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Surface Resistance to Heat and Mass Transfer in a Silicalite Membrane. A Non-Equilibrium Molecular Dynamics Study.

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1. Introduction

Zeolites are microporous materials which are ideally suited for different industrial applications, e.g. as separators or catalysts. Their applicability is determined by the dynamical and the adsorptive properties of the molecules inside their micropores.

Adsorption kinetics in zeolite has been explained as a two-step process, adsorption on the external crystal surface and subsequent inter-crystalline diffusion [1]. Recently much attention has been given to the resistance to transport of molecules at the external surface. It has been attributed to the crossing of potential barriers at the entry of the pores [1] or/and to the probability that a gaseous molecule sticks to the external surface [2]. Moreover, in the early 80's, Ruthven suggested the presence of additional heat resistances at the external surfaces that slow down the kinetics of the exothermic adsorption processes [3]. Here, using non-equilibrium molecular dynamics simulations (NEMD), we give evidences for the presence of mass and heat resistances at the external surface of a silicalite-1 membrane when n-butane is adsorbed [4].

2. Model and simulation details

The initial system was composed of an infinite membrane of silicalite-1 in contact with a gas of 250 molecules of n-butane. The external surfaces of the crystal were flat and normal to the straight channels (y directions). The silicalite was composed of 18 unit cells ([2 3 3]) and the butane molecules were modeled using a united atom model. Both were flexible and interacted with Lennard-Jones potentials. At time $t=0$ contact was made between the two phases and, by integrating the equation of motion, the gas molecules moved and part of them was adsorbed in the zeolite pores until equilibrium was reached.

A velocity rescaling thermostat was applied on the gas phase at the end of the simulation box in order to mimic the real uptake-experiments. The heat released by the adsorption process first accumulated in the crystal and subsequently flowed to the gas phase where it was removed by the thermostat. More details can be found elsewhere [4].

3. Results and discussion

The adsorption was followed until the equilibrium state and was characterized by two stages as shown in Fig.1. The first stage is governed by a large chemical driving force, which leads to a rapid uptake of butane, and the large enthalpy of adsorption ($\Delta H = -61.6$ kJ/mol butane) explains the accompanying temperature rise in the crystal.

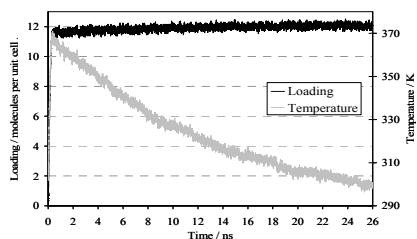


Fig. 1 Loading and average temperature of the membrane as function of time

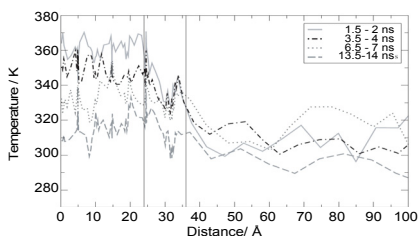


Fig. 2 Temperature profile as a function of the distance from the center of the zeolite during different periods of the second stage of the adsorption.

In the second stage the chemical driving force is very low and the thermal driving force created across the external surface relaxes slowly to zero as shown in Fig. 2. A thermal conductivity of 3.4×10^{-4} W/K was found for the surface. As the temperature decreases the chemical potential of butane goes down, leading to a corresponding slow influx of butane.

In order to study the effect of the structure of the external surface on the kinetics, additional simulations were performed considering a non-flat surface, which exhibited half zig-zag channels. The kinetics was characterized by a 25 % faster first step (smaller mass resistance), by no change in the relaxation time of the thermal driving force (second step), and by the same equilibrium state. The mass resistance is related to the probability of adsorption/ desorption of gas in zeolite. The better access to the pore openings for the second surface may thus explain the faster kinetics in this case. Heat conduction takes place by collisions, but in the absence of a net mass flux, so a constant thermal conductivity is understandable. The end state is a thermodynamic state that does not depend on the structure.

3. Conclusion

In agreement with previous analysis based on experimental results [3], we found that the adsorption kinetics of n-butane on silicalite is characterized by two non-isothermal steps. The adsorption process appears to be limited by the relaxation time of the thermal force due to the presence of a large thermal resistance at the external surface. This may help explain why non-equilibrium techniques can give much smaller diffusion coefficients than equilibrium techniques [5]. We have also found that the nature of the external surface does not affect the kinetics of the heat exchange but only the mass transfer.

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