



Study of *Trans*-1,2-Dichlorocyclohexane Absorbed in Zeolites†

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The behaviour of *trans*-1,2-dichlorocyclohexane (T12D) adsorbed inside zeolite NaY has been investigated by molecular dynamics (MD) simulations. The ratio of Si/Al is 2.35 in the NaY zeolite. The NaY zeolite is modeled using the average-T model with rigid frame. The results have clearly shown that the adsorption of *trans*-1,2-dichlorocyclohexane strongly depended on the zeolite framework structure and the presence of charge-balancing cations. Combined results show that ee conformer is favorable when *trans*-1,2-dichlorocyclohexane molecule is adsorbed in faujasite type zeolite.

Key Words: Adsorption, Zeolite, Conformational behaviour.

INTRODUCTION

The increased awareness of the environmental hazards of chlorinated halocarbons (CHCs)¹ has led to the development of new separation and catalytic conversion processes of chlorinated halocarbons. Zeolites, a framework materials containing pores, channels and cavities with molecular dimensions², have been recognized as interesting alternatives to other separation media³. As a consequence, a need is emerging for developing a better understanding on the mechanism of chlorinated halocarbons adsorption in zeolite at a molecular level. Because of "gauche effect"⁴, two conformers of *trans*-1,2-dichlorocyclohexane are in fast equilibrium, this provides a challenging system to test the conformational behaviour of guest molecule and interactions within the zeolite cavity.

After the substitution of aluminum atom to zeolite framework, the introduced aluminum causes charge defects in zeolite framework, which are compensated with nonframework cations (Na⁺, Li⁺...). The extraframework cations are believed to play a crucial role on the adsorption of guest molecules in the host framework. The precise location of faujasite zeolite extraframework cations remains uncertain⁵. The common locations of the cations in faujasite zeolite are shown in Fig. 1. SIII and SIII' are believed to be of higher potential energy⁶.

In this work, adsorptions of aa and ee conformers of *trans*-1,2-dichlorocyclohexane in zeolite Na₅₇Y (Si/Al = 2.35) are studied by molecular dynamics (MD) simulation.

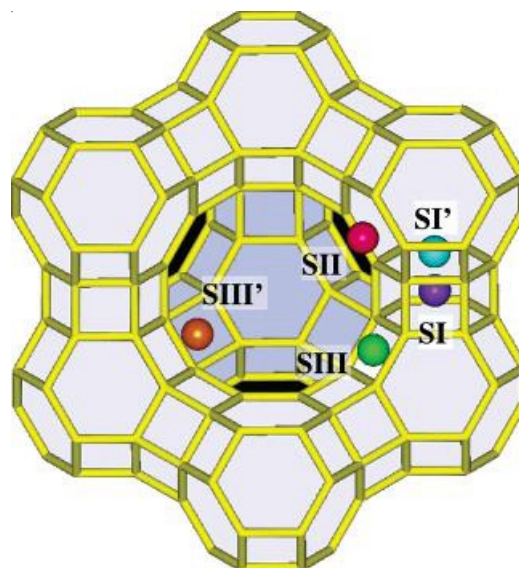


Fig. 1. Representation of the extraframework cation positions in faujasite zeolite

EXPERIMENTAL

System and simulation methods: In the present simulations, the faujasite-type (FAU) zeolites Na₅₇Y (Si/Al = 2.35) were used, in which zeolite has a composition of a united cell in Na₅₇Al₅₇Si₁₃₅O₃₈₄⁷. The dimension of a cubic united cell is 24.345 Å³. The pore dimension of zeolite sodalite cage and

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hexagonal prism is about 5.0 Å and that of super cage is 12.5 Å. One unit cell of faujasite-type zeolite was used as a simulation box, with periodic boundary conditions in all three dimensions. The zeolite was modeled by the average T model⁸ in a rigid frame.

The interactions between the sodium ions and the zeolite frame are described by the Jaramillo and Auerbach⁹ potential function, eqn. 1.

$$U_{CF} = \sum_{C,F=O} \left[A_{CO} e^{-\frac{r_{CO}}{P_{CO}}} - \frac{C_{CO}}{r_{CO}^6} \right] + \sum_{C,F=T} \frac{q_C q_F}{r_{CF}} \quad (1)$$

Trans-1,2-dichlorocyclohexane molecules are described by the following potential function:

$$U_{DCC} = \frac{1}{2} k_{stretch} (r - r_{stretch}^0)^2 + \frac{1}{2} k_{bend} (\theta - \theta_{bend}^0)^2 \quad (2)$$

Molecular dynamics (MD) simulations are performed using the DL_POLY software package¹⁰. *Trans*-1,2-dichlorocyclohexane molecules are loaded to Na₅₇Y zeolite within canonical (NVT) ensemble at room temperature (300 K). The aa and ee conformers of *trans*-1,2-dichlorocyclohexane are initially optimized by using Gaussian 03¹¹ package at MP2/6-31+G* level of theory. Cubic periodic boundary conditions (PBCs) are used throughout the simulations. The equations of motion are integrated using a time step of 1 fs with the velocity Verlet algorithm. Equilibration is performed using velocity rescaling for 2ns. The temperature is initially established and subsequently maintained using the Nose-Hoover thermostat. Configurations are saved every 0.1 ps. Following equilibration, a long equilibrium simulation is run so as to sample the structures with the temperature maintained by the Nose-Hoover thermostat.

RESULTS AND DISCUSSION

Host-Guest interaction: To have a better understanding on the effect of zeolite frame and frame extra sodium cation on guest molecules, several calculations were performed before simulations. Quantum chemistry optimizations were performed using MP2/6-311+G* for *trans*-1,2-dichlorocyclohexane-Na system to determine the interaction between Na-Cl and a σ values of 2.7250 is found suitable for the investigation of the system within zeolite Na₅₇Y.

Adsorption of *trans*-1,2-dichlorocyclohexane molecules in zeolite: Following the σ value of 2.7250, aa and ee conformers of *trans*-1,2-dichlorocyclohexane molecule are then loaded into the Na₅₇Y zeolite. Both conformers are found to be attached to sodium cations in the main pore of zeolites, as shown in Fig. 2. Molecular dynamic simulation results show that cations at SII site (in front of the 12-rings facing the cavities) play an important role in the interaction with *trans*-1,2-dichlorocyclohexane molecules. Because two Cl atoms are oriented at opposite side of the six-member ring, aa conformer is able to interact with two cations at a time. Such binding interaction is so strong that adsorbent is fixed at a definite location throughout molecular dynamic simulations. However, ee conformer demonstrates different map of interaction. Since two Cl atoms occupy the same plane in this conformer, they can interact with one cation instead of two cations. The

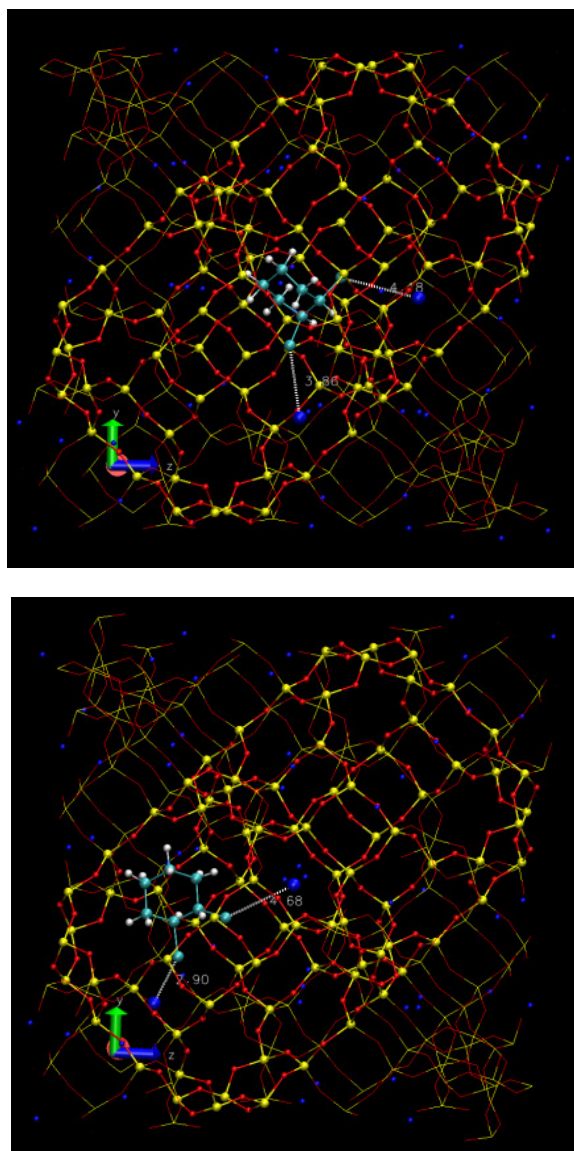


Fig. 2. Simulation snapshot for aa-*trans*-1,2-dichlorocyclohexane (top) and ee-*trans*-1,2-dichlorocyclohexane (bottom) conformer in zeolite

interaction of two Cl atoms with one cation is relatively weak and when adsorbent vibrates and approaches to a nearby cation, the cation could easily capture one Cl atom of adsorbent, which will increase tension in Cl-C-C-Cl of adsorbent. This force could break pre-existing Cl---Na⁺ interaction and finally allow ee conformer to migrates from one cation to another. The difference in migration behaviours could certainly affect the entropy of the system and also the adsorption of each conformer in zeolite. This implies that the entropy of ee conformer is much larger than that of aa conformer in zeolite, even though entropy is not calculated explicitly in our simulations.

Conclusion

Molecular dynamics simulations demonstrate that at room temperature, both aa and ee conformers of *trans*-1,2-dichlorocyclohexane can be captured by the extra framework cations in Na₅₇Y zeolite. The sodium adsorbed at SII plays an important role in the interaction with *trans*-1,2-dichlorocyclohexane molecules. Since the main interaction is Na⁺---Cl, the adsorbent is able to interact with as many sodium cations

as possible during adsorption. In case of aa conformer, two Cl atoms located on the opposite side could be easily captured by two sodium cations and this interaction is strong enough to hold *trans*-1,2-dichlorocyclohexane molecule. However, ee conformer demonstrates different behaviour when loaded into zeolite. In this conformer, two Cl atoms are not far apart and the tension force of Cl-C-C-Cl cannot be ignored. When ee conformer interacts with one sodium cation, it moves and tries to interact with two sodium cations, which enables ee conformer to migrate through zeolite. Combined results show that ee conformer is favorable when *trans*-1,2-dichlorocyclohexane molecule is adsorbed in faujasite type zeolite.

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