Measurement of Diffusion in Zeolites—A Never Ending Challenge?*

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Abstract. A review is given on the main problems associated with the determination and interpretation of molecular diffusion in zeolites. It is shown that the diffusivities may most decisively depend on the relevant space and time scales of observation, as well as on the physical state under which the measurements are carried out. Special emphasis is given to the microscopic techniques and their most recent evidence on the existence of transport resistances distributed over the intracrystalline space.

Keywords: zeolites, diffusion, diffusion measurement, equilibrium techniques, microscopic techniques, anomalous diffusion

Introduction

Diffusion is the process of irregular particle movement generated by the particles' thermal energy. It is one of the fundamental phenomena in nature. Though on quite different scales of length and time, it occurs in any type of matter (Kärger et al., 1998).

Molecular diffusion under the confinement of nanoporous materials is of two-fold interest. From the point of view of fundamental research, studying molecular diffusion in nanoporous materials provides unique insights into their host-guest interaction and the interrelation between pore architecture and propagation rates. On the other hand, the rate of molecular propagation is one of the decisive quantities affecting the effectiveness of technical processes based on the application of nanoporous materials.

From the very beginning of zeolite science and technology, molecular diffusion in zeolites was essentially studied by following the rate of molecular adsorption or desorption, after having subjected the sample under study to a pressure step in the surrounding atmosphere (Barrer and Vaughan, 1969). The introduc-

tion of the pulsed field gradient technique of NMR spectroscopy (PFG NMR) (Kärger and Caro, 1977) has initiated a critical reconsideration of the so far generally accepted results of transient uptake measurements. In many cases the uptake measurements turned out to be controlled by processes different from intracrystalline diffusion. Analysing uptake measurements without due credit to these processes had necessarily to lead to too small diffusivities. Though in the subsequent years—having unveiled this possible source of error—for numerous systems the diffusivities derived from different experimental techniques have been found to merge (Ruthven, 1984; Bülow et al., 1983; Kärger and Ruthven, 1992), there is still a large number of systems for which the diffusivities differ by orders of magnitude (Kärger and Ruthven, 1992, 1997 and 2002; Jobic, 2000). The origin of these differences is still unclear.

Since the progress in our knowledge as deduced from the application of the established measuring techniques is rather modest, novel experimental routes to diffusion studies in zeolites are more than welcome. With the Isotope Exchange Technique (Rynders et al., 1997; Mohr et al., 1999; Cao et al., 2000), Shivaji Sircar and his co-workers have substantially contributed to the spectrum of techniques applied to diffusion measurement in

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zeolite science and technology. It is the aim of the present contribution to review some of these more recent techniques of diffusion measurement and of their potentials in eventually clarifying the origin of the still remaining differences in the results of different measurements.

The "Different" Diffusivities

Quite generally, the coefficient of diffusion (the diffusivity) is defined as the factor of proportionality between the flux density and the concentration gradient of the particle species under study (Fick's 1st law). Molecular fluxes in porous media are considered with respect to a cross section, which is fixed to the pore system. Under the conditions of single-component adsorption, which we shall essentially confine to in this survey, molecular fluxes are only observable under the presence of an overall concentration gradient over the sample. This type of diffusion coefficient is generally referred to, therefore, as transport diffusivity. Obviously, transport diffusivities are defined under non-equilibrium conditions. In order to trace molecular fluxes under equilibrium, a spatially varying part of the molecules has to be labelled (e.g., by use of isotopes). In this case, the diffusivity is referred to as the coefficient of self- or tracer diffusion.

Fluxes and concentrations are macroscopic quantities. In heterogeneous systems, their significance is controlled by the scales, which they are referred to. In the case of intracrystalline diffusion, the unit areas and volumes used for the definition of molecular concentration and fluxes have to significantly exceed the unit cell (pore) dimensions, while they must be small in comparison with the crystallite (particle) dimensions. If, however, the unit volumes and areas considered are large in comparison with the individual crystallites (though being still small in comparison with the pellet/bed extension), the corresponding diffusivities are referred to as effective, long-range or pellet diffusivities. This latter definition implies fast exchange between the molecules in the intra- and intercrystalline spaces.

As an alternative to the tracer conception, molecular diffusion under equilibrium conditions may as well be quantified on the basis of the Einstein relation

$$\langle r^2(t) \rangle = 6Dt, \tag{1}$$

where $\langle r^2(t) \rangle$ denotes the mean squared distance covered by the molecules under study during the observation time t. The definition of the self-diffusivity by Eq. (1) implies that the observation time t may be subdivided in a sufficiently large number of time intervals so that the particle shift in a particular one of these time interval is independent of the particle shift in any other one. Under this condition, one may even indicate the total probability distribution of molecular displacements, the so-called propagator. According to the central limit theorem of statistics the propagator results to be

$$P(\vec{r}, t) = (4\pi Dt)^{-3/2} \exp[-r^2/(4Dt)]. \tag{2}$$

Under the above-made conditions–viz. a reasonable coarse graining by introducing the space scales of concentrations and fluxes, and statistical independence of molecular displacement in subsequent time intervals— both ways of describing molecular transport under equilibrium, i.e., Fick's first law and the propagator representation (Eq. (2)), are completely equivalent (Kärger and Ruthven, 1992). Molecular motion following Fick's first law (and being described, therefore, by a Gaussian propagator) is referred to as normal diffusion. The particular practical interest in the treatment of this type of molecular propagation results from the fact that transport under the conditions of molecular reaction is often simplified in the just dicussed way, by neglecting the differences in the molecular mobilities of the involved species, i.e., by identifying, e.g., the reactant molecules as the unlabelled and the product molecules as the labelled ones (Riekert, 1970; Kärger and Ruthven, 1992; Chen et al., 1994). Under such conditions, the self- or tracer diffusivity coincides with the mutual diffusivity.

Molecular diffusion under the confinement of nanoporous host systems, however, is well known to possibly devite from the pattern of normal diffusion. A most prominent example are host-guest systems where the molecules are confined to sufficiently narrow channels so that they are unable to pass each other, i.e., to mutually exchange their positions. As a consequence, in such "single-file" systems (Kärger et al., 1992) molecular displacements into one direction are more likely to be followed by displacements into the opposite than into the same direction. In an infinitely large channel, this correlation between subsequent displacements is unlimitedly preserved for arbitrarily large displacements and observation times. Therefore, the prerequisite of normal diffusion is not obeyed anymore. Interestingly enough, also under single-file conditions

the probability of molecular displacements is given by a Gaussian propagator (Kärger, 1993). In striking contrast to normal diffusion, however, the mean square displacement increases in proportion to the square root of time (Fedders, 1978; Kärger et al., 1992; Kehr et al., 1998):

$$\langle x^2(t) \rangle = 2F\sqrt{t}, \qquad (3)$$

rather than to the time itself (Eqs. (1) and (2)). Networks of mutually intersecting single-file systems with different access probabilities for reactant and product molecules (Clark and Snurr, 2000) have recently been considered as model systems (Neugebauer et al., 2000; Bräuer et al., 2001) for elucidating the prospects of reactivity enhancement by molecular traffic control (Derouane and Gabelica, 1980).

In practical application, zeolites with single-file features must clearly be considered to be of finite extension. As a consequence, molecular displacement and eventually the exchange of molecules from the intracrystalline space to the surroundings are found to be affected by an additional process, which may soon become rate determining (Hahn and Kärger, 1998; Rödenbeck and Kärger, 1999; Nelson and Auerbach, 1999). This process has to be associated with the displacement of the whole file, brought about by molecular ad- and desorption on the file margins. Since subsequent elementary acts of ad- and desorption are uncorrelated, it are also the corresponding displacements of the particle file in total and hence of its centre of gravity. The effect of this process on the whole particle "chain" and hence on any individual particle may therefore be described by a (normal) diffusivity, referred to as the diffusivity of the centre of gravity (D_{cm}). Quantitative analysis (Hahn and Kärger, 1998; Rödenbeck and Kärger, 1999; Nelson and Auerbach, 1999) yields

$$D_{cm} = D\frac{1-\Theta}{\Theta N} \qquad (4)$$

with N, Θ and D denoting, respectively, the site number, their occupancy and the diffusivity of a sole particle in the file. Since molecular mean square displacement by this process increases in proportion to t rather than $\sqrt{t}$, irrespective of the dramatic decrease of D_{cm} in comparison with D (N is typically on the order of 10^3), it may be shown to exceed the influence of the former mechanism (Eq. (3)) already for displacements much smaller than the crystal dimensions (Hahn and Kärger, 1998; Rödenbeck and Kärger, 1999).

Experimental Techniques of Diffusion Measurement

Conventionally, molecular diffusion in zeolites has been performed by subjecting the sample under study to a step in the pressure of the surrounding atmosphere and by recording the sample response, i.e., in general, by monitoring the time dependence of the thus induced change of the amount adsorbed, e.g., gravimentrically. Besides intracrystalline diffusion, this process may be affected by a number of different processes such as the sorbate access to the sample, sorbate permeation through the bed of crystallites, overcoming transport resistances at the external surface of the crystallites and dissipation of the heat of adsorption. On deducing intracrystalline diffusivities from the uptake curves, the experimentalist has to struggle with all these influences, i.e., either to show that they are negligibly small or to accurately take account of them when analysing the primary data. Details of the relevant procedures may be found in the literature (Ruthven, 1984; Kärger and Ruthven, 1992; Chen et al., 1994; Kärger and Ruthven, 2002).

An alternative access to diffusion phenomena is provided by PFG NMR (Kärger et al., 1998; Kärger and Pfeifer, 1987; Kärger and Caro, 1977) and quasi-elastic neutron scattering (QENS) (Jobic, 2000). In these techniques, either by studying their interaction with thermal neutrons (QENS) or by recording the time dependence of the Larmor frequency of (NMR-active) nuclei (PFG NMR), one is able to determine the propagator of the diffusants or, more accurately, of the nuclei under study. Interestingly enough, though due to quite different reasons, in both techniques the nuclei of hydrogen offer the best measuring conditions. The space scale of PFG NMR is typically between 100 nm and 100 μm, QENS is able to trace molecular displacements below a few nanometers. In both techniques, the smallest diffusivities still accessible are on the order of 10^{-14} m^2 s^{-1}, while there is essentially no upper limit. Owing to the range of observable displacements, PFG NMR is able to observe both intracrystalline and long-range diffusion, while the diffusivities attained by QENS refer to a submicroscopic scale, involving even the elementary processes of diffusion.

These two groups of experiments, viz. uptake measurements (including their relatives like the

frequency response technique (Rees and Song, 2000) or zero-length-column chromatography (Ruthven and Brandani, 2000)) and PFG NMR/QENS, differ in two essential features: Uptake measurements are carried out under *non-equilibrium* conditions and are based on the observation of *macroscopic* phenomena, like the change in the overall mass or pressure, while PFG NMR/QENS are *equilibrium* techniques, sensitive to a *microscopic* (or even sub-microscopic) scale of observation. Therefore, as techniques intermediate between these two basic groups of experiments, the following two methods have attained special interest: the isotope exchange technique (Rynders et al., 1997; Mohr et al., 1999; Cao et al., 2000) and its relatives (Quig and Rees, 1976; Cundall et al., 1981; Goddard and Ruthven, 1986) as *macroscopic* methods operating under quasi-*equilibrium* conditions, and the interference microscopy (Schemmert et al., 1999a) as a

microscopic technique monitoring the evolution of concentration profiles, i.e., features of *non-equilibrium*. While the tracer techniques have essentially evolved from the very first systematic studies of zeolitic diffusion (Barrer and Fender, 1961), the application of interference microscopy to studying zeolitic diffusion has only become possible due to most recent progress in the experimental performance (Schemmert et al., 1999b).

Figure 1 provides a survey of the years of first application of some of the most important experimental techniques for studying molecular diffusion in zeolites. Most impressively, the introduction of PFG NMR into the field in the early 70s may be seen to have initiated the development and introduction of numerous novel techniques aiming to contribute to an eventual clarification of the discrepancies between the results of the various measuring techniques.
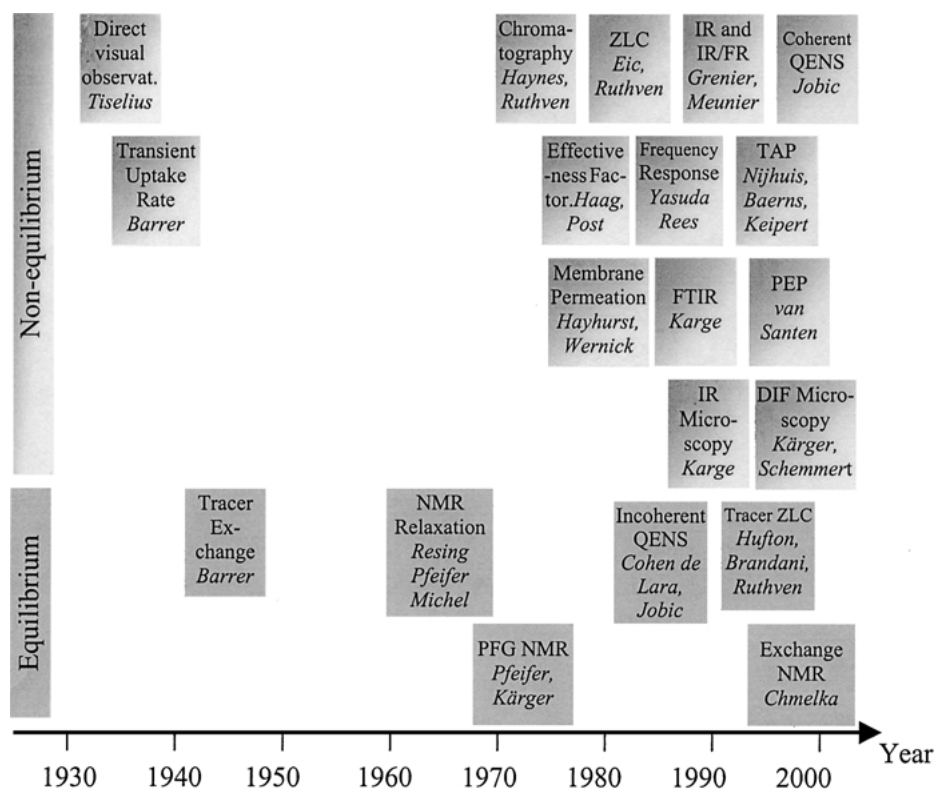

Figure 1. Years of the first application of experimental techniques for studying intracrystalline diffusion in zeolites. Names stand for following references: Tiselius (1934), Heynes (1986), Boniface and Ruthven (1985), Grenier et al. (1999), Jobic et al. (1999), Barrer and Fender (1961), Haag et al. (1981), Post (1991), Yasuda (1994), Rees and Song (2000), Nijhuis et al. (1997), Keipert and Baerns (1998), Hayhurst and Paravar (1983), Wernick and Osterhuber (1983), Karge and Niessen (1991), Schumacher et al. (2000), Schemmert et al. (1999), Resing and Murday (1973), Pfeifer et al. (1973), Michel and Rössinger (1976), Cohen de Lara et al. (1983), Jobic (2000), Hufton et al. (1994), Ruthven and Brandani (2000), Kärger and Pfeifer (1987), Favre et al. (1998).

Results of Comparative Diffusion Studies

Any application of experimental techniques implies the risk that the obtained results are obscured by influences, which so far have been remained out of the scope of consideration. Systematic studies, in which the experimentally determined quantities are compared with the theoretically expected trends and/or with complementary experiments are therefore of great importance for confirming the reliability of the methods applied.

In the case of PFG NMR, such systematic studies may be easily performed with respect to long-range diffusion. The coefficient of long-range diffusion (the effective or pellet diffusivity) is determined by the relation (Kärger and Ruthven, 1992)

$$D_{l.r} = p_{inter} D_{inter} \qquad (5)$$

where p_{inter} and D_{inter} denote respectively the relative number of molecules in the gas phase and their diffusivity. The quantity p_{inter} may be easily calculated on the basis of the adsorption isotherm and the macroporosity of the bed or pellet, while D_{inter} may be estimated on the basis of simple gas-kinetic approaches. Following the early ^{1}H PFG NMR studies of long-range diffusion (Lorenz et al., 1984) and in immediate response to Shivaji Sircar's suggestions, more recently satisfactory agreement between the theoretical model considerations and experimental data of long-range diffusion in compacted zeolites could even be attained by ^{15}N PFG NMR, whose spatial resolution is inferior to ^{1}H PFG NMR by more than one order of magnitude (McDaniel et al., 1996; Rittig et al., 2002). Such agreement has been considered as one of the primary proofs of consistency of PFG NMR (Kärger and Caro, 1977). Correlating the information of comparative diffusion studies by PFG NMR and the isotope exchange technique may be expected to provide further insight into the mechanisms of molecular transport through compacted adsorbent particles, and hence, as a consequence, into the possibilities of novel routes to the production of transport-optimised zeolite pellets for separation and catalysis. Being sensitive to a particular molecular species both PFG NMR and isotope exchange technique offer the unique possibility of investigating the behaviour of one particular species within a multicomponent system.

As a microscopic technique, PFG NMR is able to trace the rate of intracrystalline diffusion over different length scales. While in previous PFG NMR measurements of intracrystalline diffusion, the diffusivity has

essentially been found to be independent of the considered lengths of the diffusion path (Heink et al., 1990), progress in the experimental technique has meanwhile allowed to cover much larger ranges of diffusion paths. In this way, for light n-alkanes in zeolite ZSM-5, the diffusivities have been found to increase by a factor of two to three, as soon as the considered diffusion paths fall below a few micrometers (Vasenkov et al., 2001). Displacements of more than a few micrometers are found to essentially increase in proportion to the observation time. According to Eq. (1), in this case the diffusivity remains a constant, as required for normal diffusion. Similar behaviour has been observed for three different samples. It might be rationalized by assuming the existence of internal transport barriers with a mutual spacing on the order of micrometers. Since the different techniques differ in their sensitivity with respect to such transport barriers, their existence could provide an explanation of the differences in the diffusivities obtained by different techniques, as suggested already in earlier publications (Kärger and Ruthven, 1989)—though without direct experimental proof. Thus it turns out, that eventually the question for "true" intracrystalline diffusivities has to be reformulated.

In diffusion studies with zeolites, in general molecular uptake is undoubtedly assumed to proceed via the external surface. However, MFI-type zeolites like silicalite-1 or ZSM-5 are well known to appear as twins of hour-glass structure (Caro et al., 1993). This permits the option that a notable contribution to molecular uptake stems from molecules penetrating into the zeolite particles along the intergrowth boundaries. With the introduction of interference microscopy, for the first time this question could be definitely answered. In fact, all interference patterns observed with isobutane as a probe molecule (Geier et al., 2002) excluded the possibility of an uptake along the intergrowth boundaries, as observed, e.g., in the case of grain boundary diffusion in solids. Just in contrary, the internal interfaces were found to act as notable transport resistances.

Conclusions

Stimulated by huge differences in the intracrystalline diffusivities obtained by different techniques, zeolite science and technology is reinforced by a continuously increasing number of novel theoretical concepts and experimental techniques of diffusion studies. The present contribution reviews some of them, under particular emphasis of Shivaji Sircar's contribution to the field.

Irrespective of much progress in our knowledge about zeolitic diffusion, there are still a number of open questions including that for the "true" intracrystalline diffusivities in silicalite-1/ZSM-5. Thus, summing up, and coming back to the title of this contribution, the measurement of diffusion in zeolites can be expected to remain a challenging task also over the next decades.

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