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Rotational Motion of *n*-Pentane in H-ZK5

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1. Introduction

The structure type of the Zeolite ZK5 is KFI. The framework consists of two types of cages, gamma and alpha cages (Fig.1). The molecular motion is differently confined by the shape and size of these cages. The rotational motion properties of *n*-pentane in both cages of H-ZK5 have been investigated using molecular dynamics simulations.

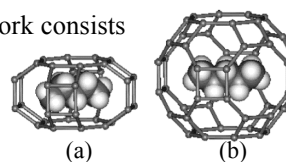


Fig. 1: Schematic of (a) gamma and (b) alpha cage in zeolite ZK5.

2. Methodology

The structure model of the zeolite H-ZK5 was obtained by an optimization using the semi-empirical method MNDO, since no experimental structure data were available. Moreover, the influence of the electric field of the proton has been examined. Two clusters were selected from the optimized zeolite structure, the neutral ($\text{Si}_2\text{O}_7\text{H}_6$) and the acid (SiAlO_7H_7) cluster. Several configurations of each cluster and a methane molecule were generated. Then, quantum calculations at HF and B3LYP level with the 6-31G(d,p) basis set were performed to estimate the interaction between the methane molecule and the cluster for each configuration. The potential energy curves of both models have been compared.

The united atoms approximation is used in which the CH_3 and CH_2 groups are treated as spherical force centers. They interacted with the corresponding force centers in other pentane molecules and with the zeolite lattice by Lennard-Jones potentials [1]. The potential for the torsional elasticity has been taken from [2]. The loading of *n*-pentane in H-ZK-5 was equivalent to an experimental [3] density of 1 molecule in each cage. The lattice including 8 unit cells was kept rigid during the simulation. The average temperature was adjusted to 298 K.

The rotation of *n*-pentane in both types of cages of ZK5 has been investigated in terms of the auto-correlation function (ACF) of the quantity $3\cos^2\theta - 1$ where θ is the angle between a fixed axis of the coordinate system and an intramolecular vector. In addition, the preferred orientation and the position of the *n*-pentane molecule especially in the gamma cage have been examined.

3. Results and Discussion

According to the equipartition theorem, at room temperature $k_B T \sim 2.51$ kJ/mol, where k_B denotes Boltzmann's constant. It can be concluded that the potential energy curves from HF and B3LYP level (Fig.2) show no significant difference between the models.

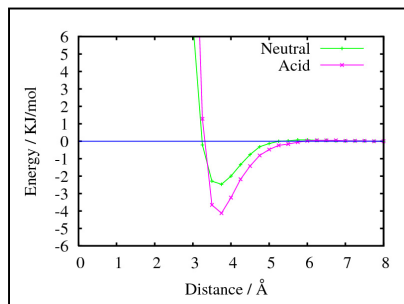


Fig. 2: Potential energy curves of both models, neutral and acid, from B3LYP/6-31G(d,p) calculation.

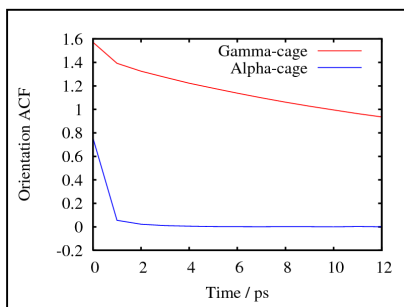


Fig. 3: Autocorrelation function of n -pentane in each cage, gamma and alpha cage, in short time scale.

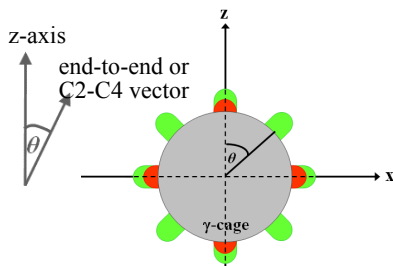


Fig. 5: The preferred orientations of n -pentane in the gamma cage represented by the vector C2-C4 and the end-to-end vector.

References

- [1] A. Loisuangsinn *et al.* to be published.
- [2] J. P. Ryckaert, A. Bellemans, Faraday Discuss. 66 (1978) 95.
- [3] V.E. Zorine, P. C. M. Magusin, R. A. V. Santen, J. Phys. Chem. B 108 (2004) 5600-5608.

Hence, a neutral lattice is a good approximation. The rapid decay of the ACF (Fig.3) of the pentane molecule in the alpha cage shows that the molecule can rotate freely with a short relaxation time compared to the molecule in the gamma cage. This situation can be ascribed to the larger shape and size of the alpha compared to the gamma cages. The preferred orientation of the molecule in the gamma cage has been investigated considering the vector C2-C4 and the end-to-end vector. The resulting distribution is depicted in Fig.4 and Fig.5. Relaxation times have also been examined.

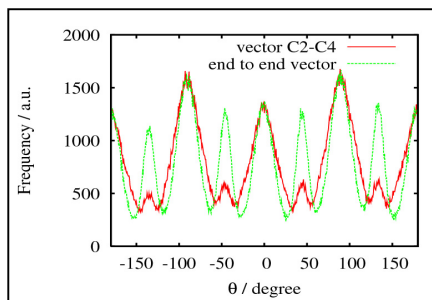


Fig. 4: Frequency of the existence of n -pentane in gamma cage at different θ represented by the vector C2-C4 and end-to-end vector.

The same orientations from both vectors were found in the region of θ equally to 0° or 90° and their symmetry region. The additional orientations of the end-to-end vector arise from the isomer conformations of the pentane molecule.

4. Conclusions

Clearly some orientations are preferred. Ongoing studies are dedicated to the flipping process between the preferred orientations and the resulting decay of the orientation ACF.