



# In-depth study of surface resistances in nanoporous materials by microscopic diffusion measurement



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## ABSTRACT

Experimental evidence leading to our present view on transport resistances on the external surface of nanoporous materials (“surface barriers”) is reviewed. First substantial arguments for the existence of surface resistances was provided by the direct measurement of intracrystalline diffusion, enabled by the application of the pulsed field gradient (PFG) technique of NMR to sufficiently large zeolite crystallites. With the advent of the techniques of micro-imaging and the thus established avenue towards monitoring transient guest concentrations, first in-depth studies of surface barriers, based on the measurement of their permeabilities, have become possible. Highlights among these studies were the detection of surface barriers formed by impermeable layers with dispersed holes, giving rise to proportionality between surface permeation and intracrystalline diffusion, and the determination of “sticking factors” which, in the present context, refer to the probability that, after colliding with the external surface, a molecule of the gas phase will surmount the surface resistance and get into the genuine pore space. The formation of surface barriers is, in conclusion, shown to be a rather complex phenomenon whose in-depth exploration necessitates efforts comprising a large spectrum of activities over essentially all fields of zeolite research and technology.

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## 1. Introduction

Nanoporous materials are well known to be key to many technologies [1,2]. In many of their applications, the rate of molecular exchange with the surroundings is among the key parameters deciding about their performance [3–7]. It is, simultaneously, an important feature of host–guest interaction under confinement making it an important physical quantity of fundamental research [7–12]. As a matter of course, molecular exchange between the pore space and the surroundings can never be faster than allowed by the rate of mass transfer in the interior of these materials, i.e. by the guest diffusivities. Over decades, however, intracrystalline diffusivities in zeolites and related nanoporous materials could only be determined by following the rate of uptake or release, by assuming that these processes are in fact limited by intracrystalline diffusion [13,14].

It was only with the introduction of the pulsed field gradient technique of NMR [15–17] that the direct measurement of intracrystalline diffusion has become possible. It came as a great surprise when, for several zeolitic host–guest systems, the thus

directly determined intracrystalline diffusivities were found to exceed those, previously estimated on the basis of “macroscopic” uptake and release measurements, by several orders of magnitude [18]. The existence of surface barriers was considered as one of the possible options for the explanation of this discrepancy. It was, however, not before the introduction of the techniques of micro-imaging that the recording of surface permeabilities allowed a direct quantification of these transport resistances.

The present contribution highlights this development up to its most recent progress. After an introduction into the different parameters of mass transfer and the options of their experimental determination in Section 2, Section 3 is devoted to various aspects of the investigation of surface barriers, including an assessment of the potentials and limitations of pulsed field gradient NMR (Section 3.1), the information available from (macroscopic) uptake and release measurements and their comparison with microscopically determined diffusivities (Section 3.2), the benefit of micro-imaging with first conceptions of the nature of these barriers (Section 3.3) and the description of how micro-imaging may be exploited to determine the probability that, upon colliding with the external surface of a nanoporous material from the surrounding atmosphere, a molecule would be able to get into the genuine pore space (Section 3.4).

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## 2. Transport parameters: definitions and options of measurement

In the context of this communication, we confine ourselves to considering the diffusional resistance of the genuine pore space of the nanoporous particle (e.g. a zeolite crystallite) under study and the transport resistance on the external surface, referred to as the surface barrier. The relevant transport parameters are the intracrystalline diffusivity  $D$  and the surface permeability  $\alpha$ .

Diffusivities may be introduced, by Fick's first law, as factors of proportionality between a concentration gradient  $dc/dx$  and the particle flux  $j$  generated by this gradient

$$j = -D_T \frac{dc}{dx}. \quad (1)$$

Here, the subscript T has been used for indicating that one is considering net mass transfer, i.e. a process occurring under non-equilibrium conditions so that the diffusivity ( $D_T$ ) is generally referred to as the transport (or Fickian) diffusivity [7]. Note that the transport diffusivity  $D_T$  is, in general, a function of the given loading  $c$ , but – as a prerequisite of its definition – it is clearly independent of the concentration gradient  $dc/dx$ . With the slightly modified notation

$$j^* = -D \frac{dc^*}{dx}. \quad (2)$$

Fick's first law is as well applicable to equilibrium conditions. Now one considers the flux of labeled molecules ( $j^*$ ) brought about by a gradient ( $dc^*/dx$ ) in the labeling of an otherwise uniform entity of guest molecules. In this case, the diffusivity ( $D$ , sometimes also noted as  $D^*$  or  $\mathcal{D}$ ) is referred to as the coefficient of self- or tracer diffusion [7]. Note, that the self-diffusivity depends, in general, on the total concentration  $c$  (i.e. the concentration of the labeled and unlabeled molecules) but, clearly, neither on the concentration  $c^*$  of the molecules which happen to be labeled nor on their gradient  $dc^*/dx$ .

Together with the definition of the respective diffusivities, Eqs. (1) and (2) do as well provide a recipe of their measurement, namely by simultaneously determining concentration gradients and fluxes. This procedure is, however, essentially confined to measurements by micro-imaging, as a consequence of the, in general, microscopic sizes of nanoporous particles. Macroscopic measurements have, therefore, to go a step further and base their analysis on the observation of overall phenomena, such as molecular uptake and release, and comparison with their theoretical predictions starting with Eqs. (1) and (2) and model assumptions. Thus, fractional uptake under diffusion limitation by a sphere of radius  $R$ , e.g., is known to be given by the relation [7,19]

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 D t / R^2). \quad (3)$$

It is important to mention that, in addition to the observation of tracer exchange phenomena (i.e. the exchange of labeled and unlabeled molecules), self-diffusivities may also be determined on the basis of the Einstein relation

$$\langle x^2(t) \rangle = 2Dt, \quad (4)$$

which states proportionality between the observation time  $t$  and the mean value of the square of the distance  $x$  over which, during this time  $t$ , the molecules have been shifted into a certain direction. Both definitions, Eqs. (2) and (4), are equivalent [20] so that, correspondingly, either of them may as well be used to determine self-diffusivities experimentally [7].

The magnitude of the transport resistance on the surface of nanoporous particles is represented by the reciprocal value of the

surface permeability  $\alpha$ . The surface permeability is defined as the factor of proportionality between the flux  $j(x=0)$  through the surface and the difference between the actual guest concentration  $c(x=0)$  in genuine pore space close to the surface and the pore space concentration  $c_{eq}$  in equilibrium with the externally applied guest pressure:

$$j(x=0) = \alpha[c(x=0) - c_{eq}] \quad (5)$$

Infinitely large permeabilities are immediately seen to correspond with an instantaneous equality of the boundary concentration with its equilibrium value since otherwise the left-hand side of Eq. (5) would yield infinitely large (and, hence, physically unreasonable) fluxes. This equality is known to hold when the influence of surface resistances on overall uptake or release may be totally excluded.

It is noteworthy that also surface permeabilities, just as the intraparticle diffusivities, may be considered under equilibrium and non-equilibrium conditions, depending on the given experimental conditions. There does not yet exist, however, a distinction in the nomenclature as introduced for the diffusivities. Surface permeabilities must also be expected to depend on the given concentrations. For tracer exchange experiments, i.e. for the determination of surface resistances under equilibrium conditions, it is simply the given equilibrium concentration which the permeability will depend on. In non-equilibrium measurements, i.e. during adsorption or release, this dependence may become more complicated: Rather than a particular concentration, a whole interval of concentrations is seen to appear in the defining relation, Eq. (5). Systematic studies with a particular host-guest system (propane in a metal-organic framework (MOF) of type Zn(tbip)) showed, however, that it was, essentially, the mean value of the concentration interval covered during transient uptake or release, on which the surface permeabilities did depend [21,22].

It is true that, in many cases, mass transfer within individual nanoporous particles may be affected by further resistances. They may be caused by stacking faults [23] in the crystal structure, hydration-induced blockage of "windows" between adjacent cavities [24] or by the interfaces between the different subunits [25–29] out of which nanoporous particles are, in many cases, known to be formed [30,31]. In such cases, however, the effective medium approach would allow us to consider, in place of the genuine pore-space diffusivity, an effective diffusivity, defined by the relation

$$\frac{1}{D_{eff}} = \frac{1}{D} + 1/\alpha_{intra} l, \quad (6)$$

where  $l$  denotes a mean value of the distance between these internal barriers and where the permeability  $\alpha_{intra}$  of these barriers is introduced in analogy with Eq. (5), now with the understanding that, on the right hand side, one is considering the difference between the concentrations on either side of the barriers.

## 3. Tracing surface resistances

### 3.1. Potentials and limitations of pulsed field gradient NMR

The pulsed field gradient (PFG) technique of NMR is able to determine the probability density  $P(x,t)$  that an arbitrarily selected (in general, hydrogen containing) molecule within the sample during an "observation time"  $t$  of typically milliseconds is shifted over a distance  $x$  of typically micrometers in a given direction (namely that of the field gradient applied) [7,32–34]. The samples under consideration in the present context are, in general, fused glass tubes containing the nanoporous host-guest system at equilibrium. The quantity  $P(x,t)$  is referred to as the mean propagator

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