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Diffusion of *n*-alkanes in zeolites: the benefit of observation over different length scales

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ABSTRACT

First results of an international research collaboration to study zeolitic diffusion are presented. By using a variety of experimental techniques, molecular diffusion paths are probed over different time and length scales. As host-guest systems the homologous series of n-alkanes in zeolites NaCaA and silicalite-1 have been selected. Since the diffusivities are found to be the smaller the longer are the diffusion paths covered during the experiments, the observed differences may be explained by the existence of transport resistances acting in addition to the intracrystalline zeolite bulk phase. In selective experiments, indications of such resistances are traced from the range of some 100 nm up to crystal dimensions.

1. INTRODUCTION

With the introduction of the "microscopic" techniques of diffusion measurement (PFG NMR and QENS) to zeolite science and the thus initiated revision of the so far generally practised procedure of "macroscopic" measurement, different measuring techniques have been repeatedly found to yield both agreement and disagreement between each other. By a concerted application of measuring techniques, viz. ZLC, QENS, PFG NMR, uptake/release and (IR and interference) microscopy, covering length scales over more than 4 orders of magnitude, an unprecedented collaborative research activity has been started to explore the origin of this situation for identical and well-specified systems. First experimental results quite coherently show that the smaller the obtained diffusivities are, the larger are the ranges over which the diffusion phenomena are recorded. Such an experimental finding indicates the

existence of transport resistances acting in addition to the zeolite bulk phase. Since the larger their influence becomes, the larger are the diffusion paths covered in the experiments, they should be subject to some hierarchical order. In the present communication we present selected experiments, dedicated to the exploration of these additional transport resistances over different space scales.

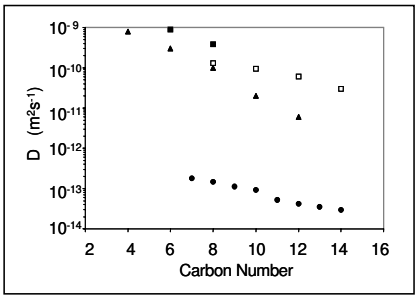

Fig. 1. Various diffusivities observed with n-alkanes at loadings corresponding to about 6 carbon atoms per channel crossing at 423 K in MFI-type zeolites: QENS □ and QENS new data ■, PFG NMR ▲, ZLC ● (zero loading).

2. EXPERIMENTAL

The measurements to which we refer in the subsequent section have been performed by quite different techniques which are specified as follows. Recent experimental progress has shifted the upper limit of diffusion paths covered by QENS up to 10 nm [1]. Moreover, in addition to self-diffusion studies by incoherent scattering, also the measurement of transport diffusion has become possible. The latter technique is based on the analysis of coherent scattering, most suitably during neutron spin echo (NSE) experiments. PFG NMR is confined to self-diffusion studies. Recent instrumental progress based on the application of ultra-high-intensity field gradients allows the observation of displacements of guest molecules from 100 nm up to micrometers [2]. Over the latter space scale, interference microscopy is able to monitor transport diffusion [3]. Spatial resolution of IR microscopy is by one order of magnitude poorer and, essentially, reflects the overall sorption and release behaviour of the individual crystal under study [4]. Uptake/release and zero-length-column (ZLC) measurements [5] are performed with assemblages of crystallites.

3. RESULTS AND DISCUSSION

3.1 Overview

Figs. 1 and 2 provide the first results of our joint research activities with a summary of the diffusivity data obtained by the various measuring techniques, available within the consortium, for the n-alkane homologues in zeolites MFI (silicalite-1/ZSM-5) and NaCaA.

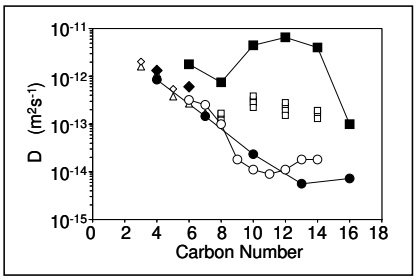

Fig. 2. Variation of diffusivity with carbon number (at 473 K) in NaCaA. NSE ■; ZLC ● and ZLC new data ○; PFG NMR data at 1 molecule/cage Δ, and at 2 molecules/cage ◊; recent PFG NMR data (1 molecule/cage) □; recent nonisothermal uptake measurements ♦.

The presentations reveal two remarkable features: (i) While the diffusivities in MFI decrease monotonically with increasing chain length, in NaCaA the data got from all the techniques present notable deviations from this pattern. These deviations are most pronounced in the QENS measurements and have been referred to the fact that there obviously exists a certain chain length for which, as a consequence of the given cage architecture, the inter-cage transition probability passes a maximum [6]. (ii) Comparing the different techniques, the resulting diffusivities are found to decrease just in the sequence in which - as described in the experimental section - the measuring techniques become more "macroscopic". Such an experimental finding may be associated with the fact that in both types of zeolites there exist additional transport resistances. The larger the displacements are, the more relevant is this statement. In the following, we are going to summarize the special messages of the different techniques of diffusion measurement with respect to the extension and intensity of these resistance mechanisms which act in addition to the "drag" exerted by the genuine inner surface of the zeolitic host systems on the diffusing guest molecules.

3.2 QENS vs. PFG NMR

On comparing Figs. 1 and 2, one must have in mind that the QENS diffusivity data in MFI shown in Fig. 1 essentially reflect self-diffusivities, while Fig. 2 displays the transport diffusivities measured by means of the neutron spin echo technique (analysing the coherent part of quasi-elastic neutron scattering). Therefore, the QENS and PFG NMR data shown in Fig. 2 do not only refer to different length scales, they also reflect different physical situations. This latter difference is, however, by far not able to explain the difference of close to two orders of magnitude in comparison with the PFG NMR data, similarly as from an equivalent comparison in Fig. 1. One has to, therefore, conclude that there have to be substantial internal transport resistances which are highly effective for the PFG NMR diffusion studies with displacements of typically micrometers. But the resistances are still of no influence for the QENS measurements with displacements in the range of nanometers. The separation of these internal barriers has to be, therefore, localized between nanometers and micrometers.

3.3 PFG NMR with varying observation times

By modifying the pulse programme of the measurement, PFG NMR is able to cover observation times from milliseconds up to seconds. As a typical result of such measurements, Fig. 3 displays the diffusivities of n-butane and n-hexane in silicalite-1 at two different

temperatures, determined during observation times which have been varied between 2 and 20 ms.

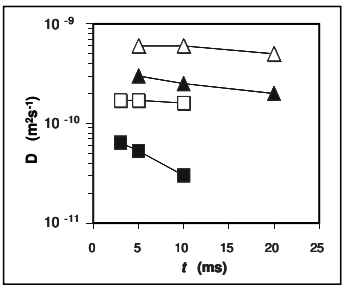

Fig. 3. Self-diffusion coefficients of n-butane in silicalite-1 (triangles) and of *n*-hexane in ZSM-5 (squares) at 298 K (filled symbols) and 353 K (open symbols), measured by PFG NMR as a function of the observation time.

Any decrease of the diffusivity with increasing observation time should indicate the existence of internal barriers which become relevant just for the diffusion paths considered in the given experiment. The most pronounced dependence is observed for the longer molecule at the lower temperature, which nicely agrees with our expectation that the larger these resistances are, the larger are the molecules which have to overcome them, and that permeation through these resistances is facilitated with increasing temperature [7]. Estimating the mean diffusion path lengths $<r(t)^2>^{1/2}$ during the observation time t by means of the Einstein relation $<r(t)^2> = 6Dt$, typical distances of the transport resistances are thus found to be of the order of 1 micrometer.

3.4 ZLC with partial loading

The crystallite assemblages typically considered in ZLC experiments are so small that any transport resistance outside of the individual crystals may essentially be neglected. The option to easily initiate or stop adsorption from the carrier gas instantaneously by a corresponding change in the partial pressure of the guest molecules in the gas flow permits an elegant way to distinguish whether overall uptake or release is controlled by internal resistances or by a transport resistance on the outer crystal surface (a "surface barrier") [8, 9]. This distinction is based on the fact that at "partial loading", i.e. as long as the sorbate distribution within the crystallites has not yet attained equilibrium, this distribution will notably depend on the uptake mechanism. In particular, for dominating surface barriers the distribution of guest molecules within the crystallite will be uniform already under partial loading conditions, while under diffusion control the sorbate concentration in an outer shell will be higher than in the centre. This latter effect will lead to a faster decay of the guest concentration in the carrier gas stream if desorption is initiated before equilibrium has been established. As an example, Fig. 4 shows the results of such a partial-loading ZLC experiment with n-decane in zeolite NaCaA. The experimentally observed partial-loading behaviour is in excellent agreement with the pattern expected for uptake limitation by internal resistances. Therefore, the diverging PFG NMR and ZLC data shown in Fig. 2 for chain lengths larger than 10 carbon atoms, should be explained by an increase of internal transport resistances (with increasing chain lengths) rather than by the impact of a surface barrier.

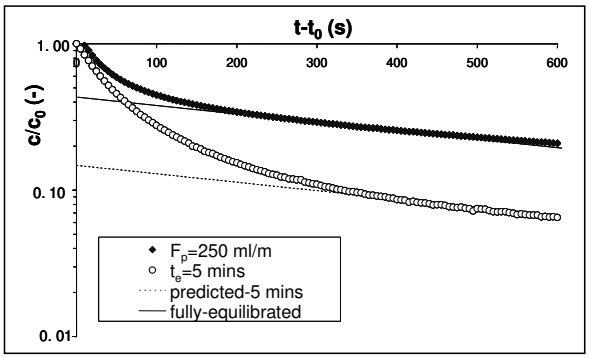

Fig. 4. Experimental ZLC desorption curves of n-decane in NaCaA (at 398 K, p=0.006 torr), fully-equilibrated sample (♦) and partially-saturated sample (○), showing a good agreement of quantitative theoretical predicition for diffusion-limited desorption with the experimental results.

3.5 Tracing surface barriers

Though with the message of the previous section surface barriers cannot be assumed to be quite generally the origin of differences between the diffusivities determined by microscopic and macroscopic techniques, the recent application of interference microscopy to studying molecular ad- and desorption on nanoporous materials [3, 4] did provide plenty of evidence that in most cases intracrystalline molecular concentrations close to the outer zeolite surface notably deviates from their equilibrium values. Moreover, the surface permeabilities which can be calculated from the fractional molecular uptake and the differences between actual surface concentrations and their equilibrium values turned out to be complex functions of both these concentrations. Hence, for an exploration and better understanding of the origin of such surface barriers the option of equilibrium studies would be of extreme importance. Again PFG NMR may provide this type of information by comparing, at a given observation time, the number of molecules which have left the individual crystallites with the mean square displacement of those molecules which are still kept within the crystal in which they have been at the beginning of the pulse programme. Obviously, the smaller the latter quantity will be, the more stringent has the restriction by the crystal surface been, i.e. the larger the surface barriers are [10]. We are going to implement this new scheme of analysis to the systems under study in the consortium.

3.6 Mesopore-generated anomalies

Most recent NMR studies with Vycor mesoporous glasses in the range of sorption hysteresis [11] have revealed a remarkable discrepancy between molecular uptake and the theoretical curves calculated on the basis of the measured diffusivities. This situation is reflected by Fig. 5 which displays the uptake curve of cyclohexane in Vycor in comparison with the theoretical curve derived from the molecular mobility. In striking contrast to the situation before onset of hysteresis (where molecular uptake may exactly be predicted on the basis of the NMR diffusivities) molecular uptake is dramatically slowed down. It turns out that now, for attaining the new equilibrium state, molecular re-distributions within the pore system rather than the rate of molecular transportation has become the rate-determining process. This type of behaviour seems to be specific for mesoporous materials. However, not only due to the option that also microporous materials may be traversed by mesopores, on

comparing macroscopic uptake and release with molecular mobilities one should not totally forget about this anomaly.

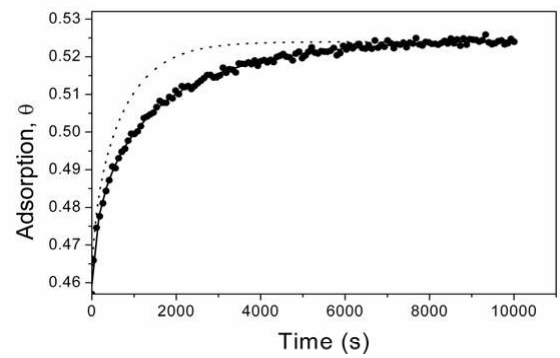

Fig. 5. Experimental transient sorption of cyclohexane in Vycor porous glass at room temperature in the range of hysteresis (points) and comparison with the uptake calculated on the basis of the inherent diffusivities (dotted line).

4. CONCLUSION

Applications of different measuring techniques to one and the same system provides the option to follow molecular diffusion over quite different length scales. As a first result of a concerted activity using different measuring techniques, a general tendency is revealed that the smaller the diffusivities are, the larger are the length scales which are traced in the experiments. In selected examples comparative studies of possible transport resistances over quite different length scales are given. It has to remain the task of further studies to apply all these different options for clarifying the origin of additional transport resistances to the considered series of systems.

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