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Encapsulation of Krypton with (K, M^{II})-A Zeolites

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The encapsulation of krypton is realized with zeolite A, having compositions $(K_{12-2x}M^{II}_x)$-A with $1.11 \leqq x \leqq 3.78$, at temperatures lower than 300 °C and a pressure of 3.7×10^6 Pa. This encapsulation condition is much milder than the usual one, 350 °C and 4.2×10^8 Pa, which is adopted in industry. Such lowerings of the encapsulation temperature and pressure are caused by bivalent cations introduced through ion-exchanges. The result is an experimental evidence to the existence of the ion-loosening effect proposed in preceding papers.

Zeolite A has, at the center of its unit cell cube, a large cavity which is nearly spherical with a diameter of 1.14 nm and can accomodate sorbed molecules. This cavity is surrounded by six 8-membered oxygen rings, which are on {100} faces of the cube and constitute windows to the cavity. In commercial molecular sieves 3A and 4A, all of these windows are blocked by potassium and sodium ions, 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 the large molecule being sorbed at higher temperature, the windows are closed and the sorbed molecules are encapsulated.[2]

An example of the practical use of the encapsulation is that of radio-active ^{85}Kr into 3A zeolite, for commercial distributions. It is a large merit that a lead container, required as a radiation shield, becomes very small for such a compactly encapsulated ^{85}Kr. Usually, krypton is encapsulated into 3A at 350 °C and a pressure of 4.2×10^8 Pa.[3,4]

It is expected that the encapsulation temperature and pressure are lowered by the ion-loosening techniques presented in the preceding papers.[5,6] The techniques consist in increasing the temperature dependence of the window size by introducing bivalent cations onto 6-membered oxygen rings. In the present paper, results of the krypton encapsulation are reported, which prove the ion-loosening effect.

Experimental

The starting material was commercial sodium-A zeolite of powder form, manufactured by Toyo Soda Co. or Union Carbide Co. Sodium-A zeolite was treated at 80 °C with an 1 mol dm^{-3} aqueous solution of KCl, repeatedly, to obtain K_{12}-A. Resultant K_{12}-A was further treated with a solution containing KCl and $M^{II}Cl_2$, of 0.2 total normality, where M^{II} is Ca, Co, Mn, or Zn. The composition of the zeolite was determined by the usual chemical analysis and atomic absorption spectrometry. The zeolite used contained M^{II} ions less than 4 per unit cell.

The dehydration process of the zeolite was studied with a quartz spring balance. The weight of the sample decreased to 75% of the initial one after vacuum baking-out for 2 h at 300 °C. After this treatment, no change was observed in the crystallinity of the sample with X-ray diffraction techniques. This degree of the dehydration, we judged, is appropriate to the practical use of the zeolite as an adsorbent. In the following experiments, the sample zeolite was dehydrated at 300 °C for 2 h under vacuum.

The sample zeolite (3—5 g) was packed in a conventional autoclave(300 cm^3) and dehydrated. Then, krypton gas at a pressure of 3.7×10^6 Pa was introduced into the autoclave, held at 300 °C, and sorbed into the zeolite. After a waiting time of 60 min, the system was slowly cooled under the pressure, to room temperature, and then a residual gas of a high pressure was evacuated from the dead space in the autoclave. The amount of gas encapsulated in the zeolite was measured by a thermal desorption method. The autoclave was heated at a rate of about 1.3 °C min^{-1}, and the amount of evolved gas was caught, through a flexible stainless steel tube, into a messcylinder placed upside-down in a water-filled vessel.

Results

Figuers 1 and 2 show the amount of krypton decapsulated as a function of temperature. The total amount encapsulated, $V_{tot.}$, depended sharply upon the content of calcium in the zeolite as shown in Fig.

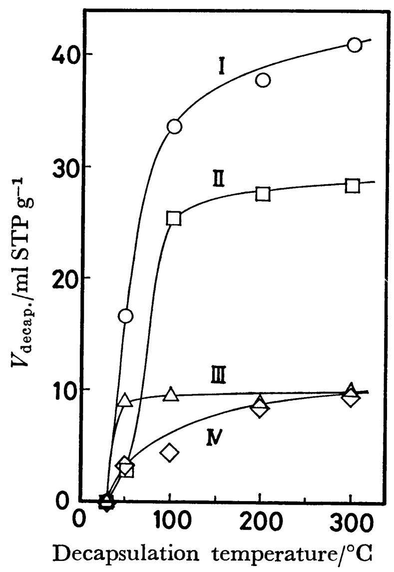

Fig. 1. Amount of Kr decapsulated as a function of temperature.
Curve I: $(K_{6.76}Ca_{2.62})$-A, Curve II: $(K_{7.84}Ca_{2.08})$-A, Curve III: Na_{12}-A, Curve IV: $(K_{5.81}Na_{6.19})$-A. Conditions of encapsulation: 300 °C, 3.7×10^6 Pa.

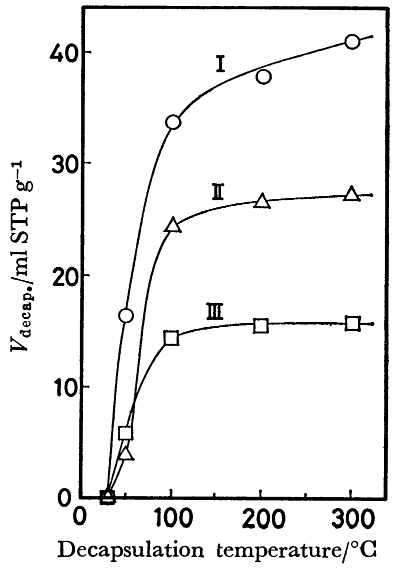

Fig. 2. Effect of encapsulation condition to the amount encapsulated with $(K_{6.76}Ca_{2.62})$-A.
Curve I: 300 °C, 3.7×10^6 Pa, Curve II: 150 °C 3.7×10^6 Pa, Curve III: 300 °C, 1.7×10^6 pa.

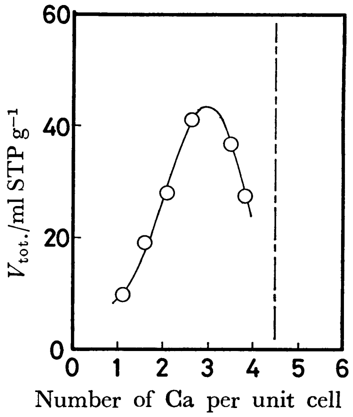

Fig. 3. Effect of calcium content to the total amount of encapsulation.

3. At a composition of 4.5 Ca per unit cell (represented by a chain line), the completely unblocked, say, open window starts to manifest itself.[7] Since krypton can freely pass through such an open window, V_{tot} should drastically decrease over this critical content. Experimentally, however, the value of $V_{tot.}$, starts to decrease when calcium content exceeds 3 per unit cell. To realize a maximum encapsulation, the content of calcium must be considerably smaller than 4.5 per unit cell.

Other bivalent cations, such as Co^{2+}, Mn^{2+}, and Zn^{2+}, have the effect as Ca^{2+}. Results are shown in Fig. 4.

Discussion

The diameter of krypton is slightly larger than that of the aperture in the K^+-blocked window. In order that a visiting krypton atom is sorbed into the large cavity, the blocking K^+ must be pushed aside to make

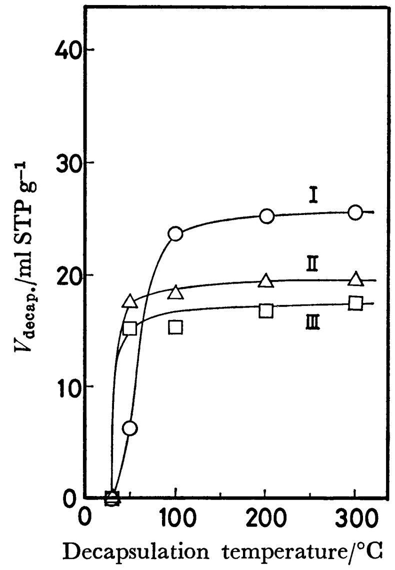

Fig. 4. Encapsulation with various kinds of (K, M^{II})-A zeolites.
Curve I: $(K_{7.08}Co_{2.46})$-A, Curve II: $(K_{6.52}Mn_{2.74})$-A, Curve III: $(K_{5.58}Zn_{3.21})$-A. Conditions of encapsulation: 300 °C, 3.7×10^6 Pa.

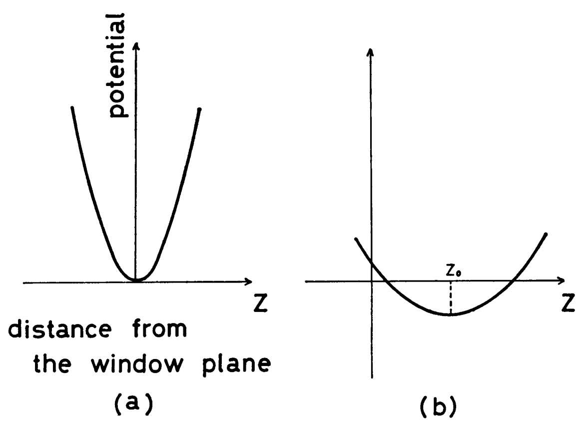

Fig. 5. Potential experienced by the window-blocking K^+.
(a) Potential in K_{12}-A zeolite. (b) Potential in (K,M^{II})-A zeolite.

a way for the visitor. In other words, an activation energy is required in krypton sorption. The magnitude of the activation energy is primarily determined by the potential experienced by the blocking K^+. The activation energy is large if the radius of curvature is small in the valley of the potential surface, while small if the radius is large. With this in view, we schematically represent the concerned potential forms for K_{12}-A and (K,M^{II})-A zeolites in Fig. 5. The abscissa, z, denotes the distance from the window plane, and z_0 the position of the potential valley in (K,M^{II})-A. A permanent widening of the aperture results from a large value of z_0, while a temperature dependent one does from an increase in the radius of curvature. Such an aperture widening, due to bivalent cations, is named as an ion-loosening effect. The ion-loosening may increase with the increasing content of M^{II}.[8] Thus, krypton can easily pass through K^+-blocked windows if the content of M^{II} exceeds 4 per unit cell, as shown in Fig. 3.

In the last place, let us discuss a problem of the storage of ^{85}Kr which is released in the reprocessing of nuclear fuel. The container tank must be air-tight and have a thick wall. (K,M^{II})-A zeolite cannot be used for such a purpose, since the zeolite will be destroyed by radiations from ^{85}Kr.[††] However, it may be used as a transient storager. For instance, zeolites encapsulating ^{85}Kr are installed in an air-tight vessel of thin wall, and then vessel is concreted by cement before the zeolites are seriously damaged by the radiation. This packing process may considerably be economical than the usual direct containment with a thick vessel of corrosion-resistive metal.

[††] Penzhorn and his coworkers are trying to encapsulate permanently.[9] In their case, zeolite A is structurally changed, and the situation is very different from ours.

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