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Aluminum Distribution in Four-Rings and Six-Rings of the Faujasite Lattice

We have previously summarized (*1*) a computer procedure for randomly siting aluminum ions in the faujasite lattice. Dempsey (*2*), working with the concept of an ordered siting of the aluminum ions, had suggested that electrostatic interaction between aluminum ions (opposed across the diagonals of the four-rings of tetrahedral sites) determined the acidity of the associated protons. Our random siting procedure focused on the definition of four types of lattice aluminum ions. Each type was distinguished by the number (0, 1, 2, or 3) of other aluminum ions opposed across the diagonals of three adjoining four-rings and hence, also by the degree of acidity of the associated protons present in the hydrogen form of the zeolite. Prominent results were an experimentally confirmed distribution of the type-ions as a function of total aluminum content and a kinetic model for dealumination based on the concepts of the random structure.

The four-rings and six-rings of tetrahedral sites have been used to define the various cationic sites (*3*). However, the relative energetics and ultimate occupancy of these sites certainly depends, in some degree, on the number of lattice aluminum ions contained in the defining rings. Our procedure of siting aluminum ions in the lattice and examining the occupancy of neighboring lattice sites, fixes the distribution of aluminum ions in these rings for the random model and may contribute to the understanding of how the anionic lattice accommodates its cations.

Four-ring distribution. The four-rings (144 per unit cell) exist in three types, i.e., those containing 0, 1, or 2 aluminum ions; the upper limit is imposed by Loewenstein's Rule (*4*). Randomness of the aluminum siting erases any distinction between those 96 four-rings contained in the hexagonal prisms and those 48 rings which are the loci of the cationic Sites-III (*3*).

The four-ring distribution can be obtained in either of two ways: (a) by a direct computer count subsequent to the random-siting of aluminum ions, and (b) by a derivation from the aluminum type-ion distribution.

The solid lines of Fig. 1 represent the distribution of type four-rings by the direct computer count. The dashed portions are extrapolations beyond the point at which the efficiency of the random-siting procedure becomes too low to be practicable. These extrapolations are consistent with a limiting slope; at aluminum contents of 0 and 96, the placement or removal of one aluminum ion destroys three type-0 or type-2 rings, respectively (and creates three type-1 rings in both cases).

The "data" points of Fig. 1 result from calculation of the number of type four-rings from the distribution of type aluminum ions. The four types of aluminum

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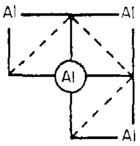
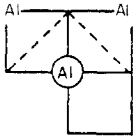
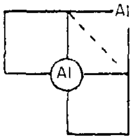
ions may be diagrammed as follows:



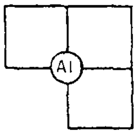
Type-3 ion



Type-2 ion



Type-1 ion



Type-0 ion

From these diagrams we may conclude that every type-3 ion accounts for $\frac{3}{2}$ of a type-2 ring; every type-2 ion, for $\frac{2}{2}$ of a type-2 ring and 1 type-1 ring; every type-1 ion, for $\frac{1}{2}$ of a type-2 ring and 2 type-1 rings; and every type-0 ion, for 3 type-1 rings. If n_i and r_j are the number of type-i aluminum ions and type-j four-rings per unit cell, respectively, this accounting leads to

$$\begin{aligned} r_2 &= \tfrac{3}{2}n_3 + \tfrac{2}{2}n_2 + \tfrac{1}{2}n_1, \\ r_1 &= n_2 + 2n_1 + 3n_0, \qquad (1) \\ r_0 &= 144 - r_1 - r_2. \end{aligned}$$

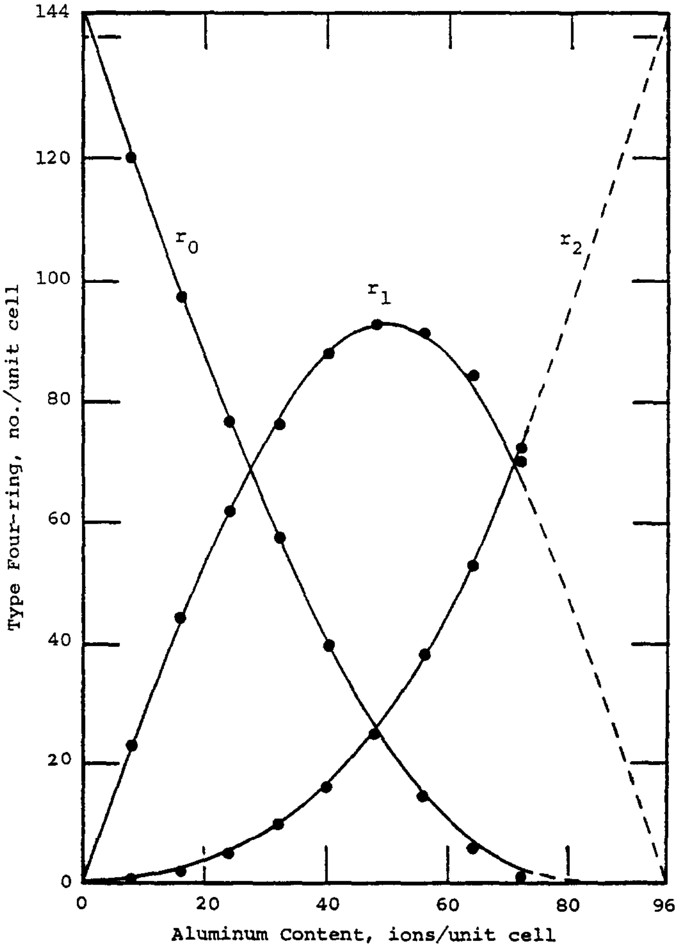


Fig. 1. Four-ring distribution.

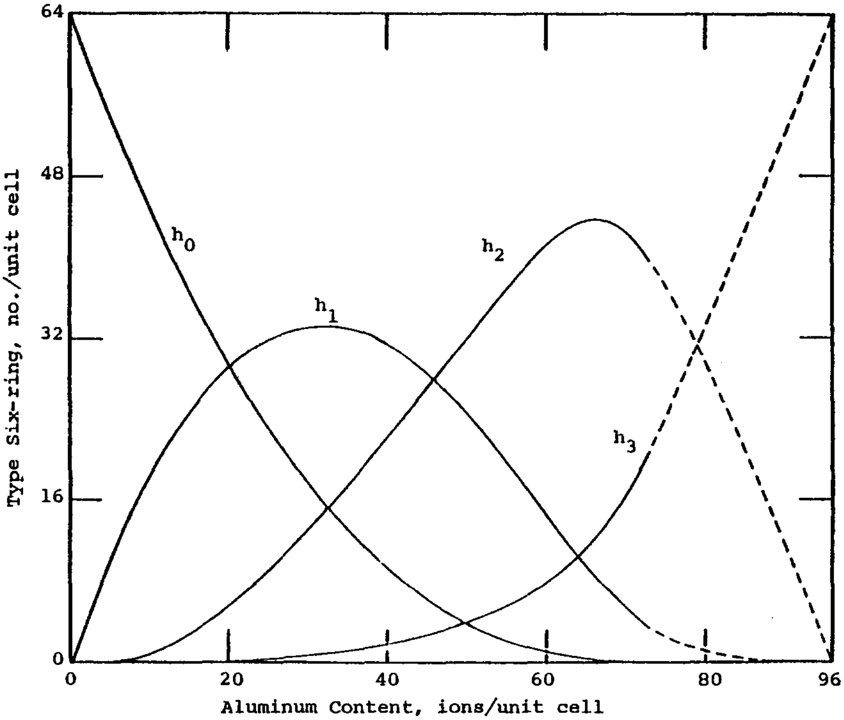


FIG. 2. Six-ring distribution.

The last equation is necessarily obtained by difference due to the procedure of only examining aluminum-filled tetrahedral sites. Values for the n_i previously obtained (*1*) for the random-siting can lead directly to the points plotted in the figure.

This counting procedure makes no assumption regarding the randomness or ordering of the aluminum ions and therefore would have general validity. Furthermore, three equivalent equations can be obtained from Eqs. (1) which are a function *only* of the total aluminum content:

$$r_2 - r_0 = 3N - 144,$$

$$2r_2 + r_1 = 3N,$$

$$2r_0 + r_1 = 288 - 3N,$$

where $N = \sum n_i$. Only two of these equations are independent; therefore, they do not fix the absolute number of type-rings. Interestingly, 48 aluminum ions placed in the unit cell will *always* create equal numbers of type-0 and type-2 rings ($r_2 - r_0 = 0$); this is consistent with the computer-derived curves of Fig. 1.

Site-III four-rings do not represent an energetically favorable placement for cations. Sodium ions have been found in sites-III of dehydrated NaX (*5*), however, the occupancy is low and many of the cations have not been located. There are no site-III cations in dehydrated NaY (5). Although we may not be able to experimentally test these distributions of four-rings at present, the situation is not quite so bleak when we come to the six-ring distribution.

Six-ring distribution. Every tetrahedral site is in two six-rings; one ring contained in a hexagonal prism and one forming the face of a sodalite cage and forming a possible cationic site (Site II). There are thus 64 six-rings per unit cell, and they may exist as four types, namely, those containing 0, 1, 2, or 3 lattice aluminum ions. The computer count, after the random siting of the aluminum ions, gives the distribution of these four types as a function of total aluminum content. The solid lines of Fig. 2 represent this count, and again, the dashed lines are extrapolations beyond the point where the random siting becomes inefficient. These extrapolations are also subject to limiting slopes (±2) due to every tetrahedral site in the structure being in two six-rings. Randomness of siting was confirmed in that the distribution of the 32 six-rings constitutive of the prisms and that of the 32 rings forming cationic Sites-II were the same.

Klyachko (*6*) has concerned himself with calculating these distributions a priori, based upon a few different arguments and methods. In general, his calculations approximate our computer results with the biggest discrepancy being in the number of type-2 rings. However, his statement that, "the unit cell can be constructed from 32 independent six-membered rings" is incorrect in that the composition of the individual rings *does* constrain the ways in which they can be joined. We believe this must create reservations about his a priori basis.

Olson's work (*7*) with hydrated faujasites gives evidence that Site-II six-rings must contain three aluminum ions before cation siting becomes energetically favorable. Thus he finds 24 Site-II cations in a NaX of 88 framework aluminum ions per unit cell and explains this observation by the presence of 24 type-3 rings, 8 type-2 rings, and no type-1 or type-0 rings. The curves of Fig. 2, if the ordinate scale is halved to apply only to the 32 Site-II six-rings, confirm his insight. Similarly, he detects no Site-II cations in either a calcium or lanthanum faujasite with 58 lattice aluminum ions per unit cell and thereby predicts there should be no type-3 six-rings; the distribution of Figure 2 corresponds to only 3.4.

Other data to test the results of this aspect of the random-siting procedure are sparse. Furthermore, more work is needed on the relative energetics of cation siting, as, for example, that of Dempsey (*8*). We hope, however, that the present results can contribute to the overall problem of cation siting within the lattice.

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