Exchange Dynamics at the Interface of Nanoporous Materials with their Surroundings

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The evolution of transient concentration profiles in nanoporous materials is shown to provide direct information about the rate of molecular exchange at the interface of these materials with the surrounding atmosphere. This includes the quantitation of a surface permeability and, related with each other, of the sticking factor, i.e., of the probability that a molecule colliding with the external surface from the outside atmosphere, will in fact enter the genuine pore system of the material under study. Owing to the recent introduction of interference microscopy to this type of systems, the relevant experimental evidence has become directly accessible and is applied to two model systems which are found to differ notably in their interface dynamics.

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Introduction.—The permanent advent of new generations and families of nanoporous materials [1] and the associated increase in the multitude of their technical application as catalysts [2], molecular sieves [3] and host systems for opto-electronic devices [4] have stimulated fundamental research over a continuously enlarging spectrum of problems related to these systems. Owing to recent progress in the power and versatility of molecular modelling, these studies are dominated by theoretical investigations [5–7] while experimental studies are, in general, impeded by the complexity of the systems to be considered and, moreover, by notable divergences between the ideal structure as revealed, e.g., by diffraction experiments, and their real structure, where one stacking fault among thousands of perfect layers may control the overall dynamics [8,9].

As a consequence, one of the most crucial questions associated with nanoporous materials, namely, the rate of molecular exchange between the intraparticle, genuine pore space and the external atmosphere has only scarcely been considered. Most of these studies [10,11] are based on molecular simulations and urgently need their confirmation or falsification by direct experimental evidence. In addition to the macroscopic techniques like uptake and release measurements, the ZLC (zero-length column) method [12] and the FR (frequency response) technique [13], more and more also microscopic techniques have been established (pulsed field gradient (PFG) NMR [14,15], quasielastic neutron scattering [6,16], IR microscopy [17,18]). By them, in principle, molecular displacements may be covered from tens of micrometers down to a couple of nanometres [6]. However, so far, the information provided by them is either taken over many crystals or, in the case of IR microscopy, over too large space scales which prohibit any detailed, i.e., spatially resolved, exploration of interface dynamics.

In fact, there are only two techniques, most recently introduced into the field of nanoporous materials, which are potentially able to explore the dynamic properties of such interfaces: single-molecule tracking [19] and interference microscopy [20,21]. So far, the former technique has only been applied to tracing molecular trajectories within the porous material without the option of monitoring their exchange with the surroundings [19,22]. It is the aim of the present letter to communicate how this information may be provided by interference microscopy. Two nanoporous host-guest systems, which turned out to provide favorable conditions for this type of analysis, shall be characterized with respect to their exchange properties between the bulk phase of the pore system and the surrounding atmosphere.

The application of interference microscopy for recording intracrystalline concentration profiles is based on the fact that the optical density of the nanoporous host system is a function of the nature and the concentration of the guest molecules. In our studies, we have used an interference microscope of Mach-Zehnder type, allowing a superposition of the beams passing the individual host particle (crystal) under study and the surrounding atmosphere [20]. In this way, changes in the integral over the optical density in observation direction (our x-coordinate) appear in changes of the interference pattern, which may immediately be transferred into the corresponding changes of the integral $\int c(x, y, z)dx$ in observation direction over the crystal, with a spatial resolution of $\Delta y \times \Delta z \approx 0.5\ \mu\text{m} \times 0.5\ \mu\text{m}$ and a temporal resolution of 10 s [21].

For one- and two-dimensional pore systems one may easily circumvent the restriction that it is the integral in observation direction rather than the local concentration $c(x, y, z)$ itself which directly results from the experiment. In this case it is sufficient to chose the direction of observation perpendicular to the channel system. Since, consequently, fluxes in observation direction are excluded, the integral $\int c(x, y, z)dx$ is nothing else than the product $c(y, z) \times l$ with l denoting the extension of the crystal in observation direction.

The mean total flux entering the crystal may be estimated as

$$J = \frac{\Delta \iiint c(x, y, z) dx dy dz}{\Delta t}, \tag{1}$$

where $\Delta \iiint c(x, y, z) dx dy dz$ is the difference in the total concentration integrals (i.e., the total amounts adsorbed) at subsequent instants of observation (of separation Δt).

Following Ref. [23], as the key parameter controlling molecular exchange between of the host-guest system and the outer (guest) atmosphere, we introduce the surface permeability α by the equation

$$j = \alpha(c_{\mathrm{eq}} - c_{\mathrm{bound}}), \tag{2}$$

correlating the flux density through the crystal surface (j) with the difference between the actual concentration of the guest molecules at the boundary of the intracrystalline pore space (c_{bound}) and the concentration in equilibrium with the external gas phase (c_{eq}). Since j has to remain finite, the limiting case of an infinitely large surface permeability is easily seen to coincide with the requirement $c_{\mathrm{bound}} = c_{\mathrm{eq}}$, representing the boundary condition for diffusion-limited uptake and release [23]. It is implied that the thickness of the boundary layer, the permeability of which is described by Eq. (2), is negligibly small in comparison with the crystal extension.

As an example, Figs. 1(a) and 1(b) display the evolution of the intracrystalline concentration profiles along a cut through the crystal center during molecular uptake of isobutane by a nanoporous crystal of type silicalite-1 [24] and of methanol by ferrierite [21]. Isobutane uptake on silicalite-1 reveals the typical pattern of so-called diffusion-controlled uptake. It is characterized by the fact that, essentially instantaneously after the onset of ad- or desorption, the boundary concentrations coincide with the equilibrium value corresponding to the pressure of the outer atmosphere of guest molecules. Already after 10 s, the actual boundary concentrations amount to 98.8% (left-hand crystal face, $y = 0$ μm) and 96.8% (right-hand-crystal face, $y = 32$ μm), respectively. Observation parallel to these two planes leaves an uncertainty on the order of at least 1 μm in the spatial resolution in flux direction. It is therefore only possible to determine a lower limit of the surface permeability. With the flux data taken from Fig. 1(a) (shaded area divided by the relevant time interval $t = 10$ s) and assuming that the difference $c_{\mathrm{eq}} - c_{\mathrm{bound}}$ between the equilibrium loading (0.67 molecules per nm^3) [25] and the actual boundary loading is less than 4% of equilibrium loading, the surface permeability can be estimated to be larger than 3×10^5 m s^{-1}.

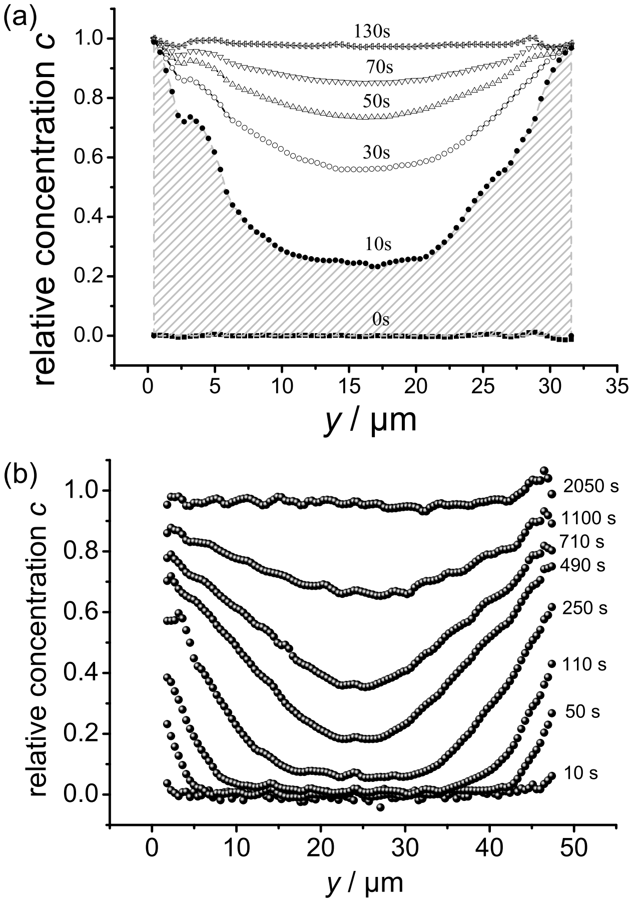

FIG. 1 (color online). Transient intracrystalline concentration profiles of isobutane in a nanoporous crystal of type silicalite-1 for a pressure step from 0 to 1 mbar [Fig. 1(a)] and of methanol in ferrierite for a pressure step from 0 to 10 mbar [Fig. 1(b)] in the surrounding atmosphere recorded by interference microscopy.

By contrast, molecular uptake on the other nanoporous host-guest system, namely, methanol in ferrierite, is characterized by a most pronounced influence of a "surface barrier", i.e., of a reduced surface permeability, acting in addition to the transport resistance of the internal pore system and appearing in the dramatic retardation of the boundary concentration in comparison with the equilibrium value (1.9 molecules per nm^3) [26]. Figure 2 displays the surface permeabilities determined from the transient concentration profiles on the basis of Eq. (2). Thus, owing to the potentials of interference microscopy, molecular exchange rates of the guest molecules at the interface between nanoporous media and the surrounding atmosphere have become accessible by direct experimental observation. Similarly, as with the coefficients of intracrystalline diffusion in nanoporous host-guest systems [2,5,6,16], the surface permeability turns out to be a pronounced function of the guest concentration. Most remarkably, over the last 10% of the considered interval of concentrations, the permeability is found to increase by essentially the same factor (namely 1 order of magnitude) as it increases over the initial 90% of the concentration range. A steep increase in the (transport) diffusivities with concentrations approaching saturation is quite common for guest molecules in nanoporous materials [27] and may be related to the corresponding steep increase of the so-called thermodynamic factor, i.e., of the logarithmic derivative $d \ln p / d \ln c(p)$ of the sorbate pressure p with respect to the

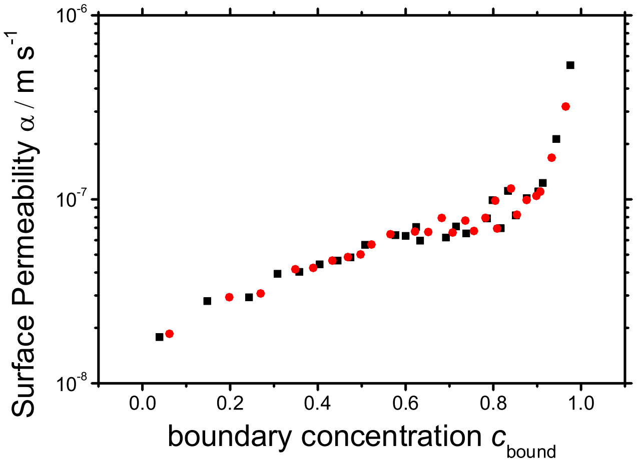

FIG. 2 (color online). Surface permeability of the ferrierite crystal for a methanol pressure step $0 \rightarrow 10$ mbar. (black squares—left-hand crystal face, red spheres—right-hand crystal face).

corresponding equilibrium concentration $c(p)$ [12,25]. Future studies devoted to the exploration of the mechanisms leading to the formation of surface barriers (or preventing their formation as in our first example) are most likely to benefit from such analogies.

Let us, at first, discuss these findings in the context of the rate-limiting processes during molecular uptake or release. For their quantification, one may introduce the time constant of equilibration [28] $\tau = \int_0^\infty (1 - m(t))dt$, where $m(t)$ denotes the relative molecular uptake (or amount released) at time t. For an estimate of the relative influences of surface barriers and intracrystalline diffusion on molecular exchange between the nanoporous material and the surrounding atmosphere we use the analytical expression for one-dimensional diffusion in a system of extension $2l$

$$\tau = \frac{l^2}{3D} + \frac{l}{\alpha} \tag{3}$$

which results for constant diffusivities and surface permeabilities from the corresponding solutions of the diffusion equation [23,28]. Thus it turns out that the resulting time constant is simply the superposition of the time constants for complete diffusion control ($\tau_{\text{diff}} = l^2/3D$) and complete control by surface barriers ($\tau_{\text{surf}} = l/\alpha$). The role of the respective resistances on the overall process may be expressed by the ratio

$$\frac{\tau_{\text{diff}}}{\tau_{\text{surf}}} = \frac{l\alpha}{3D}. \tag{4}$$

Thus, for isobutane in silicalite-1 with a mean diffusivity of about 10^{-12} m^2 s^{-1} [29] and a lower limit of the surface permeability of 3×10^{-5} m s^{-1}, we obtain a value of $\tau_{\text{diff}}/\tau_{\text{surf}} > 160$ indicating the dominating role of intracrystalline diffusion during molecular uptake and release. By contrast, for methanol in ferrierite [26], with a mean value of 3.5×10^{-13} m^2 s^{-1} for the diffusivity and of 8.5×10^{-8} m s^{-1} for the surface permeability, the resulting value of $\tau_{\text{diff}}/\tau_{\text{surf}} \approx 2$ indicates that both transport mechanisms are of relevance.

Let us now change our position and look at the surface of the nanoporous host system from the outer atmosphere. Let us, in particular, follow the collision rate of the guest molecules with the external surface and the probability with which these molecules are able to propagate into the internal pore system. From elementary gas kinetics, the number of gas phase molecules colliding with a plane surface is well known to be [30]

$$j_{\text{GS}} = \frac{1}{\sqrt{2\pi}} N_{\text{A}} \frac{1}{\sqrt{RTM}} p \tag{5}$$

with N_{A}, R, T, M, and p denoting, respectively, the Avogadro and gas constant, the absolute temperature (295 K), the molecular weight and the gas pressure.

The flux density of molecules getting from the outer atmosphere into the pore space (j_{in}), on the other hand, may be easily noted on the basis of Eq. (2). The flux density j as considered in Eq. (2) results as the net effect of the fluxes entering and leaving the pore space, i.e.,

$$j = j_{\text{in}} - j_{\text{out}}. \tag{6}$$

The flux density out of the pore system, j_{out}, results from Eq. (2) for the case of total absence of an external atmosphere, i.e., for vanishing external pressure and hence for $c_{\text{eq.}} = 0$, yielding

$$j_{\text{out}} = \alpha c_{\text{bound}}. \tag{7}$$

Since, under equilibrium conditions, $c_{\text{bound}} = c_{\text{eq}}$ and $j = 0$, combination of Eqs. (6) and (7) yields

$$j_{\text{in}} = \alpha c_{\text{eq}}. \tag{8}$$

Thus, with the ratio $j_{\text{in}}/j_{\text{GS}}$ as directly following from Eqs. (5) and (8), the "sticking probability", i.e., the probability that a molecule, after having encountered the outer crystal surface, is going to continue its trajectory in the intracrystalline pore space, has become accessible by direct experimental determination. For the systems under study and under the conditions of the reported experiments, i.e., for molecular uptake of isobutane by silicalite-1 at a pressure of 1 mbar and of methanol by ferrierite at a pressure of 10 mbar, it results to be 0.01 and 6×10^{-6}, respectively. Thus it turns out that for isobutane on silicalite-1 a notable fraction of at least 1% of the molecules colliding with the surface will continue its trajectory into the interior of the nanoporous material, while for ferrierite only a fraction of about 6×10^{-4}% of the methanol molecules encountering the entrance plane to the ferrierite crystal in y direction is allowed to enter.

Thus, direct experimental evidence is found to confirm the option that the sticking probabilities of guest molecules by nanoporous materials may cover several orders of magnitudes between close to 1 and very small values, following the predictions of macroscopic analysis [31,32].

In conclusion, interference microscopy as recently introduced into diffusion research with nanoporous materials has been shown to provide direct access to an experimental quantitation of molecular exchange at the interface of nanoporous materials with the surroundings. Thus, such important information as the relative weight of the transport resistances due to intracrystalline diffusion or surface barriers and the sticking probability of molecules encountering the system from the surrounding gas phase has become directly accessible to experimental observation. Just like the diffusivities, also the surface permeabilities (and hence the sticking probabilities) are found to vary with varying concentration of the guest molecules. This finding emphasizes the need for approaches which, in addition to the diffusivities [23], also take account of concentration-dependent surface permeabilities, as well as for attempts to explore the physical mechanisms behind them. Surface resistances are likely to be the dominating mechanism in many cases, in particular, under technical application [4].

Deposition of amorphous material on the external surface is one of the mechanisms leading to the formation of such surface resistances. This has been exemplified, e.g., in studies with zeolite crystals of type ZSM-5 [33,34]. Surface etching with hydrofluoric acid was found to reduce existing surface resistances which thus have been assigned to aluminum-enriched, amorphous surface layers. Silicalite-1 is the isomorph of ZSM-5 with dramatically reduced aluminum content [35] so that the formation of surface resistances of the type found with ZSM-5 is very unlikely. The present findings are in complete agreement with this supposition. In addition, however, the termination of the regular pore structure makes the surface layer of any nanoporous material particularly unstable. Correlating this quite general feature with its consequences for the formation of layers of reduced permeability close to the particle surface is a great challenge of material research. The option of quantitating these resistances by the procedure introduced in this Letter is among the prerequisites for the success of these efforts.

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[1] F. Laeri, F. Schüth, U. Simon, and M. Wark, *Host-Guest Systems Based on Nanoporous Crystals* (Wiley-VCH, Weinheim, 2003).
[2] N. Y. Chen, T. F. Degnan, and C. M. Smith, *Molecular Transport and Reaction in Zeolites* (Wiley-VCH, New York, 1994).
[3] S. M. Kuznicki, Nature (London) **412**, 720 (2001).
[4] M. E. Davis, Nature (London) **417**, 813 (2002).
[5] D. Dubbeldam *et al.*, Phys. Rev. Lett. **93**, 088302 (2004).
[6] H. Jobic and D. Theodorou, Microporous Mesoporous Mater. **102**, 21 (2007).
[7] F. J. Keil, R. Krishna, and M. O. Coppens, Rev. Chem. Eng. **16**, 71 (2000).
[8] J. R. Agger *et al.*, J. Am. Chem. Soc. **125**, 830 (2003).
[9] J. Kärger, R. Valiullin, and S. Vasenkov, New J. Phys. **7**, 15 (2005).
[10] M. G. Ahunbay, J. R. Elliott, and O. Talu, J. Phys. Chem. B **109**, 923 (2005).
[11] J.-M. Simon, A. Decrette, and J.-B. Bellat, Mol. Simulations **30**, 621 (2004).
[12] D. M. Ruthven and S. Brandani, in *Recent Advances in Gas Separation by Microporous Ceramic Membranes*, edited by N. K. Kanellopoulos (Elsevier, Amsterdam, 2000), p. 187.
[13] G. Onyestyak and L. V. C. Rees, J. Phys. Chem. B **103**, 7469 (1999).
[14] J. Kärger, H. Pfeifer, and W. Heink, Adv. Magn. Reson. **12**, 2 (1988).
[15] P. T. Callaghan, *Principles of NMR Microscopy* (Clarendon, Oxford, 1991).
[16] H. Jobic, J. Kärger, and M. Bee, Phys. Rev. Lett. **82**, 4260 (1999).
[17] M. Hermann, H. G. Niessen, and H. G. Karge, Stud. Surf. Sci. Catal. **94**, 131 (1995).
[18] C. Chmelik *et al.*, Adsorption **11**, 455 (2005).
[19] J. Kirstein *et al.*, Nat. Mater. **6**, 303 (2007).
[20] U. Schemmert *et al.*, Europhys. Lett. **46**, 204 (1999).
[21] J. Kärger *et al.*, Angew. Chem., Int. Ed. **45**, 7846 (2006).
[22] A. Cvetkovic *et al.*, J. Phys. Chem. B **109**, 10 561 (2005).
[23] J. Crank, *The Mathematics of Diffusion* (Clarendon Press, Oxford, 1975).
[24] D. Tzoulaki *et al.*, Angew. Chem., Int. Ed. (to be published).
[25] D. Paschek and R. Krishna, Chem. Phys. Lett. **342**, 148 (2001).
[26] P. Kortunov *et al.*, J. Phys. Chem. B **110**, 23821 (2006).
[27] D. M. Ruthven, Chem. Eng. Sci. **59**, 4531 (2004).
[28] R. M. Barrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves* (Academic, London, 1978).
[29] W. Zhu *et al.*, Chem. Eng. Sci. **59**, 3827 (2004).
[30] P. W. Atkins and J. de Paula, *Physical Chemistry* (Oxford University Press, Oxford, 2002).
[31] A. Jentys, R. R. Mukti, and J. A. Lercher, J. Phys. Chem. B **110**, 17 691 (2006).
[32] J.-M. Simon *et al.*, J. Phys. Chem. B **109**, 13 523 (2005).
[33] P. Kortunov *et al.*, Chem. Mater. **16**, 3552 (2004).
[34] J. Wloch, Microporous Mesoporous Mater. **62**, 81 (2003).
[35] C. Baerlocher, L. B. McCusker, and D. H. Olson, *Atlas of Zeolite Framework Types* (Elsevier, Amsterdam, 2007).