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

Diffusion Anisotropy in a Single Crystal of Silicalite-1 Studied by interference Microscopy

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1. Introduction

MFI-type zeolites are among the most important zeolite catalysts. Though mass transfer is known to be one of the limiting factors in the overall performance of heterogeneous catalysts [1], our knowledge about these processes is still not adequate for their importance. Diffusion measurement with MFI-type zeolites is complicated by the anisotropy of the zeolite lattice and the occurrence of twinning polymorphism [2,3] with the possibility of the formation of additional transport resistances at the twinning interfaces [4].

Though the anisotropy of the MFI pore structure has been revealed in both PFG NMR studies [5] and orientation-dependent uptake [3], our knowledge about the principal values of the diffusion tensor and about the orientation of the tensor axes within the MFI crystals is still incomplete.

The particular challenge of such studies results from the necessity of ensuring reproducible uptake and release experiments with one and the same crystal under different orientations [6-8]. Experiments of this type are only possible if the system under study remains absolutely unaffected by the different sequences of treatment. This requires a particularly sophisticated and careful handling of the zeolite single-crystal under study. The recent advent and exploitation of interference microscopy (IFM) in diffusion studies with guest molecules in nanoporous materials [9] allows us to measure, for the first time, three-dimensional concentration profiles in a single crystal of Silicalite-1.

2. Results and Discussion

The experiments were performed with 2-methylbutane as the guest molecule at a pressure of 1mbar at 294K in a crystal of Silicalite-1 (40x25x39µm) with a rounded-boat shape (see figure 1).

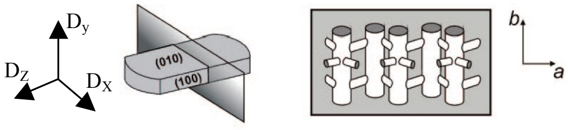

Figure 1: MFI pore system for a single crystal and the components of the diffusion tensor, Dx, Dy, Dz [10].

The diffusion coefficients are obtained by fitting the concentration profiles to a model that takes account of the surface permeability and the variation of the diffusivity with loading. The results given here correspond to the values at zero loading (Table 1).

Direction	Diffusivity ($m^2.s^{-1}$)	Surface permeability ($m.s^{-1}$)
x	$8.9 \cdot 10^{-14}$	$1.2 \cdot 10^{-7}$
y	$2.0 \cdot 10^{-13}$	$1.2 \cdot 10^{-7}$

Table 1: Diffusion and surface permeability tensor components

While the surface permeabilities are essentially identical, there is a pronounced difference in the diffusivities in x and y direction. Most interestingly, the diffusivity in crystal x-direction coincides with the diffusivity measured by Tzoulaki et al. ($D_{self} = 0.9 \cdot 10^{-13}$ $m^2.s^{-1}$) [11]. In those experiments coffin-shaped crystals have been used which are known to be composed of sub-units [3,10] where molecular uptake is dominated by transport along the zigzag channels. One might speculate, therefore, that the crystals presently under study approach the structure of real single-crystals, with the crystal x direction coinciding with the crystallographic a direction, i.e. the direction of the zigzag channels. This assumption would be supported by the notably larger diffusivities in y direction, corresponding to a reduced diffusional resistance in the straight channels. Work is in progress to confirm these conclusions by both diffusion studies with guest molecules of varying shape and structural analysis.

3. Conclusion

For the first time, diffusion anisotropy was observed experimentally in a single crystal of Silicalite-1. Nevertheless further experiments are still required to confirm this indication that the MFI particles under study may be considered as single crystals.

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