Adsorption and Diffusion of Water in Siliceous Zeolites: A Combined Monte Carlo and Molecular Dynamics Study

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Atomic-scale modeling continues to play a vital role in improving our understanding of phenomena in zeolites and other framework systems [1]. This is because, in large part, simulation provides detailed insights that are difficult to obtain from experiment alone, particularly when many variables need to be controlled in a systematic and reproducible manner. Commencing with a study of the structure and stabilities of different zeolite frameworks and compositions, it is possible to examine a variety of phenomena including molecular adsorption, diffusion, site selectivity, permeability [2].

In this study, we use classical atomistic simulation methods based on a well-tested potential model for zeolite systems [3] to investigate the relationship between loading and self-diffusion of water molecules in a number of zeolites. Such simulations have previously been performed for one, two or sometimes three systems at a time, but this is the first study to systematically examine several common zeolites at once, namely mordenite (MOR), faujasite (FAU) and its polytype EMT, MFI, and zeolite beta (BEA) and its polytypes BEB and BEC. All systems were assumed to be 100% siliceous.

The adsorption sites and equilibrium loadings of water molecules were first identified using the grand canonical Monte Carlo method with the Towhee code [5], and the diffusivities of water at various loadings at 500 K calculated by the molecular dynamics method using Moldy [6]. The SPC/E model was used to describe water molecule interactions.

Even with a small and relatively simple molecule such as water, distinct differences in the adsorption isotherms of the different zeolites are apparent (Fig. 1). Unlike the other systems, water adsorption in MOR occurs by a two-stage process. As the ambient water pressure is increased, water molecules successively adsorb at sites adjacent to the zeolite framework, up to a molecular loading of 36 molecules/unit cell. In the second stage, with all adsorption sites adjacent to the framework already occupied, water molecules form a second water shell in the larger channels until a saturation loading of slightly more than 72 molecules/unit cell ($\approx$25 mmol/g) is reached.

In addition to differences in water loading, diffusion rates and degrees of anisotropy vary with framework in a fashion consistent with the structural anisotropy of each system, with faster diffusion occurring down wide, continuous straight channels than through those connected by smaller cages or narrower T4R windows. Fig. 2 shows that the water self- diffusion coefficient (which is proportional to the slope of the curve in a mean square displacement vs time plot) is much higher in FAU and EMT than the other systems at the same temperature and pressure. For some systems, the effect of interfaces and grain boundaries were also examined. The results illustrate how simulation of zeolite systems containing thousands of atoms for millions of time steps can be carried out in a reasonable time frame on today's computers, providing a powerful tool for the design and understanding of diverse phenomena on the atomic scale.

References

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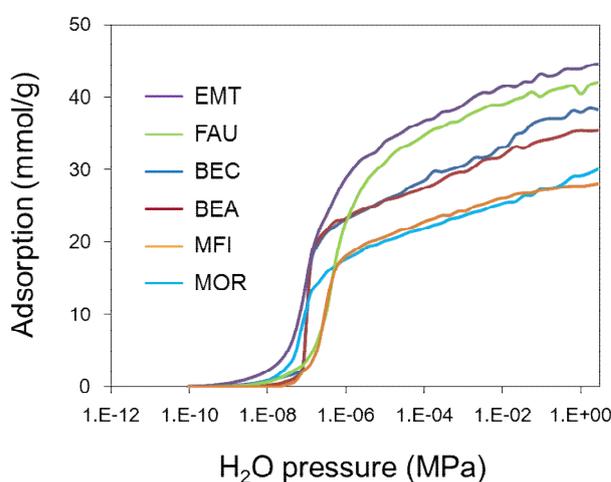[6] K. Refson, Comp. Phys. Comm. 126 (2000) 310.

FIG. 1. Adsorption isotherms for water molecules in siliceous zeolites MOR, MFI, FAU, EMT, BEA, and BEC calculated from Monte Carlo simulations in the grand canonical ensemble at 500 K.
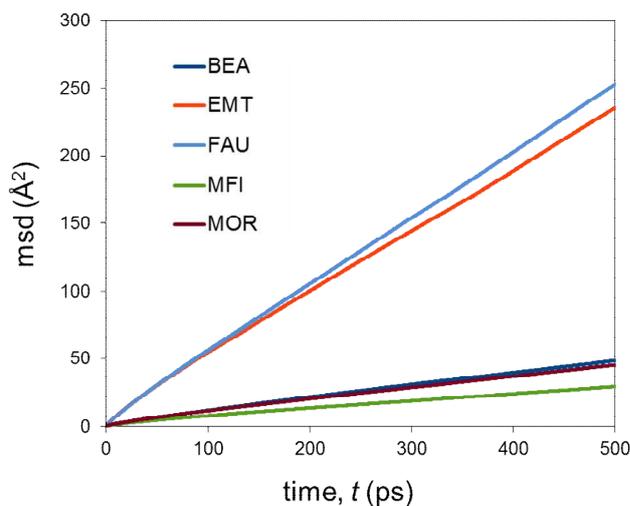

FIG. 2. Mean square displacements of water molecules in 100% siliceous BEA, EMT, FAU, MFI and MOR zeolites at 500 K for an external steam pressure of 16 Pa.