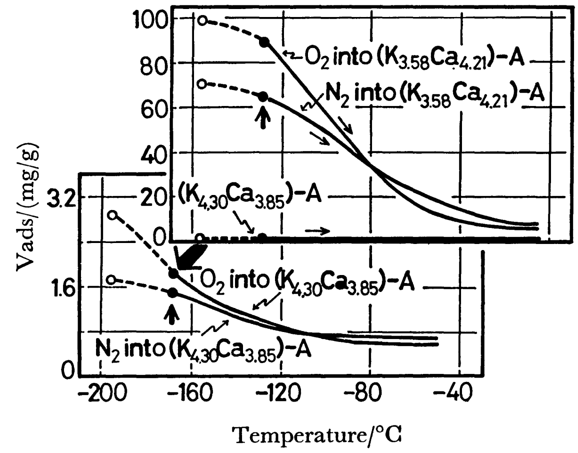


Fig. 4. Sorption isobar of N_2 and O_2 with (K,Ca)–A zeolites.
The continuous temperature rise start from the point designated by arrows; ○: measured by dipping in a liquid nitrogen bath, $P(O_2)=1.6\times10^4$ Pa (=120 Torr), $P(N_2)=9.3\times10^3$ Pa (=70 Torr), rate of temperature change, 50 °C h^{-1} for O_2, 100 °C h^{-1} for N_2.

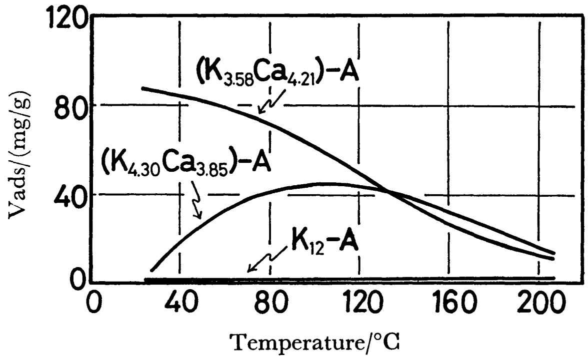


Fig. 5. Sorption isobar of n-C_4H_{10} with (K,Ca)–A zeolites.
Rate of temperature rise: 68 °C h^{-1}, pressure: 8.3×10^3 Pa (=62 Torr).

Discussion

Let us outline, for a better understanding of the sieving action, the structure of dehydrated zeolite A and cation distribution in it. Figure 6 shows its framework and cation sites. Abbreviations are used as the α-site for the site near the plane of the 8-membered oxygen ring, the β-site for the site near the center of the 6-membered oxygen ring, and the γ-site for the site near the center of the 4-membered oxygen ring. At the center of the unit cell, there exists a large cavity, named the α-cage, which is nearly spherical with a diameter of 1.14 nm and can accomodate visiting gas molecules. The 8-ring constitutes a window to the cavity, and the sieving character of zeolite A is determined by the state of the 8-ring, that is, whether the α-site is unoccupied or occupied by a cation and by what kind of cation. On the other hand, the occupancy factor on the β- and γ-sites does not directly influence the sieving character. The distribution of cations is determined by their affinities to these sites. The γ-site has a very weak affinity for all cations. Na^+ and bi-valent cations like to reside on the β-site than the α-site, while reverse is the case with K^+, Rb^+, and Cs^+.[4-10] Let us express the composition as $(M^{I}_{12-2x}M^{II}_{x})$–A, where M^{I} and M^{II} are uni- and bi-valent cations, respectively. If M^{I} is Na, one open window (unoccupied α-site) per unit cell is produced at $x=2$, while if M^{I} is K, Rb, or Cs, at $x=5$.

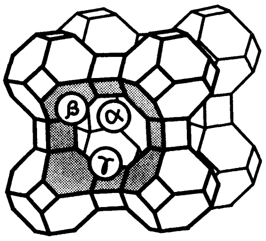


Fig. 6. Structure and cation sites of dehydrated zeolite A.

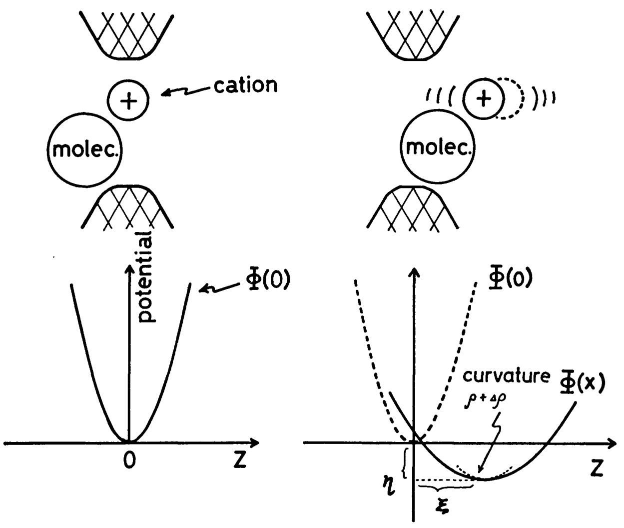
According to the percolation theory, the sieving character drastically changes in a narrow range of the concentration of the open window arround a critical value say, one per unit cell. The applicability of the theory has quantitatively been proved with (Na,Ca)–A system. In the preceding paper, the percolation theory was applied to sorptions of N_2 at 90 K and *n*-butane at 323 K with (K,Ca)–A system.[4] Then, it was concluded that there exists the third kind of window, named the conditionally-opened window, through which N_2 cannot pass at 90 K but *n*-butane, a larger molecule, can at 323 K. The 6th Ca^{2+} in Ca_6–A occupies the α-site and constitutes a conditionally-opened window.[4] Some fraction, not all, of windows blocked by K^+ also constitute conditionally-opened windows in (K,Ca)–A with a higher Ca-content.[4] This is further proved to be true by the present experiment with $(K_{4.30}Ca_{3.85})$–A.

Let us now present a model for the conditionally-opened window, of which the effective aperture-size markedly increases in a temperature range, 90—400 K. This is done by using the form of the potential surface experienced by the window-blocking cation. Here are taken into consideration potentials due to the framework and exchangeable cations but not that due to co-existing sorbed molecules. In K_{12}–A, the potential $\Phi(0)$ is to have such a sharp valley as shown in Fig. 7(a), the amplitude of thermal oscillation of the blocking K^+ is very small. A large energy may be required to push K^+ ion aside and make a way for a visiting molecule. Hence, the blocked window behaves as a perfectly closed one as far as the present temperature range concerns. In the conditionally-opened window in $(K_{12-2x}Ca_x)$–A, the blocking cation is easily displaced at a moderate temperature, and the potential $\Phi(x)$ is to have a very gentle curvature at its valley, as schematically shown in Fig. 7(b). In the figure, ξ denotes the distance of the shift of the potential minimum from the window plane, η the decrease of the potential at its minimum point, and $\Delta\rho$ the increase in the curvature of the potential surface at its valley. Values for ξ, η, and $\Delta\rho$ depend upon the distribution of cations, especially upon those in the neighborhood of the concerned K^+. If $\Phi(x)$ has a higher symmetry, ξ may be very small or zero. This is the case with Ca_6–A as shown by Firor and Seff.[11] Such a high symmetry is realized only in limitted cases with favourable compositions. With an unfavourable composition, the local configuration of cations arround a given α-site differs from site to site, so that ξ is small for some K^+ while large for others. The value of η influences the stability of the crystal but does not its sieving character which is a main concern in the present work, and is not further discussed. The larger the values for ξ and/or $\Delta\rho$, the smaller the activation energy for the passage of a visiting molecule, as can be seen from Fig. 7(b).

A window with a too large ξ behaves as a pseudo-open window. Its concentration may increase with the increasing x, except at some special values of x where $\Phi(x)$ has a high symmetry. The critical point in the percolation theory must be located at such a composition that the sum of concentrations of the open and pseudo-open windows is 1 p.u.c. This is the reason why the critical point in (K,Ca)–A system is located not at 5 but at 4.2 or so.[4]

There is another conceivable model for the activated sorption process. Breck and Smith proposed the activation of the vibration of breathing mode of the 8-ring.[2] This is unacceptable, since the framework is very rigid and one has never observed a high Debye-Waller factor of the framework. The present model, on the other hand, is in harmony with the structural observation due to Seff and his coworkers; that is, there exist loosely bound and/or displaced M^{I} cation on the α-site in (K,Zn)–A, and (Cs,Ca)–A.[12,13]

There might occur some fear that the residual water molecule influences both of the sieving character and structure. Comparing the present and previous results, one find some discrepancies in the amounts of sorption with samples of the same origine, especially with $(K_{3.58}Ca_{4.21})$–A.[4] This is attributed to the difference in the degree of dehydration. The



(a) (b)

Fig. 7. Model for the conditionally-opened window, and the potential experienced by the cation.
(a) Side view of the 8-ring window. Perfectly closed window. (b) Conditionally-opened window. The window aperture is increased with increasing ξ and $\Delta\rho$. $\Phi(x)$: The potential experienced by the window-blocking cation at composition $(\mathrm{M^{I}}_{12-2x}\mathrm{M^{II}}_{x})$–A, ξ: the distance of the shift of the potential minimum from the window plane, η: the decrease of the potential at the minimum point, $\Delta\rho$: the change in the curvature.

critical point slightly shifts to the lower Ca-content side. On the other hand, the main feature of the curve of composition *vs.* sorption capasity is not so much changed that the applicability of the present model is affected. However, the use of a clean vacuum system is essential to determine the exact value for the critical composition.

Previously, the window size was controlled solely by the kind of cation blocking the window. Now, one can finely control it by changing the form of the potential experienced by the blocking cation, that is, by changing $\Delta\rho$ and ξ values. This indirect method may be named as the cation-loosening one, though this name has a drawback that it does not include the effect of ξ. The cation-loosening can be adopted as an effective mean in tailoring molecular sieve. An example of the success in the tailoring is a highly selective sorption of PH_3 from SiH_4 with (K_4Zn_4)–A, though this was accomplished before the recognition of the method. Other examples of the tailoring are encapsulation of Kr into $(\mathrm{K,M^{II}})$–A and H_2 into $(\mathrm{Cs,M^{II}})$–A. These will be reported in the succeeding papers.[14,15]

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