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NOTES

Studies on the Dealuminization Process of Faujasite by Monte Carlo Simulation

The space group of faujasite is O_h^7 – $Fd3m$ (lattice constant a_0 = 24.91 Å). The Si and Al atoms occupy the 192(i) sites (Wyckoff notation). According to the parameters x = 0.9638, y = 0.8747, and z = 0.0525 (origin at $3m$) (*1*) the coordinates of all 192 T sites in the unit cell are determined. The shortest distance between T sites is 0.1256 a_0. The second shortest distance, the diagonal of the four-ring, is 0.1779 a_0. Whether any couple of T sites is related with nearest or next-nearest neighborhood can be distinguished easily by these two distances.

The dealuminization process is simulated by sequences of discrete stages, i.e., the Markov chain with stationary transitions and countable state space. The average number of Al atoms N per unit cell is determined by the given Si/Al ratio of the parent faujasite. For the generation of a starting state (configuration) of the Markov chain the N Al atoms are randomly positioned in a representative portion (one unit cell) of the structure, constrained only by Loewenstein's rule. The program eliminates the presence of Al–Al nearest neighborhood; i.e., those configurations created by using a random number generator in which there exist couples of Al–Al distance with 0.1256 a_0 are not accepted. The total N Al atoms in an accepted configuration are classified by having 0, 1, 2, or 3 Al next-nearest neighbors (according to the characteristic distance 0.1779 a_0). The numbers of the four-type Al $\{n_i\}$ in the configuration are then counted up by computerization as state variables. It is obvious that $n_0 + n_1 + n_2 + n_3 = N$.

Type 0 Al atoms with no Al second neighbor in the four rings exhibit strong acidity (*2, 3*). During the dealuminization, within a short period Δt the number of "strong acid" Al atoms released from the framework is Δn_0. By assuming first-order kinetics, Δn_0 is related to the rate constant for dealuminization k_0 as

$$\Delta n_0 = k_0 n_0 \Delta t. \quad (1)$$

Type 1, 2, and 3 Al atoms are considered to be "weak acid" sites (*2, 3*). For simplicity their rate constants for dealuminization are unified with k approximately. Similarly the number of type j Al atoms released from the framework within Δt is equal to

$$\Delta n_j = k n_j \Delta t \quad (j = 1, 2, 3). \quad (2)$$

The total number of Al atoms released from the framework during the period Δt can then be expressed as

$$\Delta N = (k_0 n_0 + k(n_1 + n_2 + n_3))\Delta t. \quad (3)$$

Define c as the ratio of the rate constant for dealuminization of the strong sites to that for the weak sites ($c = k_0/k$). Because the weak acid sites are removed preferentially (*4*) the value of c is then expected to be in the range of 0–1. According to (1), (2), and (3) we have

$$\Delta n_0 = \frac{c n_0}{c n_0 + (n_1 + n_2 + n_3)} \Delta N \quad (4)$$

$$\Delta n_j = \frac{n_j}{c n_0 + (n_1 + n_2 + n_3)} \Delta N \quad (j = 1, 2, 3). \quad (5)$$

The starting state decides where to go

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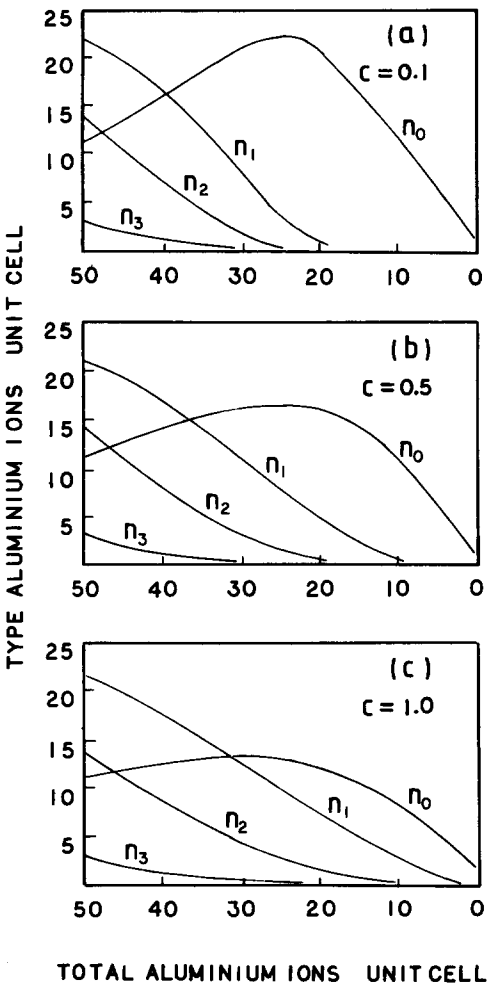

FIG. 1. The evolutions of the calculated concentrations of the different types of Al ions upon dealumination for $c = 0.1$, 0.5, and 1.0, respectively, for the Si/Al = 2.84 case.

next by a stochastic mechanism. In order to carry out a step transition we assume that the total number of removed Al atoms in one step is a small amount of ΔN. According to the given ΔN and the numbers of four-type Al atoms of the starting configuration $\{n_i\}$, the partially removed numbers $\{\Delta n_i\}$ ($i = 0, 1, 2, 3$) are determined by Eqs. (4) and (5). The one-step transition is accomplished by removing Δn_i Al atoms randomly from each n_i type i Al atoms of the starting configuration and in this way a new configuration next to the starting configuration in the Markov chain is set up stochastically. It is assumed in Monte Carlo simulation that except for ΔN Al atoms removed randomly the remainder $N - \Delta N$ Al atoms remain unchanged on the framework. Since the removal of any Al atoms affects the "acid forming" quality of all its Al next-nearest neighbors, the numbers of type Al atoms $\{n_0', n_1', n_2', \text{and } n_3'\}$ of the new configuration must recount up by computerization. The set $\{n_i\}$ represents a possible evolution of the state variables $\{n_i\}$ ($i = 0, 1, 2, 3$) under the one-step transition. By repeating the above-mentioned procedure a sample function of the Markov chain is generated step by step. The evolutions of the state variables $\{\bar{n}_i\}$ during dealuminization are obtained by taking an average from a sample space with a large enough size.

In the first set of calculations the given Si/Al ratio of the parent faujasite is 2.84 (~50 Al atoms/u.c.). The average number of removed Al atoms per unit cell for each step in the Monte Carlo simulation is set up to be 5. In order to provide accurate statistical information on the system the simulation is accomplished in a representative portion containing $2^3 = 8$ unit cells of the structure. Figures 1a–1c illustrate the evolutions of the calculated concentrations of the different type Al atoms upon dealuminization for $c = 0.1, 0.5$, and 1.0, respectively. The n_0 curves can be compared directly with the results of Mikovsky and Marshall (*4*). It can be seen that under the same parameter setups for calculations, both the Monte Carlo simulation and the approach of Mikovsky and Marshall give similar results; the evolution tendencies of n_0 upon dealuminization fully coincide and the calculated values are close to each other.

In the second set of calculations, the Si/Al ratio of the parent faujasite is taken to be 1.95 (~65 Al atoms/u.c.). Figures 2a–2c illustrate the evolutions of the calculated concentrations of the different type Al atoms.

According to the Monte Carlo simulations, one may conclude the following.

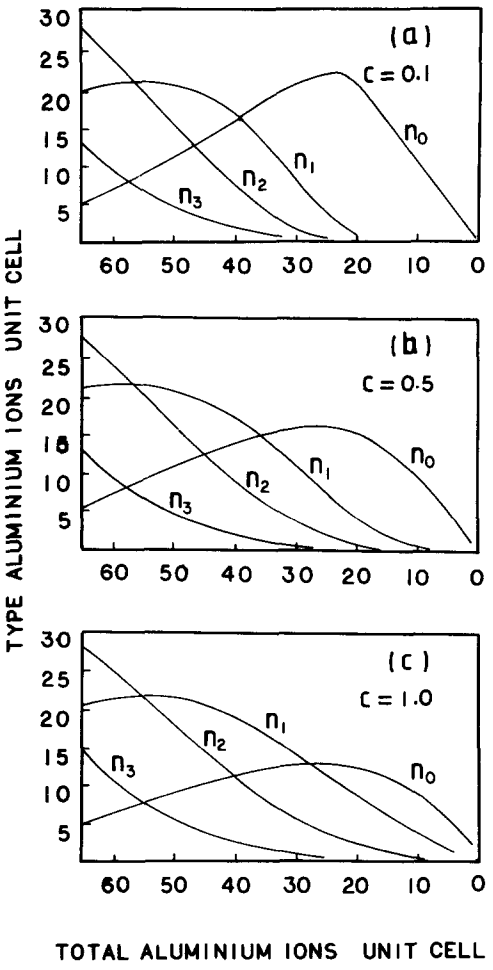

FIG. 2. The evolutions of the calculated concentrations of the different types of Al ions upon dealumination for c = 0.1, 0.5, and 1.0, respectively, for the Si/Al = 1.95 case.

(a) Dealuminated faujasites with a Si/Al ratio in the range 5.4–6.68 (30–25 Al atoms/u.c.) exhibit the maximum strong acidic center content. By examining the humps of the n_0 curves in Figs. 1 and 2, we find that n_0 goes up to a maximum that is influenced neither by the trial values of c nor by the initial Si/Al ratio of the parent material.

(b) The c dependence of the n_0 maximum value prompts the following comments. A maximum n_0 around 12/u.c. indicates $c \to 1$. A maximum n_0 around 21/u.c. indicates $c \sim 0.1$; i.e., a great disparity of the dealumination rate or chemical property between strong and weak acidic centers might be expected. There might be a practical significance of the prediction that if the ratio c can be adjusted either by pretreating the faujasite before the dealumination or by controlling the thermochemical conditions during the dealumination process, the concentration of the strong acidic center in dealuminated faujasite can then be controlled.

(c) The present work treats the dealumination as a nonequilibrium process. The approach is suitable for descriptions of metastable states and so the discussions are closer to the reality of dealuminated faujasites.

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