

## The Nature of Surface Barriers on Nanoporous Solids Explored by Microimaging of Transient Guest Distributions and Monte Carlo Simulations

*Florian Hibbe<sup>1</sup>, Lars Heinke<sup>1,2</sup>, Christian Chmelik<sup>1</sup>, Sanhita Pramanik<sup>3</sup>, Jing Li<sup>3</sup>, Douglas M. Ruthven<sup>4</sup>, Despina Tzoulaki<sup>1,5</sup>, Jörg Kärger<sup>1</sup>*

<sup>1</sup>University of Leipzig, Faculty of Physics and Geosciences, Department of Interface Physics, 04103 Leipzig, Germany, E-Mail: hibbe@physik.uni-leipzig.de

<sup>2</sup>Lawrence Berkeley National Laboratory, Materials Science Division, Berkeley, California 94720, United States

<sup>3</sup>Rutgers University, Department of Chemistry and Chemical Biology, Piscataway, New Jersey 08854, United States

<sup>4</sup>University of Maine, Department of Chemical Engineering, Orono, Maine 04469, United States

<sup>5</sup>Technical University of Munich, Faculty of Chemistry, 85748 Garching, Germany

### 1. Introduction

Nanoporous solids are attractive materials for energetically efficient and environmentally friendly catalytic and adsorption separation processes. Although the performance of such materials is largely dependent on their molecular transport properties, our fundamental understanding of these phenomena is far from complete. This is particularly true for the mechanisms that control the penetration rate through the outer surface of these materials (commonly referred to as surface barriers). Recent detailed sorption rate measurements with Zn(tbip) crystals combined with Monte Carlo simulations have greatly enhanced our basic understanding of such processes.

### 2. Experimental Results

In conventional models that describe the mass transport in porous materials the diffusion ( $D$ ) and surface permeation ( $\alpha$ ) were - in analogy to the experimental results - assumed to be controlled by different mechanisms and to vary independently of each other. To find the concentration dependences of the intra-particle diffusivities and surface permeabilities in MOFs of type Zn(tbip) follow similar patterns of concentration and temperature dependence was therefore a complete surprise[1,2].

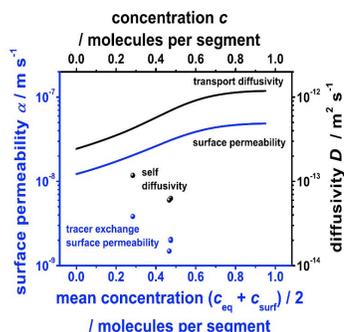


Fig. 1: Transport diffusivity and surface permeability of propane in MOF Zn(tbip) at 295 K as calculated from uptake experiments (non-equilibrium) and tracer exchange experiments (equilibrium).

An even more interesting finding was provided by considering the permeability/diffusivity ratio,  $\alpha/D$  (Fig. 1). Remarkably, the  $\alpha/D$  ratio of an individual crystal remains invariant with changes in (i) the type of the guest molecules, (ii) the loading (i.e., concentration of guest molecules), and (iii) the type of the diffusion process considered, i.e. transport diffusion (measured under nonequilibrium conditions) or self- (tracer) diffusion (under equilibrium conditions)!

These results indicate that, in contrast to the conventional picture of transport resistances at phase boundaries as homogeneous layers of dramatically reduced diffusivities, surface permeation and intra-crystalline diffusion in Zn(tbip) are evidently controlled by the same molecular mechanism [2]! The experimental evidence therefore suggests that only a very small fraction of the pores are directly accessible from the outside atmosphere. After having passed these “entrances”, however, molecules are able to diffuse at the same rate as anywhere else within the pore space. Filling of the blocked pore channels may be accomplished via structural defects (“windows” between adjacent channels) which are known to occur even in seemingly ideal crystals (Fig. 2).

Monte Carlo simulations of the adsorption of hard spheres in a crystal topology based on exactly the model developed above were carried out and compared to the experimental results: as reported in [3] transient guest profiles during uptake and release in such structures coincide with the patterns for homogeneous resistances on the material surface. In further calculations it was also possible to estimate the amount of open pores (only one pore under 2500) and the possibility for the existence of an interconnection between two cavities (5% per cavity) from the simulated profiles.

### 3. Conclusion

The surface resistance in Zn(tbip) has been shown to arise from the complete blockage of most of the pore entrances on the outer surface, while the transport resistance of the remaining open pores is negligibly small. More generally, the revealed correlation between intracrystalline diffusion and surface permeation provides a new view of the nature of transport resistances in nanoporous materials acting in addition to the diffusion resistance of the regular pore network, leading to a rational explanation of the discrepancy which is often observed between microscopic and macroscopic diffusion measurements.

### References

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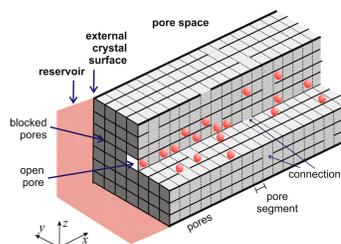


Fig.2 : Model of a Zn(tbip) crystal as derived from the experimental findings and used in the Monte Carlo simulations.