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Journal of Magnetic Resonance 185 (2007) 300–307

JMR
Journal of Magnetic Resonance

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# Exploring the surface permeability of nanoporous particles by pulsed field gradient NMR

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Received 6 November 2006; revised 8 January 2007
Available online 12 January 2007

## Abstract

A new method to determine the surface permeability of nanoporous particles is 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 equation via dynamical Monte Carlo simulations. 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. As an example, the surface permeabilities of two samples of zeolite NaCaA with different crystal sizes are determined with methane, as a probe molecule, at room temperature.

*Keywords:* Zeolites; Surface barriers; NMR; Permeability; Simulations

## 1. Introduction

Numerous technological processes in the industry of mass separation and conversion are based on the application of nanoporous materials, in particular of zeolites [1], as molecular sieves [2] and catalysts [3], respectively. In many cases, the performance of these processes is determined by the rate of molecular exchange between the nanoporous particles (the zeolite crystallites) and their surroundings. Pulsed field gradient NMR (often also referred to as pulsed gradient spin echo (PGSE) NMR) has proven to be an invaluable tool for exploring the intrinsic transport properties of such systems [4,5].

Representing the probability distribution of molecular displacements as a function of the time, the "propagator" representation [6] provides a straightforward means to discriminate between the rate of mass transfer within the crystallites ("*intracrystalline*" diffusion) and through the crystallite assemblages ("*long-range*" diffusion, sometimes referred to as "*intraparticle*" diffusion if the individual crystallites are compacted—often by means of some binder—to catalyst/adsorbent particles [7]). The coefficient of long-range diffusion may be shown [8,9] to result as the product of the relative amount of molecules in the intercrystalline space and their diffusivity. Under the precondition that the long-range diffusivity notably exceeds the intracrystalline diffusivity, the propagator may easily be separated into two constituents: a narrow one representing the displacements of those molecules which, after the given observation time $t$, have not yet left their crystallites, and a broad one (notably exceeding the crystal size) which is brought about by those molecules which, during $t$, have left the crystallites where they have resided at the beginning. The relative intensities of these two constituents (i.e. their space integrals) are directly proportional to the corresponding numbers of molecules. This means in particular that, on varying the observation time $t$ of the PFG NMR experiment, the respective relative intensities of the broad constituent represents nothing else than the values of the tracer exchange

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doi:10.1016/j.jmr.2007.01.006

curve $\gamma(t)$ for the considered observation times [10,11]. Tracer exchange curves represent the relative amount of labelled molecules which, having been initially inside the crystallites, are, after time $t$, found outside in the initially unlabelled surroundings. In contrast to the conventional way of attaining tracer exchange curves by applying, e.g., isotopes [12], the "NMR" tracer desorption technique operates in milliseconds till seconds. In [13] this option has for the first time been used to estimate the intensity of transport resistances on the surface of the individual crystallites ("surface barriers"). This estimate is based on the fact that exchange curves $\gamma(t)$ are most conveniently analysed in terms of the first statistical moment [14]

$$\tau_{\mathrm{ex}} = \int_{t=0}^{\infty} (1 - \gamma(t))\mathrm{d}t \tag{1}$$

which is easily rationalized as the time constant of molecular exchange, i.e. the mean life time of a molecule in the interior of a given crystallite. As a particular advantage of the moments method [9,14–16], the resulting first moment may be shown to be simply the sum of the first moment of each process possibly contributing to the overall behaviour. Since exchange curves are known to be rather insensitive to the particle shape, for simplifying the further analysis the crystallites are assumed to be spheres of radius $R$. Then, solution of the respective equations of mass transport [9,14–16] yields the simple relation:

$$\tau_{\mathrm{ex}} = \frac{R^2}{15D_0} + \frac{R}{3\alpha} \tag{2}$$

where $D_0$ denotes the intracrystalline diffusivity and $\alpha$ stands for the permeability of the crystal surface, the reciprocal value of which is a measure of the intensity of the surface barrier. The surface permeability is defined by the relation [17–19]:

$$j = \alpha(C_{\mathrm{surf}} - C_0) \tag{3}$$

where $j$ is the flux density through the crystal surface, $C_0$ the concentration in the crystal which would be established in equilibrium with the surrounding atmosphere and $C_{\mathrm{surf}}$ the actual concentration close to surface.

The intracrystalline diffusivity may be directly determined by PFG NMR with sufficiently small observation times, so that any disturbance by surface effects may be estimated [20] by application of the Mitra–Sen formalism [21] or neglected at all. Hence, with the determined value of $D_0$ and the mean life time $\tau_{\mathrm{ex}}$ resulting from the NMR tracer desorption curve via Eqs. (1) and (2) may be rearranged to yield, for a given value of $R$, the surface permeability.

Obviously, this way of analysis is trustworthy if the second term on the right-hand side of Eq. (2) turns out to notably exceed the first one, namely, for barrier-controlled molecular exchange. As soon, however, as both contributions are comparable (or, even worse, for molecular exchange controlled by intracrystalline diffusion) one has to take into consideration that uncertainties of a factor of two for both $\tau_{\mathrm{ex}}$ (variation of the observation time often fails to cover the total range of integration in Eq. (1)) and $R^2/15D_0$ (due to dispersion in the crystal size) are not unlikely, so that the second term of the right-hand side of Eq. (2) may turn out to be the difference between two equally large quantities with a big uncertainty. Such a situation would notably complicate if not even prevent to determine the surface permeability in the conventional manner. In the present communication we present a novel option to quantitate surface resistances by means of PFG NMR which is particularly sensitive under such conditions, where intracrystalline diffusion and surface resistance are of comparable influence on the overall transport behaviour, i.e. if the two terms on the right-hand side of Eq. (2) are of equal order.

## 2. Conception and simulation

The conventional way of estimating surface permeabilities by means of the PFG NMR technique has been sketched in Section 1. It is based on a comparison of the rate of molecular exchange between the intra- and intercrystalline space in an "NMR tracer desorption experiment" [10] with the genuine intracrystalline diffusivities. Surface resistances, i.e. the reciprocal values of the surface permeability, are obviously the larger, the more the experimentally observed exchange rates are exceeded by their estimates solely based on the intracrystalline diffusivities.

In the present communication we follow another correlation. We investigate the interdependence between the relative amount of molecules $\gamma(t)$ that during the time interval $t$ have left their crystallites, and the mean square displacement $\langle r^2(t)\rangle$ of the molecules that have remained within the crystallites during this very time interval. For this purpose, we consider a time interval $t$ during which a fixed fraction of the molecules, e.g. 50% (which means $\gamma(t) = 0.5$), have left their crystallites. The mean square displacement of the molecules remaining in the crystal may obviously be expected to be the larger, the larger are the surface resistances they have to overcome on leaving the crystallites. This is intuitively anticipated by realising that, in comparison with an infinitely extended crystallite, the mean square displacement in a finite crystallite is the more reduced, the more frequently the diffusing molecules are reflected by the crystallite surface as a consequence of a reduced surface permeability. We may expect therefore that, for a given relative amount $\gamma$ of molecules having exchanged with the surroundings, the mean square displacement of those still residing in one and the same crystallite is the smaller the larger are the transport barriers on the crystal surface.

The quantitation of this correlation may, in principle, be based on the solution of the diffusion equation with the relevant boundary conditions. The quantity directly accessible by the PFG NMR experiments, the mean square displacement, results from twofold integration over space, namely over all possible starting and final points of the molecular trajectories. Thus it is inherent to the considered type of