Estimation of Diffusional Rates in Tight Fitting Hydrocarbon-Zeolite Systems

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1. Introduction

All silica zeolites with narrow 8-membered (MR) oxygen rings are potential candidates for separations of olefin/paraffin mixtures based on molecular sieving effects. We have used classical molecular dynamics (MD) to study the structural features of five pure silica 8 MR frameworks: Si-SAS, Si-IHW, Si-ITE, Si-CHA and Si-LTA. All of the framework types studied are n-dimensional porous systems (n=1, 2, 3), with cages and channels connected through 8 MR windows. Window size fluctuations were studied in the temperature range 300-1200 K from equilibrium molecular dynamics simulations, by allowing full flexibility of the framework. Temperature influence on diffusional features of propane/propylene adsorbed in the chosen zeolites is studied using classical MD simulations and the Temperature Accelerated Dynamics (TAD) approach for the simulation of rare events introduced by Sorensen and Voter [1]. Potential energy surface effects are taken into account by comparing the results from the well known van Beest, Kramer, van Santen (BKS) [2] and the Nicholas, Hopfinger, Trouw, Iton (NHTI) [3] potentials.

2. Methods

Slow diffusivity of propene/propylene in 8 MR zeolites raises as a consequence of the close match between guest kinetic diameter and window size, making experimental determination of diffusivity a difficult task and also preventing computational MD diffusion estimates to be obtained in computer accessible time scales. Approaches based on the transition state theory (TST) are among several computational methods for the estimation of slow diffusivities [4]. The TST method is used in combination with the TAD scheme to calculate the hopping rate of propane/propylene at high temperatures, where the rate of intercage motion of the guest molecules is speeded up, thus allowing the estimation of self-diffusivities at lower temperatures by extrapolation. The flexibility of the framework plays an important role in the prediction of self-diffuvities, even more when the size of the diffusing species is close to the open space provided by the window. With this regard we have included full framework flexibility in all our calculations, by comparing the results coming from two well known models, the BKS and NHTI potentials.

3. Conclusions

The window size fluctuations of 8 MR zeolites (Fig. 1) and propane/propylene intra and intercage temperature activated motion were obtained from radial distribution functions (RDF) and mean squared displacements (MSD) (Fig. 2), respectively, were obtained

from MD-NVE trajectories, including full flexibility of the framework. The window size changes considerably at higher temperatures, changing the energetic barrier to diffusion, also, the temperature activated mobility of the guest molecules helps to overcome the cage-to-cage energy barrier, raising the frequency of intercage jumps. These effects are important when using the TST and TAD approaches for the estimation of diffusivities at lower temperatures and therefore should be considered in the systematic study of molecular diffusion through 8 MR zeolites.

References

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[3] Nicholas, Hopfinger, Trouw and Iton, J. Am. Chem. Soc. 113, 4792 (1991).
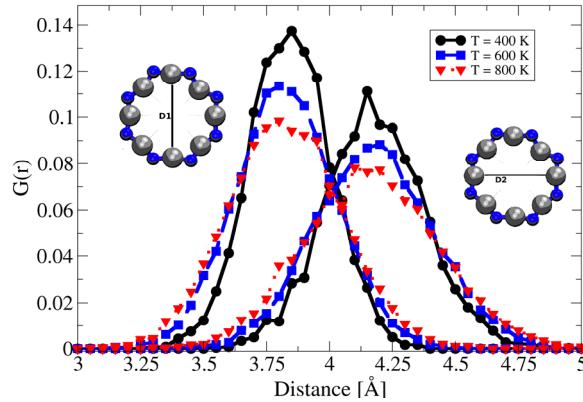[4] Voter, Montalenti, Germann, J. Phys. Chem. C, 112, 17030 (2008)

Fig. 1 Radial Distribution Functions for 8 MR O-O distances (D1 and D2) in Si-CHA obtained from MD trajectories at 400, 600 and 800 K using the BKS potential.
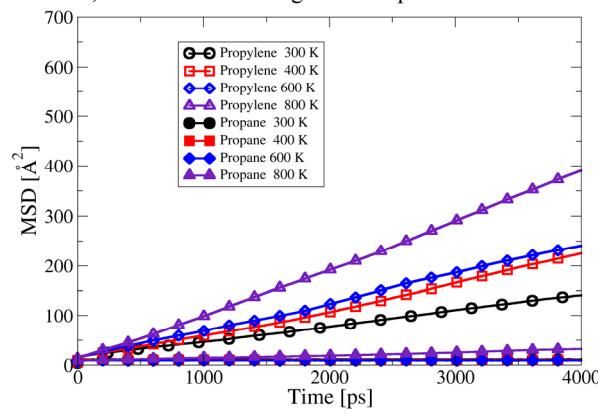

Fig. 2: Typical mean squared displacements (MSD) for Propane and Propylene in Si-CHA from conventional MD trajectories calculated with the BKS forcefield at 300, 600, 400K and 800 K. MSDs are calculated from 15 ns trajectories, which shows the difficulty to obtain intercage sampling at low temperatures, and the activation of the diffusivity at higher temperatures.