diffusion-fundamentals

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

Exploring the Influence of Surface Resistance of Nanoporous Particles on the Molecular Transport by PFG NMR

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Introduction

Understanding of the transport of guest molecules through the beds of nanoporous particles (e.g. zeolite crystallites) is required for various industrial applications, such as mass separation and catalysis. Pulsed field gradient (PFG) NMR has proven to be an invaluable tool of monitoring molecular displacements in a broad range of length scales, from below 100 nm up to tens of micrometers. This method has been successfully applied for the determination of molecular intracrystalline diffusivities in zeolites for more than 30 years [1]. However, the industrially produced nanoporous materials, in particular zeolite, may often be characterized as agglomerates of crystallites containing a large amount of various structural defects. Moreover, those nanoporous specimens are much smaller in size than laboratory-synthesised ones and usually used in form of beds, pellets or membranes. In such materials, the intracrystalline diffusion is not the only and not necessarily a predominant mechanism of mass transfer, at the length scale accessed by PFG NMR. It was found that functional properties of nanoporous materials depend largely on such phenomena as the intermolecular exchange between the intra- and intercrystalline areas and on the surface resistance of the crystalline particles to mass transfer. Due to the ability of monitoring diffusion in an extremely broad range of molecular displacements, PFG NMR has a big potential in studying the transport properties of sorbates in nanoporous crystallites. It will be shown that the combined application of PFG NMR and dynamic Monte Carlo simulations presents an especially powerful approach, which allows obtaining quantitative information on transport properties of real-world systems.

Exploring the surface permeability by PFG NMR and computer simulations.

In reference [2], a new method to determine the surface permeability of nanoporous crystals was proposed. It is based on the comparison of experimental data on tracer exchange and intracrystalline molecular mean square displacements as obtained by the PFG NMR tracer desorption technique with the corresponding solutions of the diffusion equations via Monte Carlo simulations. Namely, in addition to the conventional NMR tracer desorption analysis, in which the fraction N_{rem}/N_0 of molecules that after a given time have not yet left their crystallites is studied, the normalized effective diffusivities of the molecules D/D_0 is used. The correlations between these two values dramatically depend on the surface permeability of the crystals (fig.1). Comparison of the experimental results with Monte Carlo simulations of molecular dynamics gives the parameter $\alpha R/5D_0$. It is easily identified as the ratio of the time constants which would result in the limiting cases of intracrystalline diffusion- (large $\alpha R/5D_0$) and surface barrier-limited exchange (small $\alpha R/5D_0$). The application of the new method has been demonstrated in reference [3]. The surface permeability of zeolite crystals of type NaCaA for small alkane molecules (methane and ethane) was estimated.

Generally, the industrially produced nanoporous materials, e.g. zeolite crystallites, are much smaller in size (about a few micrometers). During accessible observation times almost all molecules of the sorbate are able to overcome distances larger than the size of the crystallites. Hence, they are able to leave the interior of the individual crystal and diffuse through the intercrystallite space, demonstrating the regime of *long-range diffusion*. In this context we are going to consider the question how under such conditions the long-range diffusivity can be influenced by the surface resistance, or what is the possibility to estimate the surface permeability from the long-range diffusion coefficient which can be measured by using PFG NMR.

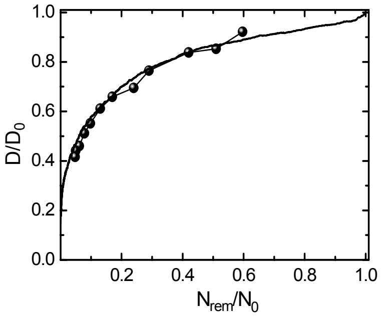

Fig. 1 Correlation plot of D/D_0 and N_{rem}/N_0 obtained for methane in zeolite NaCaA (35 μm crystal) (circles) with the corresponding theoretical curve (line). Visual comparison with the Monte Carlo simulation gives the value of the parameter $\alpha R/5D_0$. The theoretical curve with $\alpha R/5D_0=2$ is found to provide the best fit to the experimental data and provides the permeability $\alpha = (0.78 \pm 0.3)\times 10^{-3}\,\mathrm{m\,s^{-1}}$.

Conclusions

We demonstrate that combining the dynamic (lattice) MC simulations and PFG NMR measurements can lead to new insights into details of translational dynamics of guest molecules on the external surface of microporous materials. Namely, for the two zeolite specimens (5 and 35 μm) investigated, already in the as-synthesized crystals notable surface resistances have been observed. Surface permeability has been studied in dependence on temperature, sorbate and crystal size. The long-range diffusivity can also be considered as a valuable parameter to provide information about the surface resistance of the nanoporous particles. In particular, the propagator presentation may open up a new way for the experimental determination of surface barriers by means of PFG NMR.

References

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