Ion Exchange Scheme for Silver Exchange for Sodium in the Synthetic Zeolite Linde 4A

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For the Ag^+ ion-exchanged form of the synthetic zeolite Linde 4A a logical correlation has been found between the X-ray diffraction patterns and the sorptive property; this implies that the Ag^+ ion probably has a site selectivity different from that known for the K^+ ion.

It is well known that the catalytic and the sorptive properties of zeolites are markedly affected by the particular cation present, which is required to balance the negative framework charge. It was found previously that the Ag^+ ion-exchanged form (AgA) of the synthetic zeolite type A differs from other ion-exchanged forms, especially in the stability and the catalysis (*1, 2*). Hence, knowledge of the ion exchange in zeolite is important in understanding zeolitic properties. In this paper, it was attempted to gain information on the order of exchanging (i.e., site selectivity of cation) indirectly by investigating the effects on the X-ray diffraction patterns and the adsorptive characteristics of the AgA.

The unit cell composition of the Linde 4A (NaA) is $Na_{12}(12\ AlO_2\ 12\ SiO_2)$ $(NaAlO_2)_\delta \cdot nH_2O$ $(0 \leqq \delta \leqq 1)$. The sodium of $(NaAlO_2)$ has been known to have no effect upon the sorptive and the catalytic properties of the zeolite (*3, 4*). We shall therefore deal with only the 12 Na^+ ions for discussion purposes. X-ray crystallography of the NaA has shown that the Na^+ ions are distributed among three equipoints in the structure (*5*): Eight Na^+ ions occupy positions near the centers of the six-oxygen rings corresponding to (**111**) plane; three Na^+ ions lie near the centers

of the eight-oxygen rings corresponding to (**100**) plane, and the twelfth Na^+ ion is found near a four-oxygen ring corresponding to (**110**) plane. The last site appears to be the least favorable energetically and to be exchanged first with any other cation. A recent investigation (*6*) demonstrated that the Ag^+ ions probably occupy similar positions in the crystal structure to those determined for the Na^+ ions. Since the silver ion is expected to have greater influence on the intensity of diffraction peak because of having probably the high absorption coefficient for X-ray as compared with that of the sodium, the observed intensity changes of the above planes are an approximate measure of the sites replaced.

X-ray patterns of hydrated (Na-Ag)A were compared. As is shown in Fig. 1, the peak height of (**100**) plane is almost constant up to ca. 80% of the degree of ion exchange and then decreases sharply, whereas those of (**110**) and (**111**) planes decrease gradually accompanying the exchange and become constant (≈ 0) at ca. 80% or more. This clearly demonstrates that the Ag^+ ions first replace the Na^+ ions at the four- and the six-oxygen ring sites ($\leqq 9/12 = 75\%$), and next the Na^+ ions at the eight-oxygen ring sites ($>75\%$). That is, the Ag^+ ion prefers the six-oxygen ring site to the eight-oxygen ring site. This site selec-
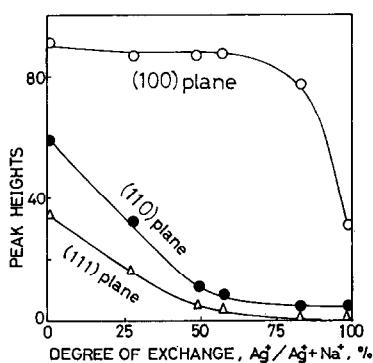
FIG. 1. X-ray diffraction peak heights of (100), (110), and (111) planes of hydrated AgA as a function of the degree of ion exchange.

tivity is contrary to that for the K^+ ion which has been made clear from the study by Breck et al. (7). This is further supported by the fact that the sorptive property is basically unlike that of the KA.

The apparent pore size in type A zeolites is altered by ion exchange. The effective pore size which is defined by critical dimension of adsorbed molecule is regarded as the size of the eight-oxygen ring, since adsorbate molecules pass through the eight-oxygen rings and are adsorbed on the internal surface of zeolite. The ions occupying the eight-oxygen ring sites, therefore, reduce the effective pore size if the ionic radius is larger than that of the Na^+. Fig-

ure 2 shows the adsorption isobars of ethane on the AgA as a function of the degree of ion exchange. That of the KA obtained by Breck is shown in the same figure. Breck et al. (7) have shown that the replacement of the Na^+ ions (ionic radius: 0.98 Å) by larger K^+ ions (1.33 Å) reduces the pore size and this reduction occurs gradually with increasing extent of exchange, and ethane is excluded by a 30% (=4/12) KA. Replacement by the Ag^+ ions (1.13 Å) does not reduce ethane sorption up to ca. 80% exchange; however, complete silver exchange (99.5%) reduces the amount sorbed to about one-half. The incomplete exclusion of ethane is due to the fact that the ionic radius of silver is slightly smaller than that of potassium. This result indicates that the 10th, the 11th, and the 12th Ag^+ ions ($\geq$83%) occupied the eight-oxygen ring sites, and this is consistent with the result in Fig. 1. Consequently, the scheme of ion exchange might be pictured as shown in Fig. 3.

EXPERIMENTAL

The original NaA zeolite was the Linde Molecular Sieves 4A powder (surface area: 659 m²/g). The silver nitrate used for ion exchange was of a guaranteed grade. The ion exchange was carried out at 85 ± 1°C
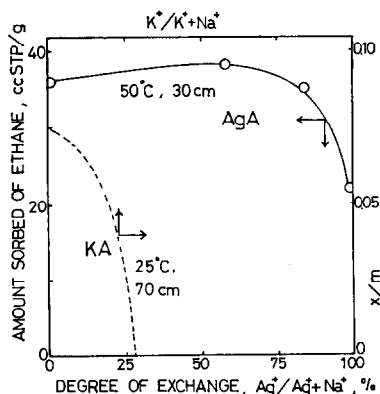

FIG. 2. Isobaric adsorptions of ethane on AgA and KA as a function of the degree of ion exchange. The data of KA (dotted line) are quoted from Ref. 7.
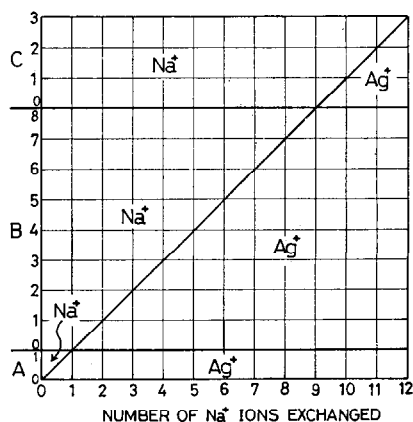

FIG. 3. A diagram of silver exchange for sodium in Linde 4A. A: Number of ions at the four-oxygen ring site. B: Number of ions at the six-oxygen ring sites. C: Number of ions at the eight-oxygen ring sites.

for 5 hr in a thermostat. Details of the procedure and the analysis of the degree of ion exchange were described elsewhere (2). The sample exchanged was stored over a saturated ammonium chloride solution to ensure a constant of zeolitic water. Exchange with silver ion to the extent of 99.5% did not destroy the crystal structure, since their surface area were almost the same as that of the NaA.

X-ray powder diffraction patterns of hydrated samples were obtained on a scintillation counter spectrometer using copper K_α radiation (Ni filter). The zeolite samples were exposed to air while their spectra were measured.

The adsorption isobars of ethane at 50°C were measured volumetrically on the sample which had been activated by removing the zeolitic water at 250°C in a vacuum of 10^{-3} mm. Commercial ethane was stated to have a purity in excess of 99.5%, and it was subjected to two freeze–pump–thaw cycles before use.

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