Site Selectivity of Cations in Zeolite by *X*-Ray Diffraction and Adsorption Studies

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Summary For the Ag^+-exchanged form of the synthetic zeolite Linde 4A interesting changes have been found in the diffraction peak intensities of some of the planes and in the adsorbed amount of ethane; this fact implies that Ag^+ probably has a site selectivity different from that known for K^+.

It is well known that the catalytic and adsorptive properties of zeolites are markedly affected by the particular cation present. We have studied the order of exchanging cations (*i.e.*, site selectivity of cation) indirectly by investigating the effect on the diffraction pattens and ethane adsorption of the Ag^+-exchanged form of Linde 4A.

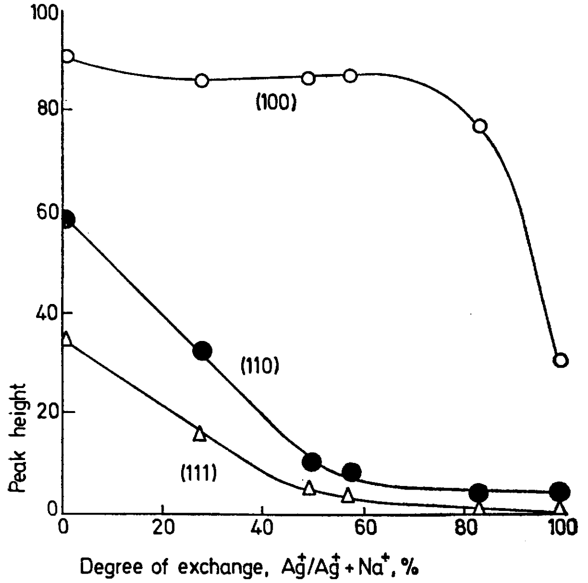

Figure 1. Effect of Ag^+ exchange for Na^+ on the *X*-ray diffraction patterns of Zeolite type A; Cu-K_α; 30 kV; 10mA.

Recent investigations demonstrated that the Ag^+ ions occupy similar sites in the crystal structure of Linde A to that determined for Na^+ and K^+ by *X*-ray crystallography,[1,2] According to Seff *et al.*,[2] eight of the twelve exchangeable Na^+ ions of Linde 4A are located near the centres of the six-oxygen rings corresponding to the (111) plane, three Na^+ ions lie near the centres of the eight-oxygen rings, (100) plane, and the twelfth Na^+ ion is statistically distributed near a four-oxygen ring, (110) plane. Since Ag^+ is heavier than Na^+, the different scattering powers would be expected to have a large influence on the reflections from the (111), (100), and (110) planes.

X-Ray powder diffraction patterns of hydrated AgA were measured. As shown in Figure 1, the peak intensity of the (100) plane is almost constant up to 80% exchange, and then decreases suddenly, whereas those of the (110) and (111) planes decrease gradually with the exchange and become constant (*ca.* 0) at >70%. This suggests that the Ag^+ ions first replace Na^+ ions at the four- and the six-oxygen ring sites ($\sim 9/12 = 75\%$), and then Na^+ ions at the eight-oxygen ring sites (>75%).

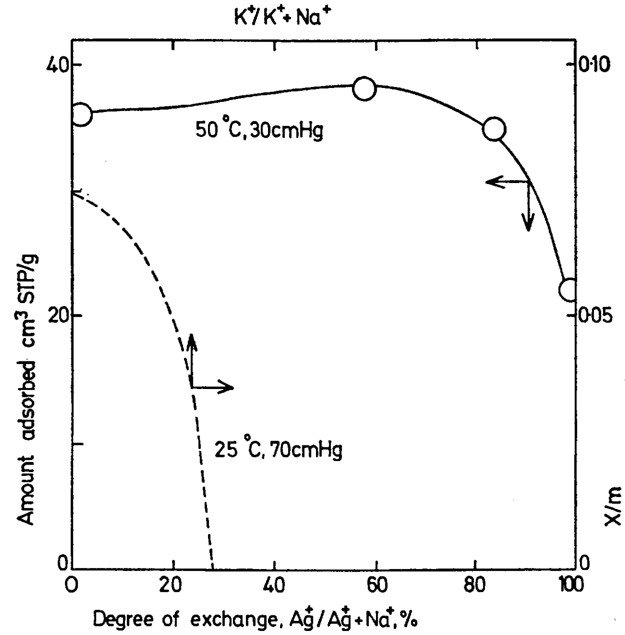

Figure 2. Effect of Ag^+ exchange for Na^+ on ethane adsorption characteristics of Zeolite type A. The dotted line is from the data for K^+ exchange from ref. 3.

Adsorption studies by Breck *et al.*[3] show in contrast that K^+ ions replace Na^+ first from the eight- and the four-oxygen ring sites. Reduction of the effective pore size of 4A, therefore, occurs immediately with increasing K^+ exchange and ethane is not adsorbed when 30% (4/12) or more exchange has occurred. However, our adsorption isobar on AgA (Figure 2) shows that only with > *ca.* 80% exchange does the amount of ethane adsorbed decrease, finally to a half. This decrease might be understood on the basis of the above tentative site selectivity; that is, the Ag^+ (1·13 Å) ions occupy eight-oxygen ring sites at >75% exchange, making the effective pore size smaller, and hindering adsorption of ethane, though not as completely as with KA because of the small ionic radius compared to K^+ (1·33 Å).

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