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The Molecular Sieving Action of Ion-exchanged Zeolites A

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K_{12}-A zeolite was ion-exchanged with Mg^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, or Pb^{2+}, and molecular sieving properties of the resultant zeolites were studied, mainly for PH_3 and SiH_4. (K, Mg)-A and (K, Mn)-A adsorbed PH_3 but not SiH_4, and hence are usable as a purifier for SiH_4. (K, Co)-A, (K, Cd)-A, and (K, Pb)-A decomposed both PH_3 and SiH_4, and are unsuitable as an adsorption purifier for SiH_4. By using adsorption columns containing (K, Mn)-A or (K, Mg)-A, breakthrough curves were obtained for PH_3 in SiH_4. The breakthroughs of (K, Zn)-A and (K, Ca)-A columns were also measured for comparison. The breakthrough point increased in the order of (K, Ca)-A<(K, Mg)-A<(K, Mn)-A<(K, Zn)-A. The mechanism of the molecular sieving is discussed. It is concluded that introduced bivalent cations increase the Debye-Waller factor of K^+ blocking the windows. A large Debye-Waller factor causes a decrease in the activation energy required for adsorbate molecule to pass through the blocked window.

Zeolite A is synthesized in its sodium form, $Na_{12}(AlO_2)_{12}(SiO_2)_{12}(NaAlO_2)_\delta \cdot nH_2O$ with $0 \leq \delta \leq 1$, whose twelve Na^+'s are easily ion-exchanged with univalent cation M^I or bivalent cation M^{II}, and $(AlO_2)_{12}(SiO_2)_{12}$ constitutes the zeolite framework. [$(AlO_2)_{12}(SiO_2)_{12}(NaAlO_2)_\delta \cdot nH_2O$ is generally abbreviated as -A.] A large cavity is located at the center of a cubic unit cell. There are three 8-membered oxygen rings per unit cell. The 8-ring is on each of the {100} faces of the unit cube, and constitutes a window to the cavity. In Na_{12}-A and K_{12}-A zeolites, all windows in them are blocked by Na^+ and K^+, respectively. Their molecular sieving properties, classified as 4A and 3A, respectively, are determined by the width of the aperture of the partially blocked window. In other words, the sieving character is directly controlled by the radius of the blocking cation.

Recently, Takaishi *et al.*[1] found another possible control mechanism. In (K,Zn)-A, the Debye-Waller factor of K^+ blocking the window is markedly influenced and increased by Zn^{2+} occupying sites other than window sites.[2] Such K^+ is easily pushed aside by a visiting adsorbate molecule, making way for the visitor.[1] PH_3 having a rather large molecular diameter is not adsorbed with Na_{12}-A, but is with $(K_{7.6}Zn_{2.2})$-A[1] in which the above mechanism operates. This result is of practical importance, being applied to the purification of SiH_4 which contains a small amount of PH_3.

In a subsequent section, the phenomenon of the indirect control is further discussed with respect to (K,Mg)-A, (K,Mn)-A, (K,Co)-A, (K,Cd)-A, and (K,Pb)-A. Their adsorption properties were measured for N_2, Ar, butane, 1-butene, *trans*-2-butene, *cis*-2-butene, PH_3 and SiH_4. The results are discussed from a practical point of view, for instance, which is the best adsorbent for the purification of SiH_4.

Experimental

Materials and Chemical Analysis. The starting material was Shōwa-Unox molecular sieve 4A powder (lot No. 490401). After the standard treatment of the sample, its composition was determined by the usual procedure.[3] The chemical formula was $Na_{11.8}H_{0.2}(AlO_2)_{12} \cdot (SiO_2)_{12}(NaAlO_2)_\delta$ with $0.2 \leq \delta \leq 0.3$. This differs from the stoichoimetric composition $Na_{12}(AlO_2)_{12}(SiO_2)_{12}$.[4,5] The deficiency of sodium may be ascribed to partial hydrolysis, though protons, which had replaced alkaline metal cations, were not analyzed. The value of δ was further examined by the following method. It has been established that $(NaAlO_2)_\delta$ molecule is contained in the β-cage (the sodalite unit) and its Na^+ cannot be exchanged with Ca^{2+}. After fully ion-exchanging Na^+ in the starting zeolite with Ca^{2+}, the residual amount of Na^+ in the resultant zeolite was determined, by activation analysis, to be 0.21 ions per unit cell ($\delta = 0.21$).

A fully ion-exchanged K_{12}-A was obtained by decanting the starting material repeatedly with 1 M KCl solutions, and washing it with distilled water. This zeolite contained 11.4 K^+ per unit cell. $(K_{12-2x}M_x^{II})$-A zeolites were prepared by treating K_{12}-A with solutions of a mixture of KCl and $M^{II}Cl_2$, of 0.2 total metal ion normality, at 80±2 °C. As for (K, Pb)-A, nitrate solution was used instead of chloride. In most cases, the composition of an ion-exchanged zeolite was calculated from that of the ion-exchanging solution and material balance. The composition of the ion-exchanging solution was determined by the titration with ethylenediaminetetraacetic acid. On the other hand, zeolites of high contents of Mg^{2+} and Mn^{2+} were obtained only after repeated treatment with pure solutions of $MgCl_2$ and $MnCl_2$, respectively. In these cases, the composition of the zeolites was directly analyzed by usual methods. Zeolites containing Mg^{2+} or Mn^{2+} in amount more than 5 ions per unit cell could not be prepared.

All chemical reagents used were S.P. grade, and common adsorbate gases contained in glass cylinders (supplied by the Takachiho Chemical Co.) had nominal purities better than 99.9% as determined by mass-spectroscopic analysis. Less common gases, such as SiH_4 and PH_3, were obtained from the Nihon Oxygen Co., and were of special high purities, *i.e.*, semiconductor grade.

Measurements of Adsorbed Amounts of Gases. Adsorption measurements were made with a McBain type quartz spring balance and electrobalance (Chan Instrument Co., Model No. RG2050). The former had a sensitivity of 0.5 m/g and an accuracy of ±0.5 mg. Prior to adsorption measurements, adsorbents were baked-out at 390 °C for 4 h under a vacuum better than 10^{-5} Torr.

Results

Amounts Adsorbed. *(K,Mg)-A Series*: Adsorptive capacities of (K,Mg)-A zeolite are shown in Fig. 1.

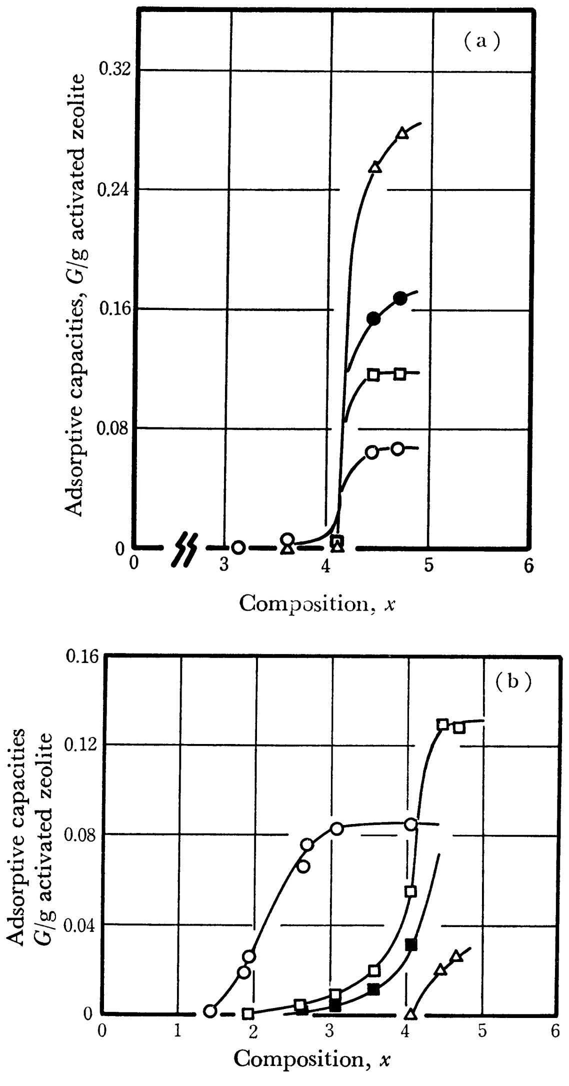

Fig. 1. (a) Adsorption of non-polar gases on (K_{12-2x}-Mg_x)-A zeolites. (△) argon, 150 Torr, −196 °C; (●) nitrogen, 130 Torr, −196 °C; (□) butane, 160 Torr, 0 °C; (○) SiH_4, 150 Torr, 0 °C.
(b) Adsorption of polar gas and unsaturated hydrocarbons on ($K_{12-2x}Mg_x$)-A zeolites. (○) PH_3, 95 Torr, 0 °C; (□) 1-butene, 160 Torr, 0 °C; (■) *trans*-2-butene, 160 Torr, 0 °C; (△) *cis*-2-butene, 160 Torr, 0 °C.

Curves in Fig. 1(a), which refer to non-polar gases, rise steeply at the same composition, for instance $x=4.1$. On the other hand, curves in Fig. 1(b), which refer to polar gas or unsaturated hydrocarbons, have gentle slopes.

(K,Mn)-A Series: Figures 2(a) and (b) show adsorption properties of (K,Mn)-A series for non-polar molecules, and for polar and unsaturated hydrocarbon molecules, respectively. Slopes of curves in Fig. 2(b) are more gentle than those in Fig. 1(b).

(K,Co)-A, (K,Cd)-A, and (K,Pb)-A Series: These were colored when either PH_3 or SiH_4 was introduced, and yielded a gas uncondensable with liquid nitrogen. The weight of the zeolite sample was irreversibly increased on contact with PH_3 or SiH_4, that is, it was not decreased outgassing at temperatures up to 350 °C. This means that PH_3 or SiH_4 was decomposed and hydrogen was produced. The higher the degree of ion-exchange, the higher the catalytic activity for the decomposition. These features are not suitable for a purifier, since the non-volatile residuals block the zeolite window and degrade the adsorption activity.

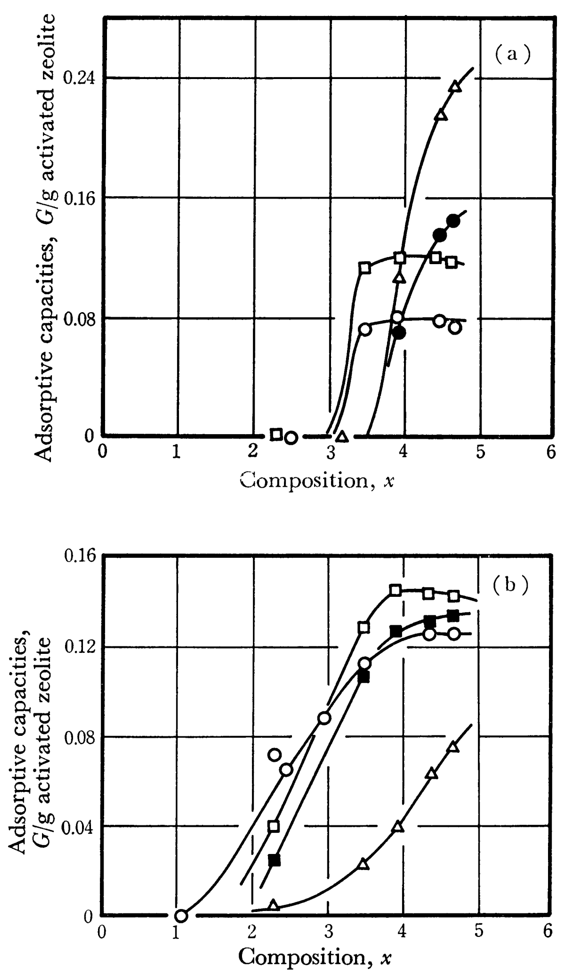

Fig. 2. (a) Adsorption of non-polar gases on (K_{12-2x}-Mn_x)-A zeolites. (△) argon, 150 Torr, −196 °C; (●) nitrogen, 130 Torr, −196 °C; (□) butane, 160 Torr, 0 °C; (○) SiH_4, 150 Torr, 0 °C.
(b) Adsorption of polar gas and unsaturated hydrocarbons on ($K_{12-2x}Mn_x$)-A zeolites. (○) PH_3, 95 Torr, 0 °C; (□) 1-butene, 160 Torr, 0 °C; (■) *trans*-2-butene, 160 Torr, 0 °C; (△) *cis*-2-butene, 160 Torr, 0 °C.

Dynamic Characteristics of the Adsorption Column. Another important property of the purifier, the dynamic property of adsorbent, was studied. Breakthrough curves of columns, containing (K,Mg)-A or (K,Mn)-A zeolite of promising compositions, were plotted for PH_3 contained in SiH_4 by the aid of gas-chromatographic techniques. The breakthroughs of (K,Zn)-A and (K,Ca)-A columns were also measured for comparison. A gas mixture of PH_3 and SiH_4 in 5.5: 10^4 volume ratio was passed through the column at a flow rate of 350 ml/min and 0 °C. Results are given in Fig. 3, which shows that the breakthrough point for (K,Zn)-A is longer than others.

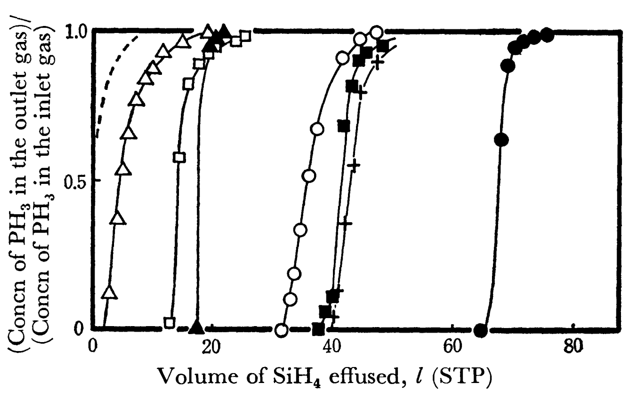

Fig. 3. Breakthrough curves of the adsorption column at 0 °C.
(---) $(K_{7.2}Ca_{2.4})$-A; (×) $(K_{4.8}Ca_{3.6})$-A; (△) $(K_{7.2}Mg_{2.4})$-A; (▲) $(K_{4.8}Mg_{3.6})$-A; (□) $(K_{7.4}Mn_{2.3})$-A; (■) $(K_{5.2}Mn_{3.4})$-A; (○) $(K_{7.4}Zn_{2.3})$-A; (■) $(K_{5.0}Zn_{3.5})$-A.

Discussion

As can be seen from Figs. 1 and 2, the curves for non-polar molecules have forms considerably different from those for polar and unsaturated. The latter two have gentle slopes and the former steep ones. This difference originates from the difference in the sieving mechanism. That is, non-polar molecules are adsorbed into zeolite A by passing through windows whose aperture width is larger than the molecular diameter. The width of the window aperture is simply determined by the ionic radius of a cation occupying the 8-ring site. The present authors have named this mechanism of the control of sieving action the direct control mechanism. In the adsorption of polar molecules, on the other hand, the following additional factor operates. The potential experienced by the ion on the 8-ring site is changed by ion-exchanges. If the change is such that the curvature of the potential surface is reduced and becomes fairly gentle, the amplitude of the oscillation of the ion, or its Debye-Waller factor, is increased. Then, the window-blocking action of the ion concerned becomes incomplete with increasing temperature. Hence, molecules having a diameter slightly larger than the width of the window aperture can be adsorbed, the rate of adsorption depending upon the incompleteness. The former phenomenon is confirmed by Takaishi *et al.*[6] in the systems of (Na,Ca)-A and (K,Ca)-A. This control mechanism of the sieving action has been named the indirect control mechanism. The above change in the potential form is induced by electrostatic forces due to cations, and hence is influenced further by the dipole or quadrupole of a visiting adsorbate. Consequently, the indirect control mechanism markedly operates on the adsorption of a polar molecule. Owing to this mechanism, zeolites having windows blocked by K^+, such as $(K_{12-2x}Mg_x)$-A with $1.5<x<3.5$ and $(K_{12-2y}Mn_y)$-A with $1.1<y<3.0$, can remove PH_3 contained in SiH_4, as well as (K,Zn)-A.[1,7] The degree of the indirect control is delicately affected by the ionicity and location of the bivalent cation, and is of the order of

$$Mn^{2+},\ Zn^{2+} > Mg^{2+},\ Ca^{2+}.^{8)}$$

Now, let us compare and discuss breakthrough points of (K,Mg)-A, (K,Mn)-A, (K,Zn)-A, and (K,Ca)-A having the similar content of bivalent cation, say about 2.3 cations per unit cell. In general, the breakthrough point is to be affected by two factors, the capacity and rate of adsorption. Experimental results are recapitulated as follows:
for the capacity

$$(Mn),\ (Mg) > (Zn) > (Ca),^{8)}$$

for the rate[7]

$$(Zn),\ (Mn) \gg (Mg) > (Ca),^{8)}$$

and for the breakthrough point

$$(Zn) > (Mn) > (Mg) > (Ca),$$

where symbols (Zn), (Mn), (Mg), and (Ca) designate zeolites containing the respective bivalent cations. The order of the breakthrough point is similar to that of the rate of adsorption. Thus, it may be said that the breakthrough point is mainly determined by the rate of adsorption in the present system. However, at composition 3.6 bivalent cations per unit cell, the breakthrough point of (Ca) is larger than that of (Mg). Hence, the point may also be affected by other factors, such as heat of adsorption for PH_3 and for SiH_4, though these values were not measured in the present work. (K,Zn)-A was concluded to be the best purifier among those studied.

Finally, let us discuss the role of the indirect control mechanism in a fine molecular sieving action for other gases. $(K_{12-2x}Mg_x)$-A with $2.4<x<4.0$ and $(K_{12-2y}Zn_y)$-A with $1.5<y<3.6$[1] can sieve 1-butene and *trans*-2-butene from *cis*-2-butene. If the shape of a butene molecule is roughly approximated by a prolate spheroid, the minor axis of *cis*-2-butene is larger than that of 1-butene or *trans*-2-butene. Then, *cis*-2-butene requires, to pass through the window, a larger displacement of the blocking K^+, or a larger activation energy. Thus, the fine separation of these isomers can be realized by the adsorption.

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