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Structures and Dynamics of Alkali Ion-exchanged ZSM-5 as Investigated by Molecular Dynamics and Computer Graphics

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Molecular dynamics method using a simple two-body interatomic potential was found to be effective for reproducing the structures of silicalite with the MFI structure and CaNaA zeolite. This method was also effective for estimating the cation position in alkali ion-exchanged ZSM-5.

Much attention has recently been given to ion-exchanged zeolites in relation to their applications to catalysts, adsorbents, and various functional materials. It has also been found that exchanged cations play important roles as the center of adsorption and catalytic reactions. It is therefore highly important to determine the position of exchanged cations to understand adsorption and catalytic reactions in zeolitic materials. In addition to the experimental methods such as X-ray crystallographic analysis, ESR, and NMR, it would be desirable to establish theoretical methods for the purpose.[1] Molecular dynamics (MD) has been widely applied for understanding the structure and physical properties of various substances including simple liquids, water, molten salts, liquid metals, glasses, and proteins in terms of the interatomic potential. Although the method has scarcely been applied for the simulation of zeolite structure,[2] MD investigations would give important information on the nature of zeolite structure with the micro pore. The objective of the present study is to demonstrate the availability of the MD method coupled with computer graphics (CG) technique for estimating the position of cations in alkali ion-exchanged ZSM-5. Ion-exchanged ZSM-5 was selected because of its importance in various catalytic reactions. It should also be noted that experimental determination of cation position is not easy for ZSM-5 because of the small number of ion-exchanged sites.

The calculations was made with the MD program developed by Kawamura.[3] The Verlet algorithm was used for the calculation of ion motions, while the Ewald method was applied for the calculation of electrostatic interactions. Temperature

and pressure were controlled by means of scaling of ion velocities and basic cell parameters under the periodic boundary condition. The total number of ions in the MD basic cell was 288 for silicalite, 320 for CaNaA, and 289 for ion-exchanged ZSM-5. The time step was 2.5×10^{-15}s. After reaching at the target temperature, the calculation was made for several thousands steps.

The two-body, central force interionic potential, Eq. 1, was used for all calculations,

$$u(r_{ij})=Z_iZ_je^2/r_{ij}+fo(b_i+b_j)\exp((a_i+a_j-r_{ij})/(b_i+b_j)) \quad (1)$$

where Z_i is the atomic charge, e the elementary electric charge, r_{ij} the interatomic distance, and f_0 a constant. The parameters a and b in Eq. 1 represent the size and stiffness, respectively, in the exchange repulsion interaction. The parameters of Eq. 1 have been determined to reproduce the structure of various crystals without the zeolitic micropore.[3] Calculations were made with DEC Micro VAX II superminicomputer, and NEC PC-9801RA personal computer, while the visualization was made with PS-390 three-dimensional color graphic terminal and MOGLI(Evans & Sutherlands) software.

Figure 1 shows an example of the MD calculations for the ZSM-5 without Al incorporation. The trajectories of Si and O atoms are close to the average positions of the ions determined by the X-ray crystal structual analysis.[4] Under the condition, the mean square displacement of ions from the positions of the X-ray analysis were 0.103 Å^2 for the O^{2-} ion while 0.039 Å^2 for the Si^{4+} ion. These values are not significant in comparison of the temperature factor in the X-ray crystal structure analysis. Consequently, the micro pore structure of ZSM-5 was reproduced by using MD with the interatomic potential for the SiO2 crystals without the micro pore. Before the application of the MD method to ion-exchanged ZSM-5, calculations were made for the CaNaA zeolite with a definite crystal

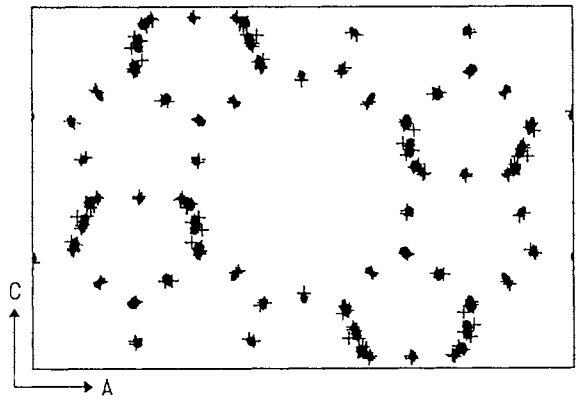

Fig. 1. Trajectories of Si and O atoms in silicalite with MFI structure calculated by the MD method at 600 K (solid lines) and average positions determined experimentally(+).

structure. Namely, the positions of Al, Si, Na, Ca, and O atoms have been determined experimentally by X-ray crystallographic analysis.[5] As shown in Fig. 2, the trajectories of Ca, Na, Al, Si, and O atoms calculated by the MD method are close to those determined experimentally, indicating that the present MD method is effective for reproducing the position of cation in ion-exchanged zeolites.

In ion-exchanged ZSM-5, the position of ion-exchanged cation has not yet been determined exactly, although a quantum chemical calculation suggests that Al ion is located at the T12 sites among the 12 possible sites of T atoms.[6] Thus, one of the 8 Si atoms in the T12 site was replaced with an Al atom, and MD calculations were made for different initial position of exchanged cation to investigate the trajectory of the cation. When the initial position was close to the possible position of the ion-exchange site in the neighbor of Al^{3+}, the ion migrated readily to the position. When the initial position was far from the ion-exchange site, high temperature was necessary to migrate the position. Figure 3 shows examples for Na-ZSM-5. Although Na ion cannot reach to the vicinity of Al cation at 300 K, the Na ion can migrate easily at 600 K to reach the ion-exchanged site. Thus, the MD

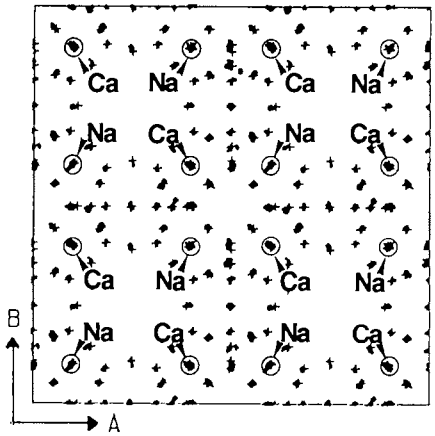

Fig.2. Trajectories of atoms in CaNaA zeolite by the MD method at 600 K (solid lines) and the average positions determined experimentally(+).

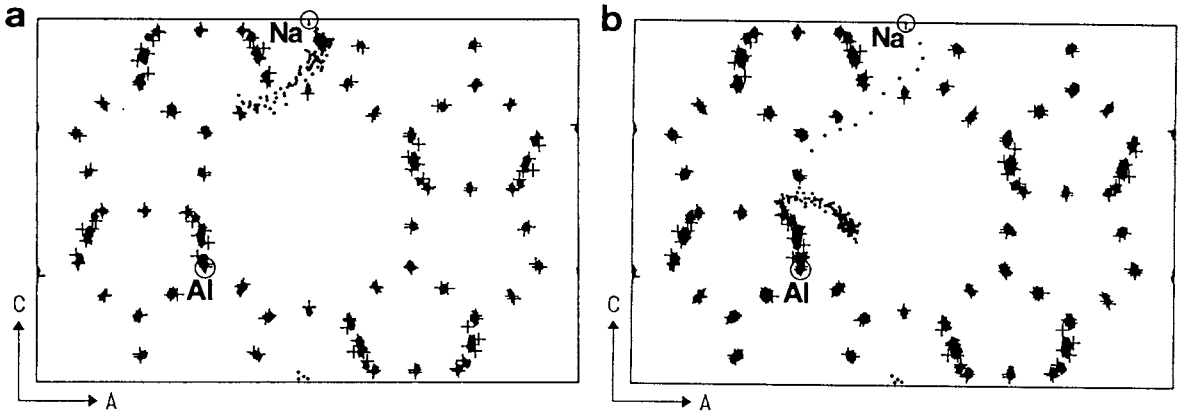

Fig. 3. Trajectories of Na-ZSM-5 by the MD method at 300 K(a) and 600 K(b).

method is effective for estimating the position of Na cation in Na-ZSM-5. Similar results were also obtained for H-, Li-, K-, and Cs-exchanged ZSM-5, and the final structures at the ion-exchanged site are visualized in Fig. 4. Although H^+ or Li^+ ion with small ionic radius located in the vicinity of oxygen anions, Na^+, K^+, and Cs^+ ions with larger ionic radius spread out of the micro pore of ZSM-5. It should also be noted that adsorption data of O_2 and N_2 on alkali ion-exchanged ZSM-5 are consistent with the pictures.[7)]

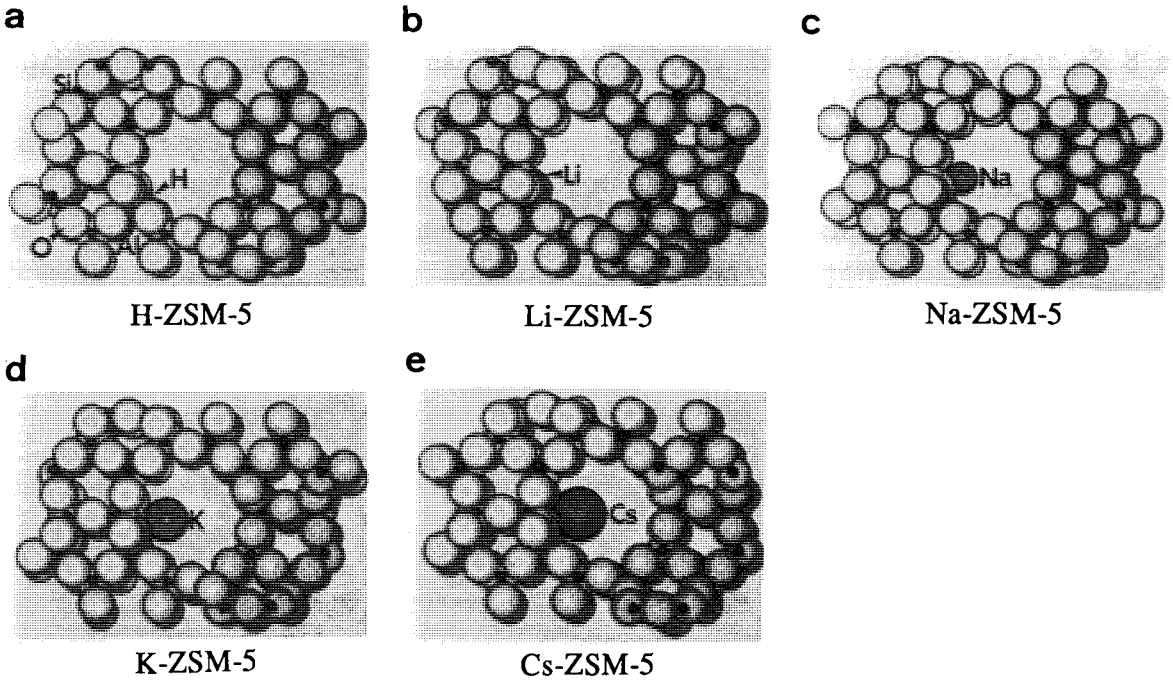

Fig. 4. Computer Graphic Pictures of Alkali ion-exchanged ZSM-5.
(a) H-ZSM-5 (b) Li-ZSM-5 (c) Na-ZSM-5 (d) K-ZSM-5 (e) Cs-ZSM-5

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