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Simulation Studies of CH_4, CO_2, H_2 and D_2 in FAU and MWW Framework Type Zeolites

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1. Introduction

The sorption dynamics of methane, carbon dioxide, hydrogen and deuterium in digitally reconstructed frameworks of FAU and MWW type zeolites is investigated via atomistic computer simulations. The loading dependence of the self-diffusivity proved to be affected by the energetic inhomogeneity of the sorption sites or/and their topology in the particular crystal. Also, collective (Maxwell – Stefan) and, hence, transport diffusivities are examined on the basis of sorbate–sorbate interactions.

2. Methodology

The charged crystal framework of zeolite $Na_{86}X$ is digitally reconstructed based on X-ray diffraction spectra. In the modeling, distinct coulombic charges were attributed to all atoms in the framework. The distribution of counterions among the various kinds of sites present in the unit cell was determined through simulated annealing.

A mass transport study of hydrogen and its isotope deuterium in $Na_{86}X$ was undertaken using molecular dynamics (MD) at 77 and 100 K. A classical simulation treatment of the sorbates at these temperatures is made possible by virtue of the quantum mechanics-based correction due to Feynman and Hibbs imposed on the conventional Lennard-Jones potential for all types of interactions in the systems under study. Our calculations have been designed to allow direct comparison with measurements of transport in these systems via quasielastic neutron scattering [1]. In the rigid model matrix of this work, during the MD runs, molecules were not hindered from accessing the sodalite interior; nevertheless, no molecule was trapped inside a sodalite cage for all loadings used. Classical MD simulations were undertaken for CH_4 and CO_2.

CH_4 and CO_2 were also simulated in the MWW zeolite type, represented by its purely siliceous analogue, the ITQ-1.

3. Results

Our MD results in NaX show that the self diffusivity D_s of CH_4 decreases as the loading increases; this is in agreement with earlier PFG – NMR intra-crystalline self-diffusivity measurements by other groups [2]. On the contrary, the self-diffusivity of D_2 and H_2 in NaX, which is predicted in good agreement with recent QENS measurements [1], exhibits a monotonic increase with loading. The energetic heterogeneity experienced by deuterium molecules in NaX proves to be responsible for this peculiar behaviour: the computed partial molar configurational internal energy of the sorbate molecules indicates

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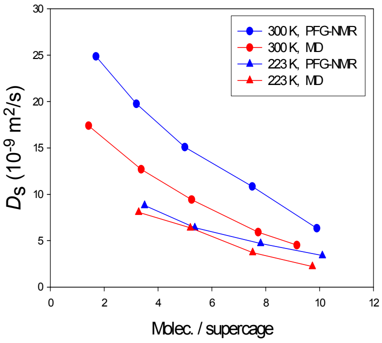

Fig. 1: Comparison of self-diffusivity data obtained via PFG-NMR [2], with MD for CH_4 in NaX.

the existence of low-energy sites which are preferentially filled at low occupancy. To a good approximation, D_s values of H_2 and D_2 at the same loading and temperature in NaX exhibit a ratio of $\sqrt{2}:1$, as would be expected on the basis of the difference in molar mass from simple kinetic theory.

In ITQ-1 at 300 K, the D_s of CH_4 goes through a maximum, while that of CO_2 decreases monotonically with loading. A mesoscopic Diffusion through Spatial Discretization (DSD) approach recently developed in our group [3] may offer a plausible explanation of this trend. The loading dependence of collective (Maxwell – Stefan) and transport diffusivities of CO_2 and CH_4 in ITQ-1 and also of D_2 and H_2 in NaX were interpreted on the basis of the sorbate – sorbate interaction strength by invoking the simple model of Reed and Ehrlich [4].

The molecular dynamics predictions were compared to quasielastic neutron scattering (QENS) measurements from the same zeolite – sorbate systems. Both microscopic methods for probing the diffusivity of sorbed molecules show similar trends for the loading dependence of self, collective, and transport diffusion coefficients.

4. Conclusion

Common gas molecules exhibit a variety of loading dependences of their self- and collective diffusivities in the zeolites NaX and ITQ. These dependences can be predicted by MD simulation, validated through QENS measurements, and rationalized on the basis of sorbate-zeolite and sorbate-sorbate energetics.

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