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Molecular Dynamics Studies on Thermal Behavior of a FAU-type Zeolite

Ting Jun HOU[1], Ming Juan JI[2], Hui LIU[1], Xiao Wei HUANG[1], Xue Qi YE[2], Xing Yun LIU[1], Xiao Jie XU[1]*

[1]Chemistry Department, Beida-Jiuyuan Molecular Design Laboratory, Peking University, Beijing 100871
[2]Graduate School of Chinese Academy of Sciences, Beijing 100039

Abstract: Molecular Dynamics (MD) simulations of siliceous FAU-type zeolite were carried out at various temperatures, to investigate its thermal behaviors. From the study, we found that pure silicon faujasite showed different thermal behaviors below 1500K and above 1500K; its cell volume gradually shrinks with the rising of the temperature below 1500K, the cell volume of the zeolite changes little above 1500K.

Keywords: Zeolite, molecular dynamics(MD), thermal behavior.

Introduction

Zeolites are generally crystalline aluminosilicates. Their frameworks are composed of interconnected TO_4(T=Si, Al) tetrahetral networks which have numerous molecular dimensional micropores. It is known that zeolite frameworks can vibrate thermally or be distorted by change of temperature or the presence of sorbed molecules. The catalytic properties of the zeolites and the stability of the framework are greatly affected by the temperatures. It is thus meaningful to model the flexible frameworks in a simulation in order to understand the properties of the zeolites. FAU-type zeolite called zeolite-Y or zeolite-X according to their Si/Al ratio are widely used as industrial catalyst because of their high catalytic activity and excellent shape selectivity.

In the present work, we have carried out MD simulations of siliceous FAU-type zeolite at various temperatures, to investigate its thermal behaviors. Because of the difficulty in experimentally determining Al distributions in disordered zeolite, it is difficult to determine the simulating parameters of FAU-type zeolite with varying Si/Al ratio and simulate their properties. The catalytic activities of FAU-type zeolite changed greatly with their Si/Al ratio, but their thermal behaviors have some similarities. In the present work, we have carried out MD simulations of siliceous FAU-type zeolite at various temperatures to investigate its thermal behaviors. From the ideal model, we may disclose some useful structural information of this kind of zeolite at various temperatures.

This study will also provide a basis for the future study of zeolites with various structures and compositions.

Method

In our MD simulations, the potential parameters came from Burchart[1]. Interatomic potential functions consisted of bond term, Urey-Bradly term, Coulombic term, van der Waals short range repulsion term and van der Waals attraction term. MD simulations were carried out using the Cerius[2] molecular simulation package. In our study, the temperature was varied over the range of 100-1800K, and the pressure was controlled at 1 atm throughout the MD calculations. The simulation cell corresponding to one crystal unit contains 576 atoms (192 Si and 384 O). The initial structrue was constructed according to the experimental structure[2], but the model did not comprise Al atoms and cationic atoms. Then the model was minimized by using molecular mechanics. In the minimization, the symmetry of the zeolite remained, a pressure constraint with 1 atm was applied on the zeolite. **Table 1** showed the cell parameters of the zeolite with Si/Al ratio equal to 3 and the pure silicon faujasite. From this table, it can be seen that cell parameters of the pure silicon faujisate did not change very largely compared with the real zeolite. After the minimization, the molecular dynamics was performed. In the simulation, the periodic boundary conditions were adopted. Initial simulations were performed to relax the system for 5000 steps at various temperatures with a time step of 1 fs (1.0×10^{-15}s). After the equilibration, a production run of 10000 steps with a time step of 1 fs (1.0×10^{-15}s) was performed, and various time-averaged properties were evaluated.

Table 1. The cell parameters of the real zeolite and the pure silicon faujasite

	a(A)	b(A)	c(A)	α(°)	β(°)	γ(°)
Structure1(Si/Al=3)	24.71	24.71	24.71	90	90	90
Stucture2(Si/Al=∝)	24.23	24.23	24.23	90	90	90

Results and discussion

MD simulations over the temperatures range of 100-1800K were carried out. **Figure 1** shows the time-averaged temperature dependence of cell volume. From the simulations, we can see that pure silicon faujasite shows some particular thermal behaviors. Below 1500K, its cell volume gradually and slightly shrinks with the rising of the temperature, but above 1500K, the cell volume of the zeolite changes little. Meanwhile, the cell length of the zeolite shows similar variations with the cell volume (see **Figure 2**). The pure silicon faujasite has different thermal behaviors below and above 1500K, which is a thermal transition temperature. Although the cell volume and the cell length slightly shrink below 1500K, but their thermal extraction coefficient is relatively small. Moreover, below 1500K, its cell volume and cell parameters do not show any drastic

changes. From this point of review, its thermal stablity is very good.

Figure 1 Temperature dependence of cell volume obtained for the MD simulations

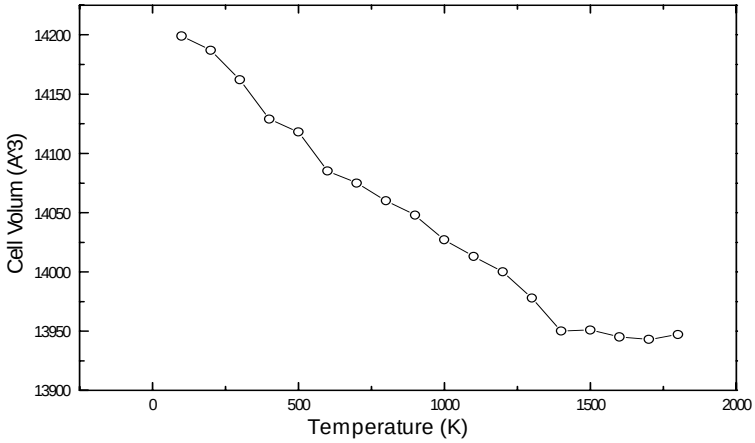
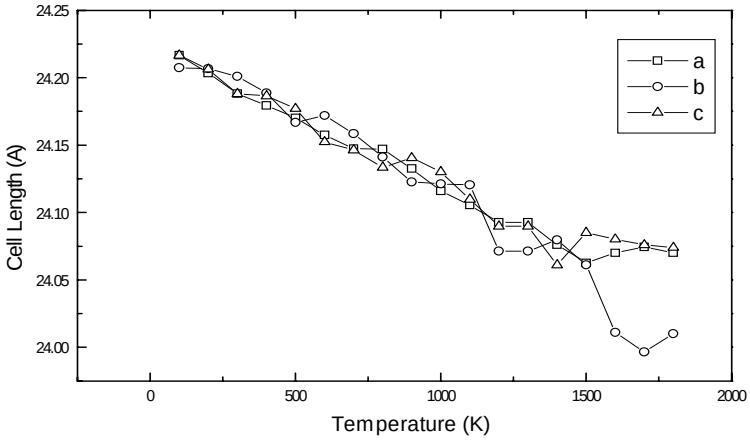


Figure 2 Temperature dependence of the cell parameters obtained for the MD simulations



The MD simulations of FAU-type zeolite at various temperatures disclose its regularities of thermal behaviors. In this work, we only used the pure silicon faujasite model. This is an ideal model which does not include Al and some cations. It would generate deviations from the real models. The molecular simulation of the real zeolites is very difficult. The first problem is that we can not determine the definite position of the Al atoms, how to get accurate force field parameters of Si and Al is not solved at present. The second important problem is how to treat the cations in zeolite, how to determine its position and how to correctly handle its flowing property are very important. We have

ever offered some theoretical methods for determining the positions of the framework Al and in-cell cations[3,4], our further work is to try to carry out some studies on real FAU-type zeolites.

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References

1. E. de Vos Burchart, PhD thesis, Technische Universiteit Delft, **1992**.
2. H. B. Werner, *The American Mineralogist*, **1964,** *49*, 698.
3. P.C. Yang, X.J. Xu, *et al. Acta Phys.-Chim.* (In press).
4. P.C.Yang, X.J. Xu, *et al. Acta Phys.-Chim.* (In press).

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