

## The Coupled Transport of Heat and Mass across a Silicalite Surface. Non-Equilibrium Molecular Dynamics Simulations of *n*-Butane.

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### 1. Introduction

It is well known that the surface can pose a barrier to transport. Heat and mass transport across surfaces are then described by contact resistivities. Less well known is that the coupling coefficient can be large in these cases, and that the simple transport laws will therefore fail to capture the phenomena [1]. Experimental investigations of such transports are very difficult, because of the small surface thickness, typically a few nanometers. In the following we report on non-equilibrium molecular dynamics simulations that were done to investigate and quantify these resistivities. The transports of *n*-butane onto and into an external surface of silicalite were investigated as an example of a typical separation system.

### 2. Model and simulation details

The system was composed of an infinite membrane of silicalite-1 in contact with gas of *n*-butane. The external surfaces of the crystal were flat and normal to the straight channels (*y* directions). The silicalite was composed of 36 unit cells [2 6 3], and the butane molecules were modelled using a united atom model. Both compounds were flexible and the atoms interacted with Lennard-Jones potentials. In order to obtain the different surface resistivities, stationary mass and heat fluxes were applied along the simulation box (through the gas, the surface and the zeolite crystal). Details about the simulations can be found elsewhere [2].

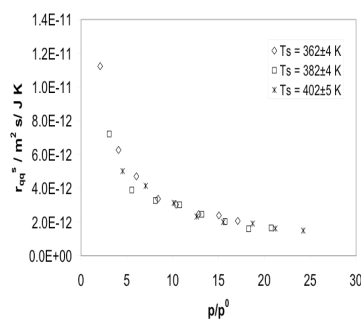


Fig. 1: Surface heat resistivity as a function of the gas pressure

### 3. Results and discussion

The surface total resistivity to heat is shown in figure 1. We see a decrease as the surface temperature or the gas pressure increases. The stationary state mass resistivity of the total surface was, on the contrary, rather independent of the temperature and of the

gas pressure. The structural details of the surface had a large influence on this resistivity, explaining why other effects were insignificant.

For the first time we report the coupling coefficient between heat and mass transport. The simulations gave a negative coupling resistivity, increasing with an increase in the gas pressure. This coefficient will explain for example the kinetics of adsorption during non-isothermal adsorption, as it gives the effect of a thermal driving force on the mass flux. The negative value means that a positive thermal force hampers a mass flux. In this sense, the coupling coefficient adds to the thermal resistance to mass flow.

A further analysis of the resistivities showed that the main contribution to the thermal resistivity came from the side of the surface that is facing the gas. The side that is facing the silicalite was decisive for the mass as well as the coupling resistivities.

These resistivities were described by non-equilibrium thermodynamics. This theory is valid for heterogeneous systems. The surface, even on small scales like here, is dealt with as a separate thermodynamic system. The theory gives a systematic description of transport phenomena into and across a surface that is bounded by two homogeneous phases.

#### **4. Conclusion**

We used molecular dynamics simulation to get access to the resistivity coefficients for transport of heat and mass across the external surface of silicalite-1 in contact with a gas of n-butane. We pointed out the role of the coupling phenomena between heat and mass transport, and the fact that it cannot be neglected in the description of adsorption kinetics.

#### **References**

- [1] S. Kjelstrup, D. Bedeaux, *Non-Equilibrium Thermodynamics of Heterogeneous Systems*, World Scientific, London, 2007
- [2] I. Inzoli, S. Kjelstrup, D. Bedeaux, J.M. Simon, Transport coefficients of n-butane into and through the surface of silicalite-1 from non-equilibrium molecular dynamics study, in print in *Microporous and Mesoporous Materials*.