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LETTER TO THE EDITORS

Randomness and Order of Aluminum Siting in the Faujasite Lattice

We would like to emphasize a few points concerning the siting of aluminum ions in the faujasite lattice, in response to Dempsey's most recent communication (*1*). We also would like to place the concepts of a random structure and an ordered structure into the overall context of trying to understand the nature of the zeolite crystal and its dealuminization.

The seminal idea of our approach (*2*) is the suggestion (*3*) that electrostatic interaction between aluminum ions, mutually opposed across the diagonals of the lattice four-rings, is the major determining factor for the acidity of the associated protons. Because any given aluminum ion is in three adjoining four-rings we *must* distinguish four types, namely those with 0, 1, 2, or 3 diagonal aluminum neighbors. Thus, in principle, we have four degrees of acid strength of the cationic protons. This situation obtains *regardless* of the randomness or ordering of the aluminum ions. In fact, particular distributions of these type-ions may ultimately prove useful in helping to define a degree of order or disorder.

At this point we stress the observation that the distribution of type-ions determined by a computerized random-siting procedure is quantitatively consistent with thermogravimetric deammoniation of the ammonium form of the zeolite (*2*). Obviously, it is of great importance to determine the type-ion distributions for ordered structures and examine their possible correlation with thermogravimetric data—a simple matter once the indexing of the structure is accomplished.

Our siting procedure for determining the type-ion distribution has been mildly criticized by Dempsey for not including "end effects." However, we had met this criticism. Our repeating unit of the lattice was four hexagonal prisms (48 tetrahedral sites, one-quarter unit cell) tetrahedrally arranged to form a sodalite unit. On each prism another sodalite unit and its three defining prisms were constructed and indexed. Random siting of aluminum was first performed onto these (4 × 36) external sites before siting was performed in the basic unit. Our statistics were based on up to 500–560 siting cases at each aluminum content.

For modeling the rate of removal of lattice aluminum, our basic assumption obligates us to continue to distinguish four types of ions—it has been previously noted that "weak-acid" aluminum ions are removed preferentially over the "strong-acid" type (*4*). If the rate of removal of the type-i ion is characterized by a first-order rate constant k_i and the relative concentrations of the type ions are used as guides to the number and types of neighboring combinations, we may write

$$\frac{dn_0}{dN} = \frac{k_0 n_0}{\Sigma k_i n_i} - n_1 F,$$

$$\frac{dn_1}{dN} = \frac{k_1 n_1}{\Sigma k_i n_i} + (n_1 - n_2)F,$$

$$\frac{dn_2}{dN} = \frac{k_2 n_2}{\Sigma k_i n_i} + (n_2 - n_3)F,$$

and

$$\frac{dn_3}{dN} = \frac{k_3 n_3}{\Sigma k_i n_i} + n_3 F.$$

In these equations, the n_i are the concentrations of type-i aluminum ions, N is the total aluminum content (Σn_i),

$$F = \frac{(k_1 n_1 + 2k_2 n_2 + 3k_3 n_3)}{(\Sigma k_i n_i)(n_1 + n_2 + n_3)},$$

and the summations are to be performed over the four types of sites ($i = 0$ to $i = 3$).

The relative values of the k_i and an initial distribution of the type ions are necessary for the numerical integration of these equations. Moreover, their generality permits the type-ion distribution to be obtained from either the random-siting model or the ordered structures as defined by Dempsey.

In light of the foregoing, any dealuminization sequence (*1*) must be consistent with the accepted relationship between acidity and ease of aluminum removal and should reflect the statistical nature of simultaneous first-order rate equations. The individual "possible sequences" of Dempsey do not meet these requirements, although we may conceive our rate-equation solutions as being equivalent to weighted averages of all possible sequences.

Dempsey has been trying to rationalize the existence of "strong" and "weak" acid sites as manifested in the experiments of Beaumont and Barthomeuf (*5*). We need only point out that although we are conceptually committed to four types of sites, catalytic or acid-titration experiments may distinguish a lesser number which we must obtain by appropriate "lumping." We had tried to simplify the exposition in our previous note (*2*) by labeling type-0 sites as "strong acid forming" and types 1, 2 and 3 as "weak acid forming." The dealuminization equations listed in that note were derived from those above by setting $k_1 = k_2 = k_3 = 1$ and $0 \leqslant k_0 \leqslant 1$. Simplifications of this type, at this stage, depend greatly on the data available but these simplifications must only be made after exploiting the underlying concepts, which we have tried to do in deriving the dealuminization equations.

Dempsey has also suggested that $(n_0 + n_1)$ be considered as the concentration of strong sites. This is a perfectly reasonable suggestion but developing the idea requires a complete reintegration of the dealuminization equations. His re-plotting of our data is invalid in that the concentration of type-1 ions was determined under the assumption that they were weak sites ($k_1 = 1$) in the dealuminization. Of course, we do have the option, if warranted, of "lumping" differently for the dealuminization than for the catalytic process.

Finally we would like to echo Dempsey's sentiments on the importance of further work on the kinetics of aluminum removal. The applicability of all the concepts discussed here rests upon such work as do correlations of the catalytic capabilities of these materials.

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