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Catalysis Today 23 (1995) 417–423

CATALYSIS TODAY

Atomic processes in the thermal destruction of zeolites as investigated by molecular dynamics and computer graphics

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Abstract

The destruction processes of various zeolites, such as a silicalite with the ZSM-5 structure (SiO_2-MFI), Cu-ZSM-5, and a silicalite with the faujasite structure (SiO_2-FAU), with increasing temperature were investigated by using molecular dynamics and computer graphics methods. The mobility of atoms in SiO_2-MFI was increased and the framework became unstable, as the temperature was increased. Finally the framework was destroyed to an amorphous phase. Increasing the Al content led to a decrease in the heat-resistance in Cu-ZSM-5. The change in the Si–O, Al–O, and Cu–Al distances as well as the change in the pairs of Si–O bonds are discussed to clarify the mechanism of Cu-ZSM-5 destruction. The destruction process of SiO_2-FAU was also investigated in order to understand the effect of framework structure, and it was suggested that the presence of the 4-membered ring provides one of the reasons for the inferior heat-resistance of SiO_2-FAU to that of SiO_2-MFI.

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1. Introduction

Zeolites are industrially important catalysts because of their applications to cracking, hydrocarbon isomerization, alkylation, and methanol-to-gasoline processing etc., and some interesting research projects have been carried out [1–3]. A detailed understanding of the deactivation processes of zeolite catalysts, in addition to that of the active sites and the reaction process, are desirable to develop novel zeolite catalysts. Framework destruction is one of the reasons for the deactivation of catalysts. In fact, many zeolite catalysts with high activity and high selectivity have not been commercialized because of their lack of heat-resistance. Since it is not always easy to clarify the destruction processes of zeolite frameworks experimentally, theoretical methods are desirable in addition to elaborate experimental work in order to understand the mechanism of zeolite destruction.

Song and co-workers applied molecular dynamics (MD) to investigating the destruction process of an A-type zeolite framework with increasing temperature [4,5]. The radial distribution functions of T–T, T–O, and O–O (T = Si or Al) and the distribution of T–O–T bond angles were discussed at several temperatures. Moreover, the structural transformation process from an A-type zeolite to a cristobalite-type structure was investigated with increasing temperature. However, in their studies Si and Al atoms were not distinguished, and the same potential function and the same parameters for Si and Al atoms were

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SSDI 0920-5861(94)00158-8

used. Therefore, the effect of the different motions between Si and Al atoms and the effect of the Si/Al ratio could not be examined. Industrially, an atomistic understanding of these effects is important in order to develop novel zeolite catalysts with high heat-resistance.

Previously, we have profitably applied MD and computer graphics (CG) methods to understand the structure and dynamics of various materials, including supported metal catalysts, oxide superconductor films, supercritical fluids, and carbon nanotubes, in addition to different zeolites, such as materials with LTA, FAU, MOR and MFI frameworks [6–11]. In the present study, by using MD and CG methods we investigated the destruction processes of a silicalite with a ZSM-5 structure (SiO_2-MFI), Cu-ZSM-5, and a silicalite with a faujasite structure (SiO_2-FAU), with increasing temperature to clarify the effects of not only the different motions of Si and Al atoms and the Si/Al ratio but also the framework structure.

2. Method

MD calculations were carried out with the XDORTO program developed by Kawamura [12]. The Verlet algorithm was used for the calculation of atomic motions, while the Ewald method was applied to the calculation of electrostatic interactions. Temperature and pressure were controlled by means of scaling the atom velocities and unit cell parameters under 3-dimensional periodic boundary conditions. The calculation was performed for 2000–20000 steps with a time step of $2.0–2.5 \times 10^{-15}$ s. The two-body central force interatomic potential, Eq. (1), was used for all calculations. In Eq. (1) the first and second terms refer to Coulomb and repulsive interactions, respectively.

$$u(r_{ij}) = Z_i Z_j e^2 / r_{ij} + f_0 (b_i + b_j) \times \exp\{(a_i + a_j - r_{ij}) / (b_i + b_j)\} \qquad (1)$$

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 of the atoms, respectively, in the repulsive interaction. Table 1 shows the potential parameters of each atom (O, Si, Al, and Cu) which were employed in this study. Calculations were performed with Hewlett-Packard HP9000 Model 715/33 and Silicon Graphics INDY R4400 workstations, while the static visualization was done with the Insight II program developed by BIOSYM Technologies Inc., USA. The dynamic visualization was made with the MOMOVIE program and the RYUGA program developed in our laboratory on OMRON LUNA-88K and Hewlett-Packard HP9000 Model 715/33 workstations, respectively.

Table 1
Potential parameters of O, Si, Al and Cu

Atom	Z_i	a_i/Å	b_i/Å
O	−2.0	1.629	0.085
Si	4.0	1.012	0.080
Al	3.0	1.076	0.080
Cu	1.0	0.801	0.080

3. Results and Discussion

3.1. Destruction process of SiO_2-MFI

The dynamic behavior of atoms in ZSM-5 type silicalite was calculated at several temperatures, such as 300, 1000, 5000, 10000, and 15000 K to investigate the destruction process with increasing temperature. In the MD simulation, the destruction temperature cannot be predicted quantitatively, because the framework destruction of zeolites occur experimentally over months or years and the MD method can only deal with phenomena occurring during a period of picoseconds. Therefore, instead of long-term calculations, the MD simulations were performed at higher temperatures so as to simulate the destruction processes. Moreover, it is necessary to elaborate potential functions and parameters to quantitatively predict the destruction temperature. Song and co-workers reported that the framework of A-

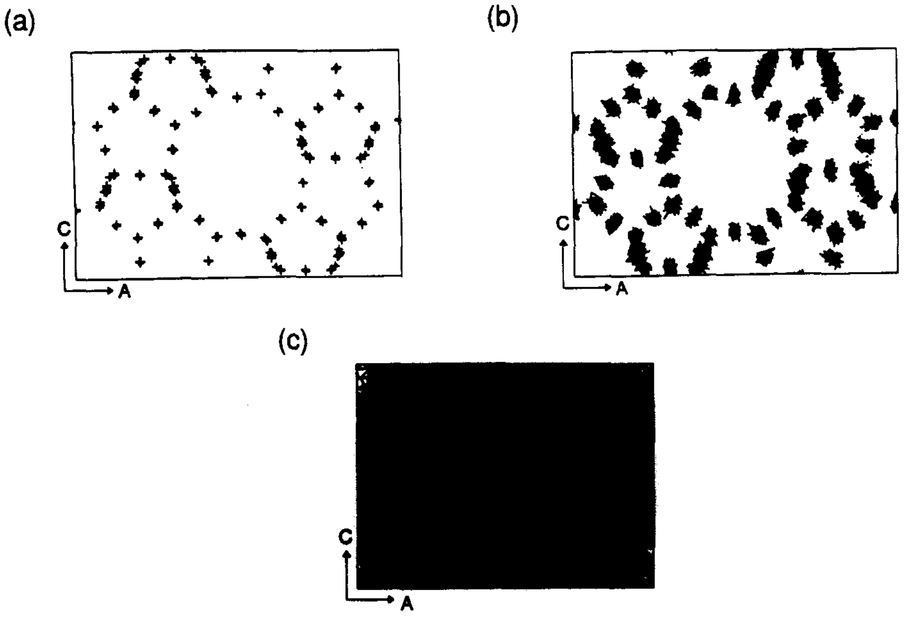


Fig. 1. The trajectories of Si and O atoms in SiO_2-MFI at 300 K (a), 5000 K (b) and 1500 K (c) during 2000 steps.

type zeolite was destroyed at 2100 K in their MD simulation [4,5], and this destruction temperature is much higher than that derived from the experimental results (< 1000 K). Although a long-term calculation is not possible at this moment, the effect of potential parameters on the destruction temperature is also discussed at Section 3.4.

Fig. 1 shows the trajectories of Si and O atoms in SiO_2-MFI at 300, 5000, and 15000 K during 2000 steps of MD calculations. The ' + ' symbols in Fig. 1 denote the equilibrium positions of atoms reported by X-ray crystal structure analysis [13], while the solid lines denote the trajectories of the atoms during the simulations. The trajectories of Si and O atoms at 300 K were close to the average positions determined by X-ray crystal structure analysis [13], and the atoms vibrated near average positions without atomic diffusion. The mean square displacements of atoms from the positions determined by X-ray crystal structure analysis were 0.062 $Å^2$ for the O atoms and 0.014 $Å^2$ for the Si atoms, which are not significant when compared to the temperature factor in the X-ray crystal structure analysis. At 5000 K, although the atoms vibrated near the average positions, they moved more vigorously because of the higher thermal motions. As the temperature was increased further, the zeolite framework became unstable. Finally, the atoms diffused randomly, and the structure changed to an amorphous phase at 15000 K. At this temperature, the structure of SiO_2-MFI was completely destroyed.

Fig. 2 shows CG pictures of the destruction process of ZSM-5-type silicalite at 15000 K. The 5-membered rings of the silicalite were distorted at 1.0 picosecond (ps), and the 10-membered rings were crushed at 3.0 ps. Finally, the structure was completely converted to an amorphous state. It was found that the collapse of the 5-membered rings is an initial step of the destruction of SiO_2-MFI. The applicability of MD and CG methods to understanding the atomistic mechanism of zeolite destruction was clarified.

3.2. *Destruction process of Cu-ZSM-5*

The effect of the different mobility of Si and Al atoms and the effect of the Si/Al ratio on the destruction process of ion-exchanged ZSM-5 is an important topic in the development of novel catalysts with high heat-resistance. The destruction process of Cu-ZSM-5 (Si/Al = 95, 47) was

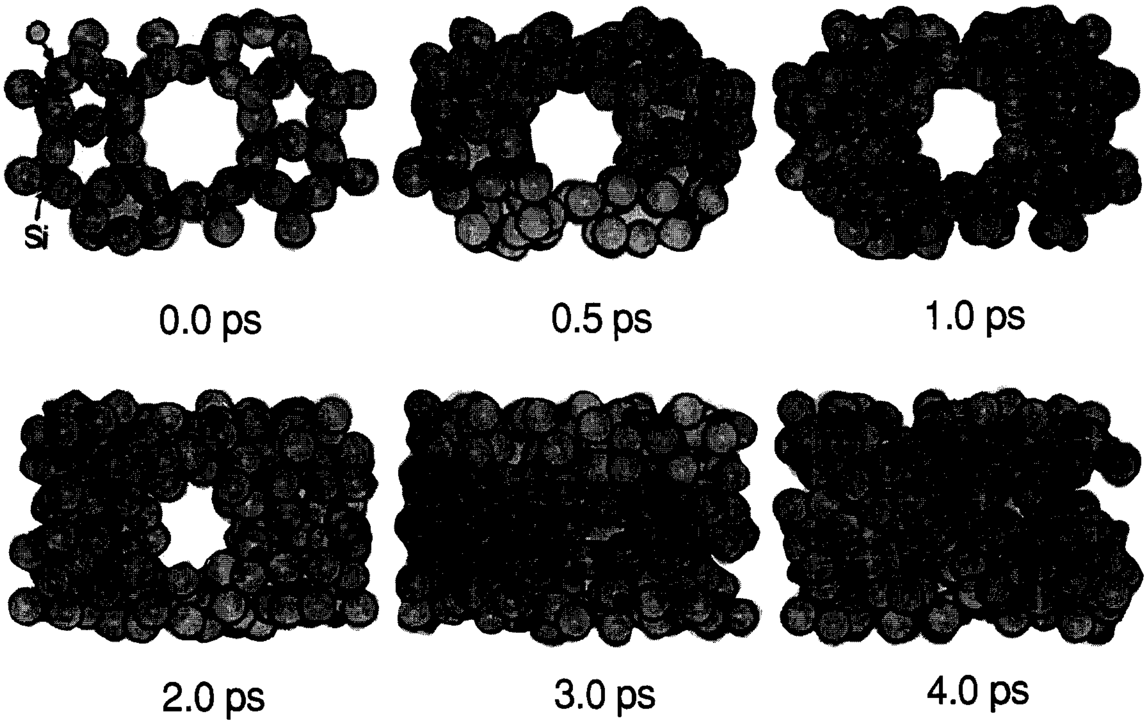


Fig. 2. The destruction process of SiO_2-MFI at 15000 K.

investigated with increasing temperature. The locations of substituted Al ions and extra-framework cations in ZSM-5 have not been reported in the literature based on X-ray crystallographic studies to the best of our knowledge, although two possible extra-framework sites have been proposed for ZSM-5 [14]. Schröder and co-workers [15] have performed energy minimization calculations and have shown that a random Al substitution is possible since the substitution energy for different sites falls in a close range of energy values. Quantum chemical calculations by Fripiat and co-workers [16,17] have indicated that the T12 and T2 sites are the preferred sites of Al substitution. In this background, we have substituted a part of eight T12 sites corresponding to Si/Al ratios of 95 and 47, and charge compensated the anionic framework with 1 and 2 Cu^+ cations, respectively. The location of Cu^+ cation was determined by the MD calculation, and the detailed method is described in ref. [18].

The dynamics of atoms in Cu-ZSM-5 (Si/Al = 95) were simulated at several temperatures, such as 300, 1000, 5000, 10000, and 15000 K. The structure of Cu-ZSM-5 was maintained at 300 K, and all of the atoms vibrated near the initial positions. Fig. 3 shows the trajectory of atoms in Cu-ZSM-5 at 7000 K. All of the framework Si, Al, and O atoms remained near their initial positions; on the other hand Cu^+ ions moved freely and dynamically in Cu-ZSM-5. The high mobility of exchanged cations in ion-exchanged ZSM-5

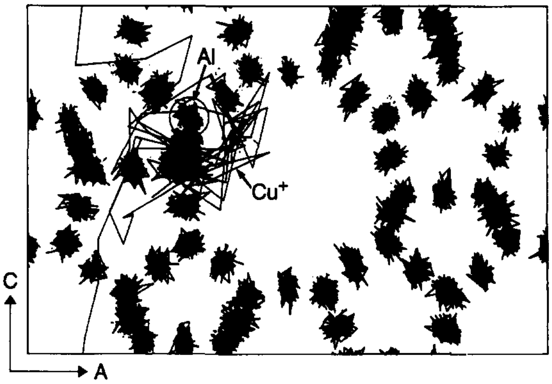


Fig. 3. The trajectory of atoms in Cu-ZSM-5 (Si/Al = 95) at 7000 K.

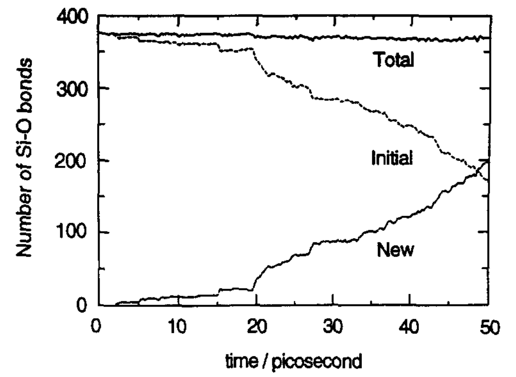


Fig. 4. The change in the numbers of Si–O bonds in an unit cell of Cu-ZSM-5 (Si/Al = 95) at 11000 K.

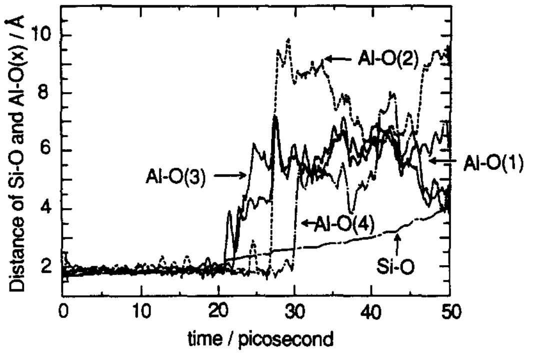


Fig. 5. The change of the Si–O and Al–O distances in Cu-ZSM-5 (Si/Al = 95) at 11000 K.

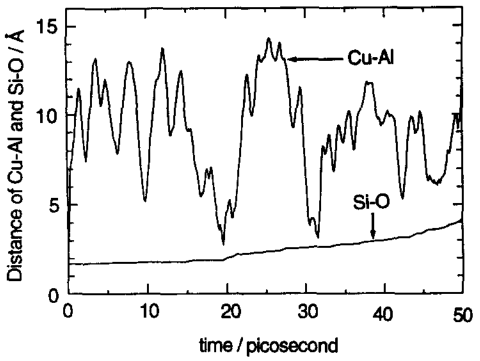


Fig. 6. The change of the Cu–Al distance in Cu-ZSM-5 (Si/Al = 95) at 11000 K.

was also confirmed by the experimental results [19]. As the temperature was further increased, the structure of Cu-ZSM-5 became unstable, and finally the structure was destroyed at 11000 K. It was found that the destruction temperature of Cu-ZSM-5 was lower than that of SiO_2-MFI.

During the destruction process of Cu-ZSM-5, the original Si–O bonds were broken, while new Si–O bonds were constructed. Fig. 4 shows the change in the pairs of Si–O bonds in a unit cell of Cu-ZSM-5, when Cu-ZSM-5 was destroyed at 11000 K. The total number of Si–O pairs was almost maintained during the MD simulation, while the number of original Si–O pairs was suddenly decreased at 20.0 ps. In contrast, the number of new Si–O pairs was increased after 20.0 ps. The destruction process of Cu-ZSM-5 was clearly observed from the exchange of Si–O pairs.

The change of the average Si–O and Al–O distances in Cu-ZSM-5 (Si/Al = 95) was calculated at several temperatures to explore the different diffusivity of Si and Al atoms in Cu-ZSM-5. Here, the distances between the atoms of Si–O pairs or Al–O pairs that were bonded initially were averaged. Both Si–O and Al–O distances were not significantly changed and the structure of Cu-ZSM-5 was maintained below 1000 K. Fig. 5 shows the change of the Si–O and Al–O(x) (x = 1–4) distances in Cu-ZSM-5 at 11000 K. The Al atom is attached to four O atoms in Cu-ZSM-5. The Al–O(3) was suddenly expanded at 20.0 ps, while the distance between Si and O was gradually expanded after 20.0 ps. This suggests that the destruction of Cu-ZSM-5 is initiated by the collapse of the Al–O bond in Cu-ZSM-5. As a consequence, the collapse of the Si–O bonds follows that of the Al–O bonds.

Fig. 6 shows the change of the Cu–Al distance in Cu-ZSM-5 (Si/Al = 95) at 11000 K to clarify the role of the dynamics of Cu^+ cation in the destruction mechanism. The Cu^+ cation diffused freely and extensively in Cu-ZSM-5 from the beginning of the MD simulation. At 20.0 ps the distance between Cu and Al was a minimum (about 2.7 Å), indicating that the Cu^+ cation attacked O atom directly attached to the Al atom. 20.0 ps is the starting time of the Cu-ZSM-5 destruction in this MD simulation, as described previously. Therefore, the attack of the Cu^+ cation on the O atom attached to the Al atom was found to be the cause of the dealumination, namely the destruction of Cu-ZSM-5.

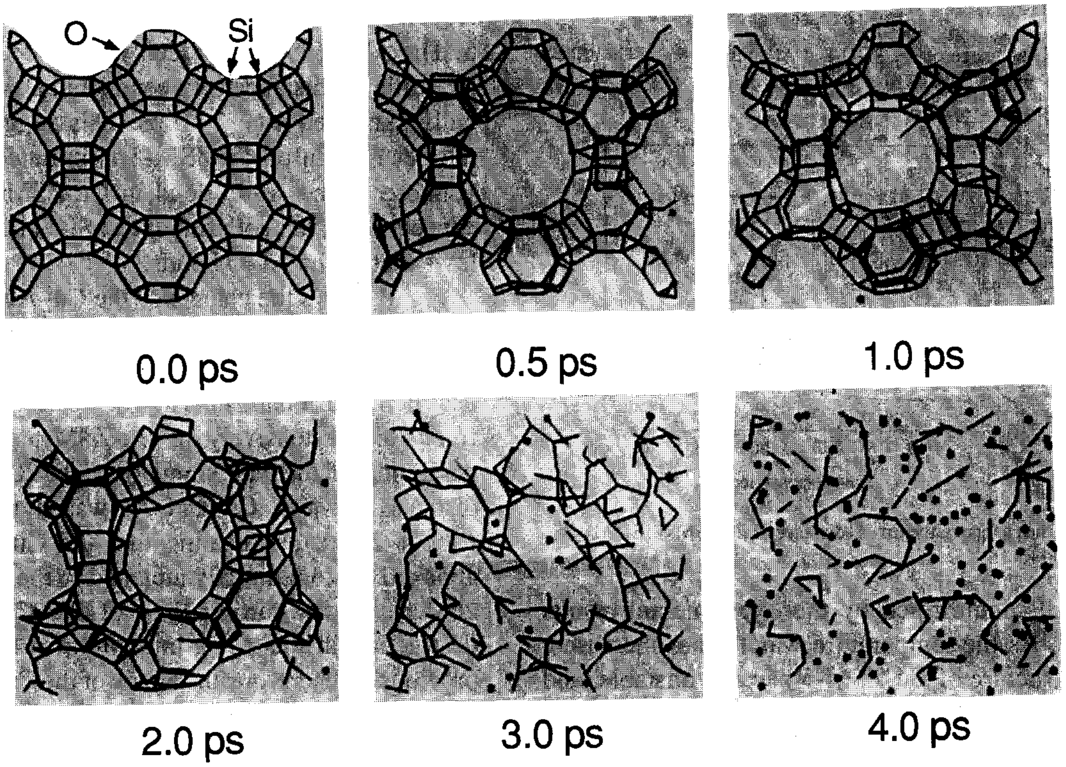
The destruction process of Cu-ZSM-5 (Si/Al = 47) was investigated to evaluate the effect of Si/Al ratio on the destruction mechanism. The destruction temperature of Cu-ZSM-5 (Si/Al = 47) was lower than that of Cu-ZSM-5 (Si/Al = 95). Thus, increasing the Al content was found to lead to a decrease in the heat-resistance of Cu-ZSM-5. This result agrees with the generally accepted knowledge of the heat-resistance of zeolites; however, a systematic experimental study of the destruction of Cu-ZSM-5 with increasing temperature is desired.

Table 2
Potential parameters of O, Si and Al for the partial ionic model

Atom	Z_i	$a_i/\text{Å}$	$b_i/\text{Å}$
O	−1.2	1.474	0.085
Si	2.4	0.916	0.080
Al	1.4	0.974	0.080

3.3. Destruction process of SiO_2-FAU

ZSM-5 has 10-membered straight and sinusoidal channels as well as 5- and 6-membered rings, while faujasite has 12-membered windows, and 4- and 6-membered rings. Because the framework structures of these zeolites is very different, a comparison between the destruction processes of SiO_2-MFI and SiO_2-FAU may help us to understand the effect of framework structure. The dynamic behavior of atoms in SiO_2-FAU was investigated at several temperatures. As the temperature was increased, the structure of SiO_2-FAU became unstable, similarly to SiO_2-MFI. Finally, SiO_2-FAU was completely destroyed at 14000 K. SiO_2-FAU shows inferior heat-resistance than SiO_2-MFI. Fig. 7 shows the destruction process of SiO_2-FAU at 14000 K. Here, the sticks indicate Si–O–Si bonds and the O atoms occur close to the centers of the sticks. After the original Si–O bond was broken, the Si atom is drawn as a dot. The 4-membered rings of SiO_2-FAU were distorted at 2.0 ps, and the 12-membered windows were crushed at 3.0 ps. Finally, the structure was com-



0.0 ps

0.5 ps

1.0 ps

2.0 ps

3.0 ps

4.0 ps

Fig. 7. The destruction process of SiO_2-FAU at 14000 K.

pletely destroyed to an amorphous state. The collapse of 4-membered rings was the initial step in the destruction process of the SiO_2-FAU framework, and that process was significantly different from that of SiO_2-MFI. Therefore, the presence of the 4-membered ring was suggested to be a contributor to the inferior heat-resistance of SiO_2-FAU.

3.4. Effect of potential parameters on the destruction process of zeolites

The above results suggest the effectiveness of a combination of MD and CG techniques when studying the destruction process of various zeolites. In the above calculations, however, for simplicity the full ionic model was employed as shown in Table 1. A partial ionic model as shown in Table 2, which is more realistic, was also employed, and the destruction process of the zeolites were investigated for clarifying the effect of potential parameters on the destruction process. The potential parameters in Table 2 were adjusted to reproduce the potential curves determined by Kramer and co-workers [20]. The destruction temperatures of the zeolites were significantly decreased. For example, SiO_2-MFI was destroyed at 6000 K which was much lower than 15000 K, as shown in Fig. 2. However, the essential features of the destruction process were not changed. Although only a qualitative discussion of the destruction process is provided by this MD study, long-term calculations and more sophisticated potential functions may allow quantitative predictions of the destruction temperatures.

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