JOURNAL OF CATALYSIS 44, 170–173 (1976)

Random Aluminum-Ion Siting in the Faujasite Lattice

The recent continuing discussion on the behavior and character of acid faujasites (*1*, *2*) has involved a very suggestive concept, viz., that acidic behavior depends upon "the number of four-rings of tetrahedral sites containing two aluminum ions" (*2*). However, if we center our attention on the individual aluminum ions, instead of the four-rings, we may distinguish four types of ions. The concentrations of these type ions may be fixed after randomly siting aluminum ions in the lattice, and then may be used as a basis for modeling their *relative* rates of removal, i.e., dealuminization. Furthermore, the type ions appear to be experimentally differentiable.

Minimum approach and maximum electrostatic interaction can be achieved by lattice aluminum ions across the diagonals of the four-rings of tetrahedral sites. The ability of a sited aluminum ion to delocalize its associated protonic charge thus depends on the number of other aluminum ions diagonally opposed to it. Because every tetrahedral site is in three adjoining four-rings, we may, in principle, distinguish four types of aluminum ions, i.e., those having 0, 1, 2, or 3 diagonally opposed aluminum neighbors. By implication, then, we have four degrees of acid strength of the associated protons, but for simplicity, hydrogen ions associated with type-0 aluminum ions are to be identified as "strong" acid, and those associated with types 1, 2, and 3, as "weak" acid in keeping with the arguments of Dempsey (*2*).

By indexing a repeating unit of the faujasite lattice, and by using a random number generator, we have by computerization randomly sited aluminum ions in the lattice and determined the distribution of the above four types as a function of the aluminum content.

Figure 1 shows the concentrations of the type aluminum ions so determined. Attesting to the randomness of siting, the type aluminum ions, at any given aluminum content, were found to be binomially distributed about the probability of finding a diagonally opposed neighbor, i.e., one-third the average number of diagonally opposed aluminum ions. For present purposes, we observe that a Y-zeolite of 50 aluminum ions per unit cell is characterized by about 10 type-0, 23 type-1, 15 type-2, and 2 type-3 ions.

In a dealuminization process, the "weak-acid" aluminum ions (types 1, 2, and 3) are removed preferentially over the "strong acid" type-0 (*1b*). Also, the removal of any aluminum ion affects the "acid forming" quality of all its diagonal aluminum neighbors. By using the relative concentrations of type ions as the key to the number and type of neighboring combinations, and by assuming first-order kinetics, the following description may be derived:

$$\frac{dn_0}{dN} = \left[\frac{1}{cn_0 + \alpha}\right]\left[cn_0 - n_1\left(\frac{\beta}{\alpha}\right)\right],$$

$$\frac{dn_1}{dN} = \left[\frac{1}{cn_0 + \alpha}\right]\left[n_1 - (n_2 - n_1)\left(\frac{\beta}{\alpha}\right)\right],$$

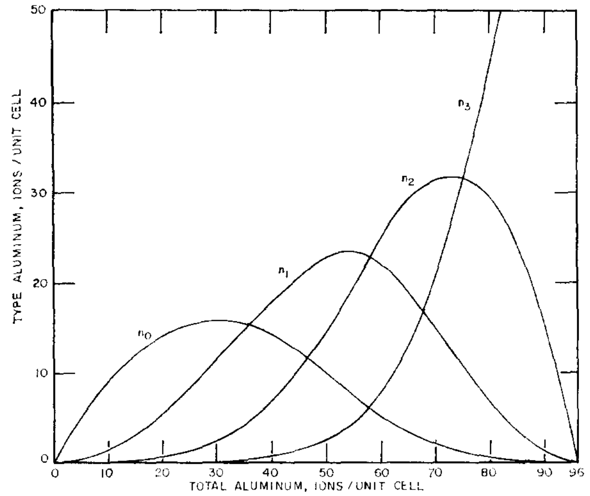

FIG. 1. Lattice aluminum-ion distribution.

$$\frac{dn_2}{dN} = \left[\frac{1}{cn_0 + \alpha}\right]\left[n_2 - (n_3 - n_2)\left(\frac{\beta}{\alpha}\right)\right],$$

$$\frac{dn_3}{dN} = \left[\frac{1}{cn_0 + \alpha}\right]\left[n_3 + n_3\left(\frac{\beta}{\alpha}\right)\right].$$

In these equations, n_i is the number of type-i ions per unit cell; N, the total aluminum content $(\sum_i n_i)$; c, the ratio of the rate constant for dealuminization of the "strong" sites to that for the "weak" sites; α, the number of weak sites $(n_1 + n_2 + n_3)$; and $\beta = n_1 + 2n_2 + 3n_3$.

The above equations can be reduced to quadratures and numerically integrated using, as initial conditions, the distributions of the random-siting model. For our exemplary Y-zeolite, the results are shown in Fig. 2. The solid lines show the concentrations of the type aluminum ions upon dealuminization, under the constraint of $c = 0$, i.e., only the "weak-acid" aluminum ions are being removed. The dashed lines show the concentrations of the "strong-acid" sites (n_0) for parametric values of c. The general observation is that, starting

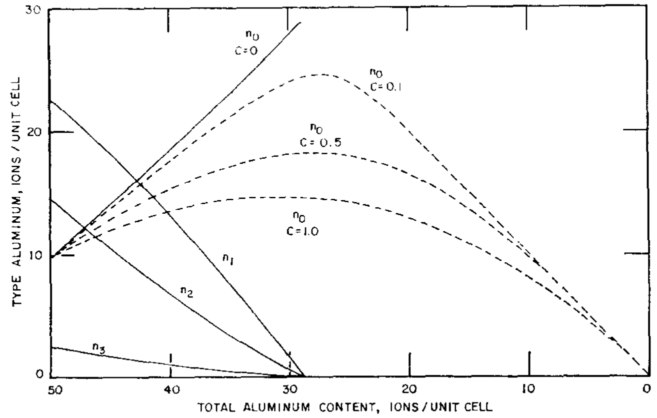

FIG. 2. Dealuminization of Y-zeolite.

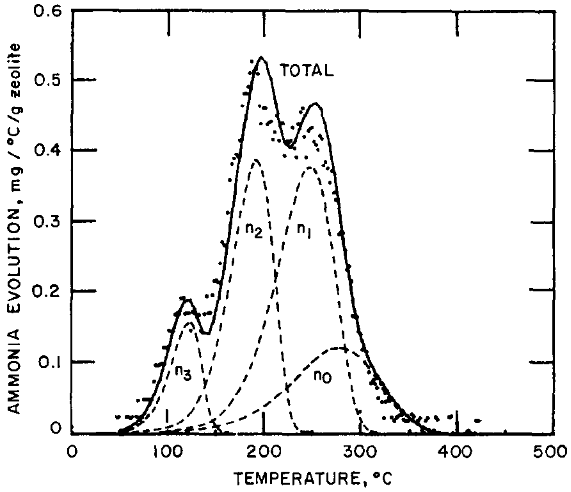

FIG. 3. Ammonium-ion decomposition.

with a Y-zeolite, the number of strong-acid sites proceeds through a maximum upon dealuminization, with an absolute maximum (when $c = 0$) in the neighborhood of 29 ions per unit cell.

Empirical justification for these models comes from thermogravimetric analysis (TG) (*3*). We have found that the decomposition of cationic ammonium ions reflects the distributions of type aluminum ions as defined above. Data points of Fig. 3 show, as a function of temperature, the rate of ammonia evolution from our exemplary ammonium Y-zeolite determined at a heating rate of 0.5°C per minute. The solid curve is a computed total rate of evolution of ammonia and the dashed curves are individual contributions to the total rate which are to be associated with the four types of aluminum ions. These computed curves were obtained by means of a kinetic analysis of the TG data (*4*)—an analysis which, incidentally, maintains consistency in establishing kinetic parameters over a range of heating rates from ~0.04 to 20°C per minute. The areas under the curves yield excellent agreement with the model predictions:

	Ions per Unit Cell	
	Model	TG
Type-0	10.1	9.7
Type-1	22.8	20.4
Type-2	14.6	15.3
Type-3	2.5	4.6

The kinetic parameters observed for sites in the ammonium Y-zeolite have been used to interpret the deammoniation behavior of EDTA-extracted materials, thus implying that dealuminization does not alter the character of the type sites. In such materials, the relative amount of type-0 aluminum ions increases greatly with dealuminization, as predicted. For example, in a nominally 60% dealuminized Y-zeolite of 72% crystallinity, 87% of the aluminum ions were found to be type-0. The lack of crystallinity retention prevented the unqualified reduction of these results to a unit-cell basis.

Behind the derivation of the dealuminization equations lie the questions as to whether, during dealuminization, the crystal can maintain its integrity and to what degree, if any, the character of the type sites depends upon the possible creation of lattice vacancies (*5*). These questions are presently being answered by a growing body of evidence (*6*) which imputes the healing of such vacancies to silicon migration, thereby tending to maintain crystalline integrity. Our work is entirely consistent with these developments.

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Received January 30, 1976