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Studies on the Catalytic Properties of Synthetic Zeolite A. V.[1]
Site Selectivity of Silver Ion in (Ag^{ex}, Ca^{ex})-A

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Synopsis. The X-ray diffraction pattern and the propane-adsorption capacity of (Ag^{ex}, Ca^{ex})-A zeolites were determined as a function of the degree of ion exchange. From the change in diffraction intensity and the molecular sieving effect, it was deduced that Ag^+ ion prefers site I to site II.

It is well-known that synthetic zeolites A replaced by various cations are very useful as catalyst and adsorbent. The physicochemical property of zeolite A has been investigated in detail by many workers, but many points concerning the cation positions and the exchange scheme remain unclarified. We reported that Ag^+ ions were introduced into Na-A in an order of exchanging cations differing from that known for K^+ ions,[2] though both cations have a similar ionic radius larger than Na^+ ion. In this paper the site selectivity of Ag^+ ion in the (Ag^{ex}, Ca^{ex})-A* system is discussed.

The unit cell composition of $Ca^{ex}_{1.00}$-A is denoted by Ca_6 ($12AlO_2$ $12SiO_2$) nH_2O (M_{12} instead of Ca_6 for the monovalent cation form). From X-ray crystallography[3] and sorption study[4,5] of (Ca^{ex}, Na)-A, it was shown that all the $6Ca^{2+}$ ions occupy positions near the centers of the six-oxygen rings (site I) corresponding to the (111) plane. Other positions occupied by monovalent cations are sites near the centers of the eight-oxygen rings (site II) corresponding to the (100) plane, and site near a four-oxygen ring (site III) corresponding to the (110) plane.[6] In the hydrated Na-A, there are $4Na^+$ ions in site II and $8Na^+$ ions in site I. No X-ray structural data for (Ag^{ex}, Ca^{ex})-A seem to have been published. A recent study[7] suggests that Ag^+ ions occupy similar positions to those of Na^+ and K^+ ions.

The scattering power of silver for X-ray is much greater than that of calcium. Thus, when $Ca^{ex}_{1.00}$-A is replaced by Ag^+ ions, the intensity change in the X-ray diffraction of the above planes of (Ag^{ex}, Ca^{ex})-A should indicate the sites replaced by Ag^+ ions. As is shown in Fig. 1, the peak intensity of the (111) plane of hydrated samples decreased sharply with an increase in the degree of exchange, and reduced to zero at *ca.* 60%, while the intensity of the (100) plane did not decrease until 40% and then decreased gradually. This suggests that Ag^+ ions first occupy site I ($\leqq 8/12 = 66\%$), and then site II ($\geqq 5/12 = 41\%$). That is, Ag^+ ion prefers site I to site II. This is supported by the results of molecular sieving properties of (Ag^{ex}, Ca^{ex})-A and (K^{ex}, Ca^{ex})-A as given in the following.

Figure 2 shows the adsorption isobars of propane on (Ag^{ex}, Ca^{ex})-A and (K^{ex}, Ca^{ex})-A as a function of the degree of exchange. Since site II of $Ca^{ex}_{1.00}$-A is vacant, propane is rapidly diffused into the zeolite cavity and is adsorbed. In the case of K^+-exchange, propane was excluded by a $K^{ex}_{0.41}$, $Ca^{ex}_{0.59}$-A ($=5/12$). As is well known,[4] this is due to the siting of the initial K^+ ions into site II, which diminishes the apparent pore size. Takaishi *et al.*[5] have also confirmed from molecular sieving effects of (Ca^{ex}, K)-A with various adsorbates that K^+ ion prefers site II to site I. On the other hand, the replacement by Ag^+ ions permitted propane-sorption up to 70% ($\approx 8/12$) exchange, and then suddenly interfered with the sorption to *ca.* one fifth. This clearly indicates that the filling-up of site II by Ag^+ ions is completed after site I is completely filled

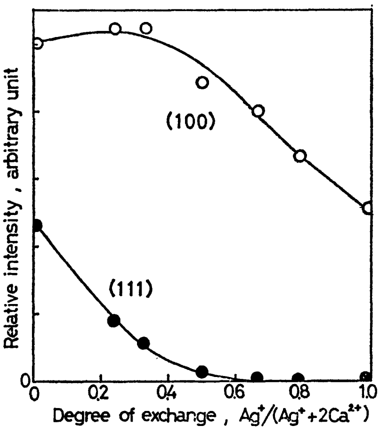

Fig. 1. Relationship between X-ray powder diffraction intensity and the degree of ion exchange.

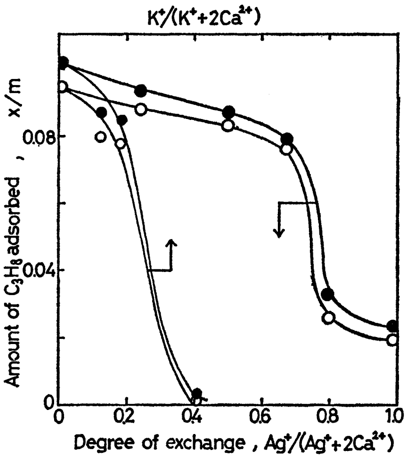

Fig. 2. Effects of silver and potassium exchanges for calcium on the sieving property.
○: 100 Torr, ●: 250 Torr, *x/m*: amount adsorbed in grams per gram of adsorbent.

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* The nomenclature of cation-exchanged zeolite A obeyed Barrer's rule.[1] Superscript ex of M^{ex} indicates that M^{n+} ion was indroduced by ion-exchange.

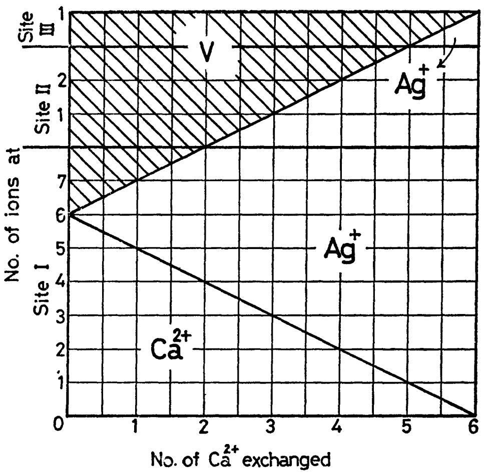

Fig. 3. Distribution of cations in (Ag^{ex}, Ca^{ex})-A. V: Vacancies.

with $8Ag^+$ ions. That is to say, Ag^+ ion prefers site I to site II, in contrast with K^+ ion. This can be well interpreted by X-ray observation, and is consistent with the result of the (Ag^{ex}, Na)-A system.[2] The incomplete hindrance of $Ag^{ex}_{0.70-1.00}Ca^{ex}_{0.30-0}$-A for propane-sorption is due to the small ionic radius of Ag^+ (1.26 Å) compared to K^+ (1.33 Å).

From these results, the following diagram can be given to the dehydrated (Ag^{ex}, Ca^{ex})-A (Fig. 3). Such a diagram may be used as a guide line to future structural studies, and the true locations of Ag^+ ions should be determined only by X-ray structural analysis.

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Experimental

$Ca^{ex}_{1.00}$-A was prepared first from the original sodium-form zeolite A (Na-A) (Linde Molecular Sieve 4A powder). (Ag^{ex}, Ca^{ex})-A and (K^{ex}, Ca^{ex})-A were then prepared. The ion-exchange was carried out at 85±1 °C for 10 hr as already described.[1] Precaution was taken to shield the sample from light during ion-exchange and operations. The crystallinity of the samples was confirmed from the specific surface area to be unchanged by ion-exchange.

The X-ray powder diffraction pattern of the hydrated sample was obtained on a scintillation counter spectrometer using filtered Cu K_α radiation. The samples were exposed to air at room temperature while their spectra were measured.

The propane-adsorption was measured volumetrically at 0 °C on the sample activated at 250 °C in a vacuum at 10^{-3} Torr. Commercial propane (purity$>$99.5%) was subjected to two freeze-pump-thaw cycles before use.

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