

Dynamics of Exchange at Gas-Zeolite Interfaces I: Pure Component *n*-Butane and Isobutane

M. Chandross*,† E. B. Webb III,† G. S. Grest,† M. G. Martin,‡ A. P. Thompson,‡ and M. W. Roth§

Mail Stop 1411, Sandia National Laboratories, Albuquerque, New Mexico 87185, Mail Stop 1111 Sandia National Laboratories, Albuquerque, New Mexico 87185, and Texas A&M University, Department of Physical and Life, Sciences, Corpus Christi, Texas 78412

Received: August 15, 2000; In Final Form: February 23, 2001

We present the results of Molecular Dynamics and Monte Carlo simulations of *n*-butane and isobutane in silicalite. We begin with a comparison of the bulk adsorption and diffusion properties for two different parameterizations of the interaction potential between the hydrocarbon species, both of which have been shown to reproduce experimental gas–liquid coexistence curves. We examine diffusion as a function of the loading of the zeolite, as well as the temperature dependence of the diffusion constant at loading and for infinite dilution. Both force fields give accurate descriptions of bulk properties. We continue with simulations in which interfaces are formed between single component gases and the zeolite. After reaching equilibrium, we examine the dynamics of exchange between the bulk gas and the zeolite. In particular, we examine the average time spent in the adsorption layer by molecules as they enter the zeolite from the gas in an attempt to probe the microscopic origins of the surface barrier. The microscopic barrier is found to be insignificant for experimental systems. Finally, we calculate the permeability of the zeolite for *n*-butane and isobutane as a function of pressure. Our results underestimate the experimental results by an order of magnitude, indicating a strong effect from the surface barrier in these simulations. Our simulations are performed for a number of different gas temperatures and pressures, covering a wide range of state points.

I. Introduction

Zeolites are microporous materials that are ideally suited to a number of different industrial applications such as catalytic cracking or hydroisomerization of hydrocarbon molecules as well as ion exchange in desiccant or purification applications. Zeolites with medium pore sizes, such as silicalite (structure type MFI),¹ are additionally useful for separations processes, as their openings are approximately the same size as the kinetic diameter of many small molecules. As such, the utility of any given zeolite in a separations application is strongly dependent on the preferential adsorption, as well as the relative diffusivities of the sorbed species.

There exists a large body of theoretical^{2–6} and experimental^{7–14} work that investigates the diffusion properties of small alkanes in zeolites. Simulations are generally performed with either Molecular Dynamics (MD) or Monte Carlo (MC) methods,¹⁵ both of which give calculated diffusivities that agree well with each other, although the MC methods, not having a true time dependence, rely on transition state theory for rate constants. The experimental situation is much less clear. Experimental diffusion constants can be measured through both microscopic and macroscopic methods, with the calculated diffusivities differing by an order of magnitude or more between the two methods. Although macroscopic studies measure the diffusion

of the molecules indirectly, as in supported membrane studies where the diffusion is calculated from the permeation flux, the microscopic measurements directly follow the mean-squared displacement of individual molecules. This is the same method that is traditionally used in simulations, and it is for this reason that simulations tend to agree more with microscopic diffusion studies rather than macroscopic. It has been suggested that the difference between the macroscopic and the microscopic measurements lies in the improper assumption of Fickian diffusion in the former¹⁶ or the difference between the diffusion of gas-phase and adsorbed components,¹⁷ but this discussion lies outside the scope of this paper. With the above in mind, when both macroscopic and microscopic measurements are available for comparison with our simulations, we only use the microscopic measurements.

Simulations of molecular adsorption on zeolites have traditionally been MC studies of adsorption isotherms.^{18–22} Although MC methods are much more efficient for computing equilibrium properties of the gas/zeolite system than MD, MC is not well suited for calculating time dependent properties. We are primarily interested in the dynamics of exchange between the gas and adsorbed phases through direct analysis of molecular trajectories which are not available from MC interface simulations. In fact, although our MC studies include a gas phase in the simulation, most do not, instead relying on parameterized equations of state that equate a calculated chemical potential with a gas pressure.²² It is for these reasons that we have focused our transport studies on MD simulations. We have verified that MD simulations equilibrate to the state points as given by the

* Mail Stop 1411, Sandia National Laboratories, Albuquerque, New Mexico 87185.

† Mail Stop 1111 Sandia National Laboratories, Albuquerque, New Mexico 87185.

‡ Texas A&M University, Department of Physical and Life, Sciences, Corpus Christi, Texas 78412.