diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Loading Dependence of Diffusion in Zeolites: Combined Benefits of Microscopic Measuring Techniques and Theoretical Approaches

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1. Introduction

Nanoporous materials are widely used as catalysts and adsorbents in applied chemistry and technology. Zeolites, with their well-defined, uniform and molecular-sized pore system, are one of the most important examples of such materials. Molecular transport is of crucial importance for many of their applications. One of the challenging tasks in chemical engineering is the design and optimization of zeolite-based processes by employing computer simulations. Hence, for precise predictions it is essential to have a detailed fundamental understanding of the transport processes.

In the present work, molecular transport in two prominent representatives of zeolite structure types was investigated using IR microscopy (IRM) and interference microscopy (IFM). The results were compared with the predictions of theoretical approaches.

2. Experimental

IFM is based on following the change of the optical density of a zeolite crystal during molecular uptake and provides the possibilty to calculate two-dimensional intracrystalline concentration profiles with an unprecedented high spatial resolution. The overall sorption rates of individual zeolites were also measured by IRM. One important feature of IRM is the ability to pinpoint adsorbates by their characteristic IR bands.

3. Results and Discussion

Ferrierite consists of a two-dimensional system of mutually intersecting channels with different window sizes. The characteristic properties of the investigated ferrierite-methanol system have been examined in a previous work [1]. The main finding was that, due to blockage of the larger pore entrances, the transport can be considered as to proceed like in a one-dimensional system along the smaller channels with cage-window structure. The analysis of the measured transient concentration profiles by direct application of Ficks 2nd law allowed the determination of the loading dependence of the transport diffusivity *D*. The thermodynamic factor derived from the adsorption isotherm was used to calculate the "corrected" diffusivity D_0. Both quantities increase strongly with loading. This finding agrees well with results of computer simulations in zeolites with similar pore topology

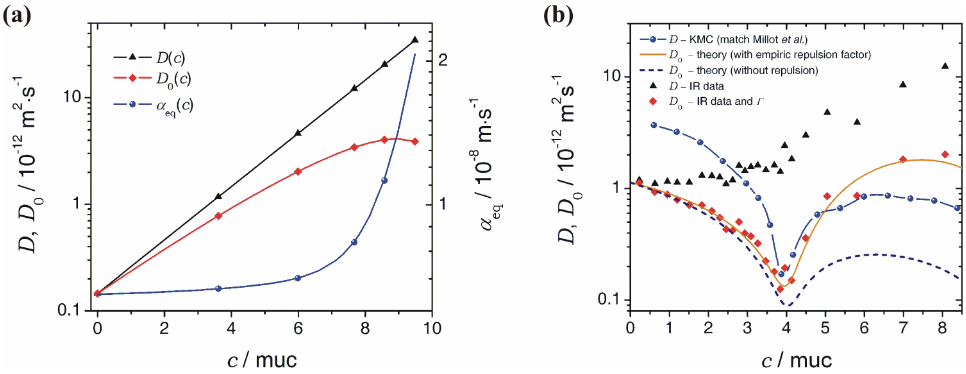

Figure 1. (a) Methanol in Si-ferrierite: loading dependence of D [1], D_0 and α_{eq}. **(b)** *Iso*-butane in silicalite-1: loading dependence of diffusivity determined from IRM measurements. The agreement with the prediction of theoretical models [2] is remarkable.

(i.e. LTA, CHA). The increase of D_0 might be explained by a decrease of the energy barrier for diffusion through the 8-ring windows, caused by the repulsive forces between molecules within a cavity. A surface resistance was found to reduce the uptake rates. The surface permeability at equilibrium, α_{eq}, was calculated from IR tracer-exchange experiments assuming $D_0 \approx D_{tracer}$, which is typically true for zeolitic cage-window structures.

The diffusivity of *iso*-butane in the intersecting channels of silicalite-1 has been determined from IR uptake experiments. $D_0(c)$ was calculated analogously. In contrast to methanol in ferrierite, D_0 decreases with loading, approaching a minimum at 4 molecules per unit cell (muc). At a loading of 4 muc, all intersections, acting as preferred adsorption sites for *iso*-butane, are occupied by one molecule. The consequences on the diffusivity have been investigated by theoretical considerations and KMC simulations [2]. The agreement with the theoretical model is remarkable, especially when molecular repulsions are taken into account. The numbers derived in KMC simulations, which were tuned to match the experimental data of Millot *et al.*, are approximately 3 times larger. This discrepancy might result from the internal structure of the investigated crystals.

4. Conclusion

The measured loading dependence could be successfully related to results obtained in computer simulations. This study underlines the benefit of combining experimental investigations with theoretical modelling. Simulation results are important in understanding the transport process. However, the influence of the non-ideal real-structure on molecular uptake can only be accessed by experiments which in turn might help to optimize the theoretical models.

References

[1] P. Kortunov, L. Heinke, S. Vasenkov, C. Chmelik, D.B. Shah, J. Kärger, R.A. Rakoczy, Y. Traa and J. Weitkamp, *J. Phys. Chem. B* **110** (2006) 23821-23828.

[2] R. Krishna and D. Paschek, *Chem. Eng. J.* **85** (2002) 7–15.