Evidence for the Site Selectivity of Silver in Zeolite A

By MASAHIRO NITTA,* KIYOSHI OGAWA, and KAZUO AOMURA
(*Faculty of Engineering, Hokkaido University, Sapporo, Japan* 060)

Summary Although their monovalent cations are of similar size, the Ag^+- and K^+-exchanged forms of Ca^{ex}-A show a different molecular sieve action; thus Ag^+ has a site selectivity different from K^+.

IN a previous report,[1] we have suggested that, in (Ag^{ex}, Na)-A, Ag^+ preferentially occupies the six oxygen ring sites (β-sites) in the zeolite A crystal structure, in contrast with the site selectivity of K^+ determined by Breck.[2] However, it was unclear whether this site selectivity of Ag^+ occurs in any other cation systems, that of K^+ having already been confirmed in other cation systems.[3] We now report further evidence for the site selectivity of Ag^+ in (Ag^{ex}, Ca^{ex})-A.

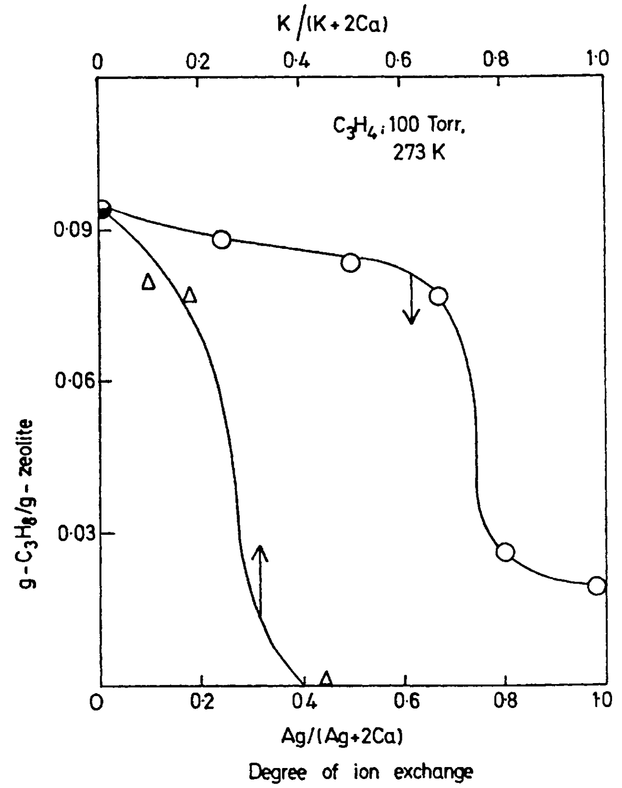

FIGURE. Effects of Ag^+ and K^+ exchange for Ca^{2+} on propane adsorption of zeolite A.

$Ca^{ex}_{1\cdot00}$-A was prepared from Linde 4A, and then (Ag^{ex}, Ca^{ex})-A and (K^{ex}, Ca^{ex})-A were obtained. All of them had good crystallinity. The apparent pore size of $Ca^{ex}_{1\cdot00}$-A is about 4·3 Å, which indicates a large window (eight oxygen ring) aperture, and it is decreased when the cation occupies the eight oxygen ring sites (α-sites); 4·0 Å for Na-A, 3·3 Å for K-A. This is responsible for the molecular sieve action.

The isobaric adsorptions of propane on (Ag^{ex}, Ca^{ex})-A and (K^{ex}, Ca^{ex})-A as a function of the degree of exchange are shown in the figure. When K^+ (of large ionic radius) occupies the α-sites, propane (kinetic diameter 4·3 Å) is not adsorbed. K^+ first enters 33% of the α-sites and then enters the other sites. With (K^{ex}, Ca^{ex})-A, a similar-shaped adsorption curve has been observed for n-butane adsorption by Takaishi.[3] On the other hand, for (Ag^{ex}, Ca^{ex})-A, propane adsorption drops suddenly after 75%. This indicates that the Ag^+ first enters into β-sites and then other sites which are independent of the window aperture, and last into the α-sites. An incomplete drop on the curve of (Ag^{ex}, Ca^{ex})-A is probably due to the slight difference in ionic size between Ag^+ (ionic radius, 1·26 Å) and K^+ (1·33 Å); *i.e.*, a small residual adsorption on $Ag^{ex}_{0\cdot99}Ca^{ex}_{0\cdot01}$-A occurs as a result of incomplete closure of the window.

The site selectivity of Ag^+ was confirmed by a conventional *X*-ray study of hydrated (Ag^{ex}, Ca^{ex})-A according to the method previously described.[1]

We propose that site selectivity of the exchangeable cation is determined by the ionic size. For example, it is suggested that Ba^{2+} (1·35 Å), larger than Ag^+, was first introduced into α-sites in zeolite A,[4] in contrast to Ca^{2+} (0·99 Å) occupying β-sites from the beginning of exchange.[2,3]

(*Received*, 16*th September* 1974; *Com.* 1171.)

---

[1] M. Nitta, S. Matsumoto, and K. Aomura, *J.C.S. Chem. Comm.*, 1974, 552.

[2] D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed, and T. L. Thomas, *J. Amer. Chem. Soc.*, 1956, **78**, 5963.

[3] T. Takaishi, Y. Yatsurugi, A. Usa, and T. Kuratomi, *J.C.S. Faraday I*, in the press.

[4] A. Dyer, W. Z. Celler, and M. Shute, Advances in Chemistry Series, 101, 436.