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Exploring the influence of the surface resistance of nanoporous particles on molecular transport

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Abstract

Molecular transport through the nanoporous particles, in particular, zeolite crystallites, is influenced both by intracrystalline diffusion and surface resistance. In comparison to zeolite crystallites with ideal structure, molecular transport in real-world zeolite particles may often be influenced by the surface barriers resulting from various defects at the surface of the crystallite. The potentials of the combined use of the pulsed field gradient NMR and dynamic Monte Carlo simulations for exploration of the surface permeability of nanoporous particles are demonstrated.

Keywords

Zeolites, surface barriers, NMR, long-range diffusion, simulations

1. Introduction

The industrial processes of catalysis and mass separation are mainly based on using nanoporous materials as adsorbents. In many cases, the performance of these processes is determined by the transport of the sorbate molecules through a nanoporous material consisting of individual crystallites. A detailed knowledge of the diffusion properties of such materials is therefore a necessary prerequisite of their efficient use. The pulsed field gradient (PFG) NMR has proven to be an invaluable tool for monitoring molecular displacements in a broad range of length scales, from below 100 nm up to tens of micrometers. Representing the probability distribution of molecular displacements as a function of time, the "propagator" representation provides a straightforward means to discriminate between the rate of mass transfer inside each individual crystallite (*"intracrystalline"* diffusion) and through the crystallite assemblages (*"long-range"* diffusion). This method has been successfully applied for the determination of molecular intracrystalline diffusivities in nanoporous systems such as zeolites for more than 30 years [1]. The most important earlier studies were performed with specially synthesised large crystals of such a size that during the experimental diffusion time the sorbate molecules were not able to leave their individual host crystallites [1-3]. Thus, the main mechanism studied was intracrystalline molecular diffusion within the single crystals. Nanoporous materials used in industrial application, in contrast, usually consist of much smaller particles of no well-defined shape and with a broad size distribution. Moreover, these particles may often be composed of agglomerates containing a large amount of structural defects, including surface defects of various origins, rather than of ideal crystals. In such materials, intracrystalline diffusion is not the only and not necessarily the predominant mechanism of mass transfer. In recent years, the attention has therefore been considerably shifted to length scales of the order of the crystalline size and larger. 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. It has been shown that the combined application of PFG NMR and dynamic Monte Carlo simulation presents an especially effective approach providing quantitative information on transport and structural properties of nanoporous materials [4]. In the present paper the new possibility to estimate the surface permeability of nanoporous crystallites based on PFG NMR measurements and computer simulation will be overviewed.

2. Exploring the surface permeability by PFG NMR tracer desorption technique

In reference [5], 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 [1], in which the fraction of molecules that after a given time have not yet left their crystallites N_{rem}/N_0 is studied, the normalized effective diffusivities of the molecules D/D_0 is used. The method is found to be particularly sensitive in the "intermediate" regime, when the influence of intracrystalline diffusion and surface resistances of the nanoporous crystal on molecular transport are comparable and the conventional method fails. The correlations between these two values dramatically depend on the surface permeability of the crystals (fig.1).

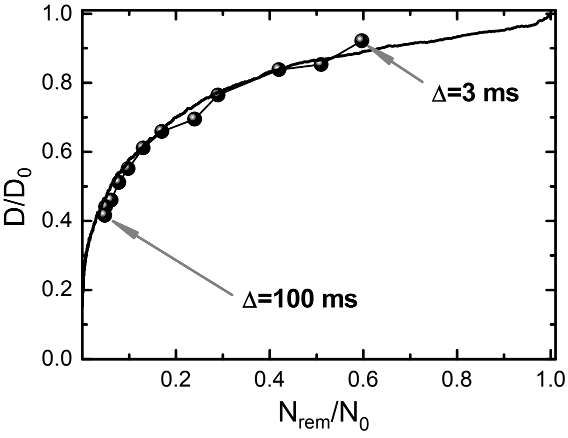

Fig. 1 Correlation plot of restricted diffusion (D/D_0) and tracer desorption (N_{rem}/N_0). Arrows point to minimal (3 ms) and maximal (100 ms) observation time of PFG NMR experiment. Visual comparison of the experimental data obtained for methane in zeolite NaCaA (for the 35 μm crystal) with the corresponding theoretical curve obtained by dynamic Monte Carlo simulations 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 value $\alpha = (0.78 \pm 0.3)\times 10^{-3}\,\mathrm{m\,s^{-1}}$.

Comparison of the experimental results with Monte Carlo simulations of molecular dynamics gives the parameter $\alpha R/5D_0$, where α and R denote, respectively, the surface permeability and the crystal radius. This expression 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 [6]. The surface permeability of zeolite crystals of type NaCaA for small alkane molecules (methane and ethane) was estimated. For the two zeolite specimens (5 and 35 μm) investigated, already in the as-synthesized crystals notable surface resistances have been observed. Surface permeabilities have been studied in dependence on temperature, sorbate and crystal size. Fig.1 presents the correlations of simulation data with the experimental findings for methane in NaCaA-type crystals of 35 μm diameter at room temperature. A complete set of the data obtained for these crystals is provided by Table 1 [6].

	methane		ethane	
	100°C	25°C	100°C	25°C
D_0 / m^2 s^{-1}	$(1.6\pm20\%)\times10^{-9}$	$(1.4\pm20\%)\times10^{-9}$	$(4.6\pm20\%)\times10^{-10}$	$(3\pm20\%)\times10^{-10}$
$\alpha R/(5D_0)$	1	2	0.4	0.6
factor of uncertainty *F*	10	1.5	1.5	3
α /10^{-3} m s^{-1}	0.85	0.78	0.068	0.051

Table 1. Summary of the experimental data determined for methane and ethane in zeolite NaCaA with crystal size 35 μm at different temperatures: intracrystalline diffusivity D_0, weight parameter $\alpha R/(5D_0)$ reflecting the relation of the relative contribution of diffusion and barrier resistance to overall molecular exchange, and surface permeability α. The parameter $\alpha R/(5D_0)$ results as the best visual fit of the experimental data to the theoretical curves (Fig.1). The accuracy of this fitting procedure is reflected by an uncertainty factor *F*. It is defined by the requirement that the real value of $\alpha R/(5D_0)$ and, essentially, also of α will be found with a probability of more than 80% in the interval of confidence, the limits of which are determined by multiplying the table data by $1/F$ and *F*, respectively.

3. Long-range diffusivity in beds of nanoporous particles

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 overcome distances larger than the size of the crystallites. Hence, they are able to leave the interior of the individual crystallite and diffuse through the intercrystallite space (“long-range” diffusion, sometimes referred to as “intraparticle” diffusion if the individual crystallites are compacted – often by means of some binder – to form a catalyst/adsorbent “particle”). The PFG NMR tracer desorption analysis is based on the time dependence of this fraction of molecules that, after a given time, have not yet left their crystallites. Therefore, the NMR tracer desorption analysis can not be applied for that small industrial samples. Often, the determination of the surface resistance turns out to be difficult to perform, since the industrially produced specimens are characterised by a large crystalline size distribution. Moreover, the much more complicated shape than generally found with laboratory synthesized crystallites provides additional problems. 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.

As a first step to respond to this problem, we performed dynamic Monte Carlo simulations of the diffusion in a bed of nanoporous particles. The structure of the two-dimensional model bed which we have used is presented in the fig.2.

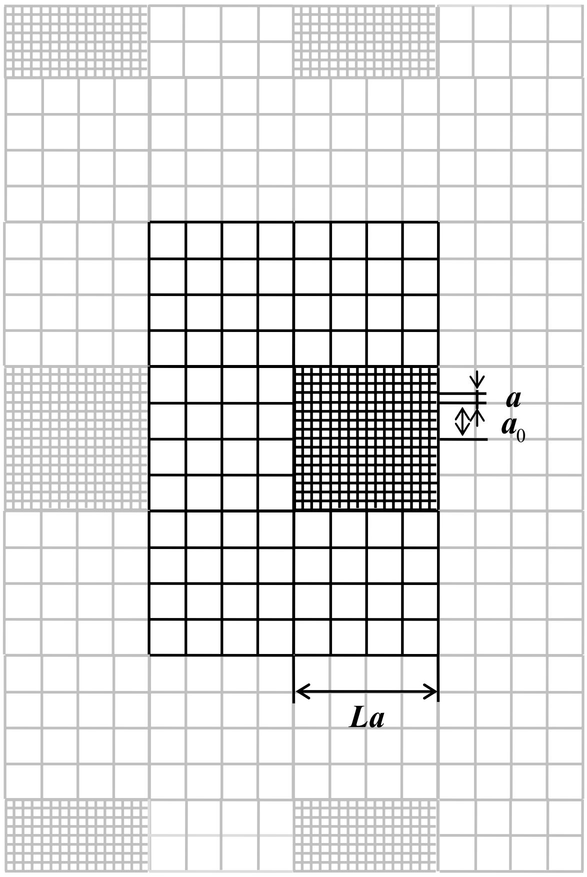

Fig.2 Two-dimensional model bed. Periodical structure is organized by repetition of the simulation unit consisting of the square crystal with the edge length *La* and the outer space (indicated by bold lines). The diffusion step length in the outer space exceeds the intracrystalline diffusion step length by a factor 4: $a_0=4a$.

In the simulations, we operate with a unit step length *a* and a time unit τ characterizing the time interval between two subsequent attempts to perform a diffusion step of length a on a square lattice of extension $La \times La$. Each (of the four possible) step directions is selected with equal probability. The probability that the step is actually performed is assumed to be given by the Boltzman factor $\exp\left(-\varepsilon_{diff}/RT\right)$, where ε_{diff} is the activation energy of intracrystalline diffusion. The diffusion step length a0 in the outer space exceeds the diffusion step length inside the crystal by a factor $\lambda >> 1$, i.e. $a_0=\lambda a$. That means, in particular, that we imply Knudsen diffusion to be the prevailing mechanism so that the magnitude of the effective mean free path (diffusion step length in outer space) remains constant with varying temperature.

The probability of jump from the boundary sites of the crystallites into the intercrystalline space is given by a factor $\exp\left(-\varepsilon_{des}/RT\right)$ with ε_{des} denoting the heat of adsorption, i.e. the difference in the potential energies of the diffusants in the free space between the crystals and the intracrystalline space. Moreover, the factor $\exp\left(-\varepsilon_{barr}/RT\right)$ is introduced, which additionally reduces the rate of both escape from the crystal and entrance into the crystal.

Thus, ε_{barr} represents the height of an energy barrier (the “surface barrier”) which the molecules have to overcome on both leaving and entering the crystal. In contrast to ε_{des}, the magnitude of ε_{barr} does in no way affect the distribution of the diffusants under equilibrium. Fig.3 displays the results of the simulations for $\varepsilon_{des} = 3\varepsilon_{diff}$ considering the cases without and with surface barriers.

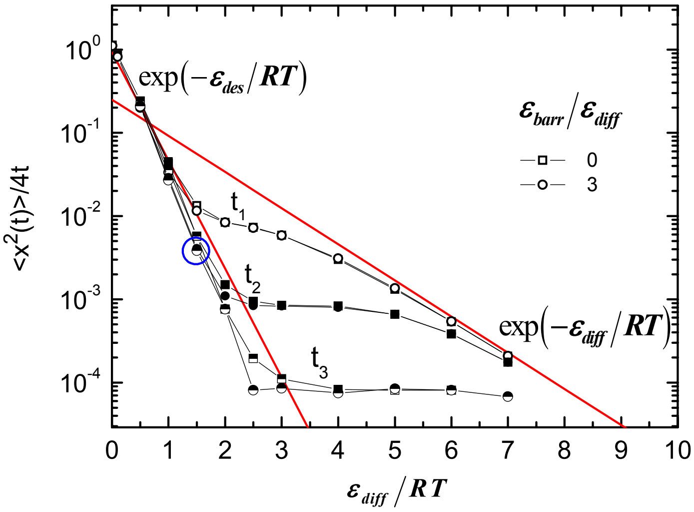

Fig.3 Dependence of the apparent diffusivity, calculated from the mean squared displacement, as a function of the temperature. Open, full and half-full points correspond to different observation times $t_1 < t_2 < t_3$ ($t_1=10^5$, $t_2=10^6$, $t_1=10^7$ Monte Carlo steps). The simulations have been performed with $\varepsilon_{des} = 3\varepsilon_{diff}$ and for $\varepsilon_{barr} = 0$ (squares) and $\varepsilon_{barr} = \varepsilon_{des} = 3\varepsilon_{diff}$. The large circle highlights the data point at $\varepsilon_{diff}/k_B T = 1.5$ which refers to the presentation in fig.4.

In complete agreement with the well established formalism of PFG NMR diffusion studies with zeolites [1], these diffusion regimes can be clearly distinguished. The regime of intracrystalline diffusion at the lower temperatures is merely controlled by the activation energy of diffusion. In the regime of restricted diffusion, at higher temperatures, the mean square displacement approaches the particle size. At higher temperatures, the displacements substantially exceed the particle dimensions establishing the regime of long-range diffusion. The slope of this part of the plot arises from the temperature dependence the equilibrium distribution of the diffusing molecules, which is directly related to the desorption energy. As to be required [7], diffusivities in the plateau are inversely proportional to the observation time.

While in the limiting cases of both intracrystalline diffusion and long-range diffusion there is essentially no difference between the diffusivities determined with and without an additional surface barrier, this difference becomes significant in the transient range from restricted to long-range diffusion. The difference becomes particularly obvious in the so-called propagator presentation shown in fig.4, i.e. in a plot of the probability distribution for molecular displacements during the PFG NMR experiment.

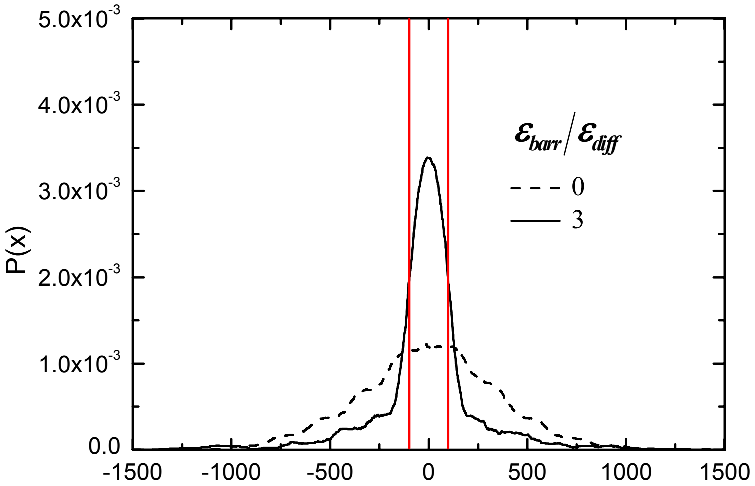

Fig.4 Probability distribution of the molecular desplacements (the “propagator” [8]) for the molecules moving through the two-dimentional model system with and without surface barriers for $\varepsilon_{diff}/RT = 1.5$ and 10^7 Monte Carlo steps (large circle in fig.3). The extension *La*=100 of a crystallite (edge length) is indicated by the two vertical lines.

Since the propagator is nothing else than the Fourier transform of the PFG NMR spin echo attenuation [8], the simulation results shown in fig.4 may open up a new way for the experimental determination of surface barriers by means of PFG NMR. The corresponding combined experimental and theoretical work is still in progress.

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