

Diffusion in Nanoporous Materials in the Focus of an IUPAC Initiative: On the Benefit of Microscopic Measurement

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(Received: 2025/08/26, Published online: 2025/11/03)

Nanoporous host materials are key to numerous technological applications in value-adding processes such as matter separation, purification and conversion, with the performance controlled by the rate of exchange between the interior of the nanoporous particles (“crystallites”) and their surroundings. Detailed knowledge about this process is, hence, among the primary prerequisites for a knowledge-based enhancement of the performance of these applications.

As a rule, exchange processes between the interior of the sorbent material and its surroundings are brought about by a sequence of elementary steps, including intracrystalline diffusion, the permeation through (possibly existing) barriers in the crystal interior and on their external surface and through the bed of crystals. The sensitivity of the techniques of measurement of the diffusion-determining parameters may, hence, be focused on quite different phenomena. This has given rise to a specification of the different measuring techniques by the diffusion path lengths typically covered by the molecules during the respective measurement. On considering diffusion in nanoporous materials it has thus become common use to distinguish between “macroscopic” and “microscopic” techniques for diffusion path lengths considered in the measurement through a bed of crystals or within the individual crystals. Measurements with a single crystal without resolution of its interior are referred to as “mesoscopic” techniques and “submicroscopic” ones are sensitive to the elementary steps of diffusion.

In some way, corresponding with the multitude of processes by which the overall rate of sorption or desorption may be controlled, there exist quite a number of different techniques applied for diffusion studies in nanoporous materials – essentially each of these techniques may have some advantages in comparison with the other ones. And there are good reasons for using each of these techniques, even if it is just the low acquisition costs and ease of use. All the more important is the mutually coordinated handling of all these measurement options. With precisely this objective in mind, in 2015 an IUPAC (International Union of Pure and Applied Chemistry) Task Group has been founded, with the aim “to provide a first comprehensive set of guidelines for measurements and reporting of diffusion properties of chemical compounds in nanoporous materials serving for catalytic, mass separation and other relevant purposes” [1],[2].

As a first step in this initiative, in 2021 there appeared a special issue of the Adsorption Journal with contributions from leading representatives of the different measuring techniques on overall close to 500 pages [3]. The issue was, most importantly, complemented by a paper dealing with diffusion theory and molecular modelling and its relevance for experimental measurement [4]. Finally, in December 2024, as a kind of a condensate of the individual contributions in the special issue of the Adsorption Journal, the IUPAC Technical Report aspired to within the framework of the project initiative has been published [5].

Looking back on the development of the different techniques of measurement, the advent of pulsed field gradient NMR as the first technique of microscopic measurement and, subsequently, the option of microimaging for following the propagation of diffusion and reaction fronts in the individual crystals gave rise to particularly productive steps in our understanding of diffusion in nanoporous materials.

They shall thus be a second focus of the talk. Figs. 1 and 2 show examples of two recently tested applications of these techniques, with information possibilities that have not yet been achieved by any of the other measurement methods [6],[7].

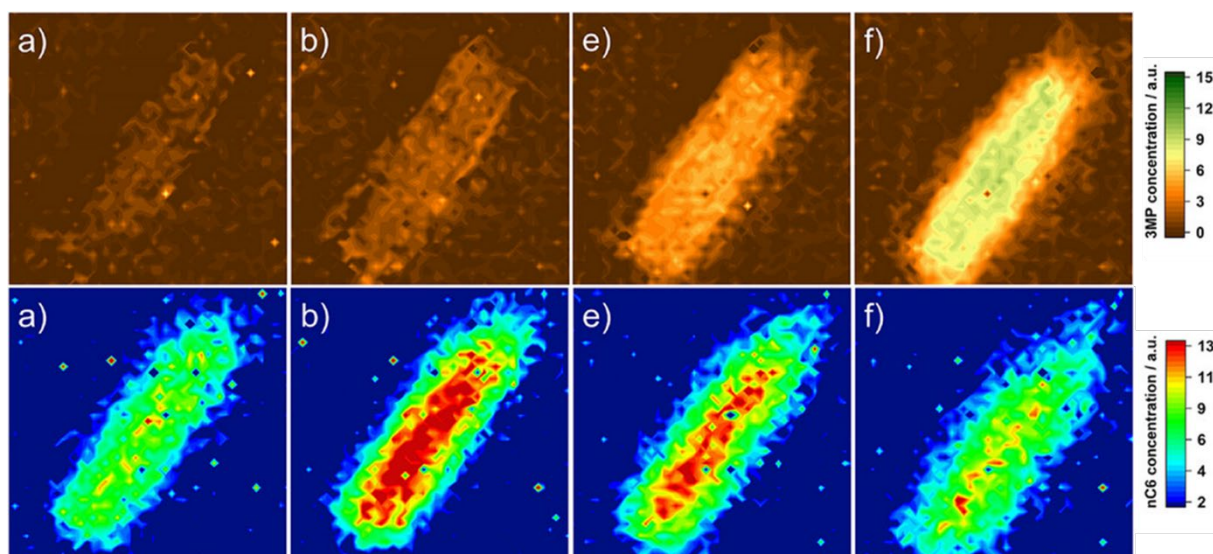


Fig. 1. IR microimages of the concentration of 3-methyl pentane (top) and of *n*-hexane (bottom) in a zeolite crystal of type ZSM-5, following a pressure step in a surrounding (equimolar nC6/3MP) atmosphere from 0 to 0.02 mbar. The images were captured at about ca. (a) 10 s, (b) 1 min, (c) 10 min and (d) 30 min after start of the uptake. Microimaging is seen to allow the direct monitoring of the phenomenon of “overshooting”, with the *n*-hexane concentrations (b, c) notably exceeding their final (equilibrium) value (d) [6].

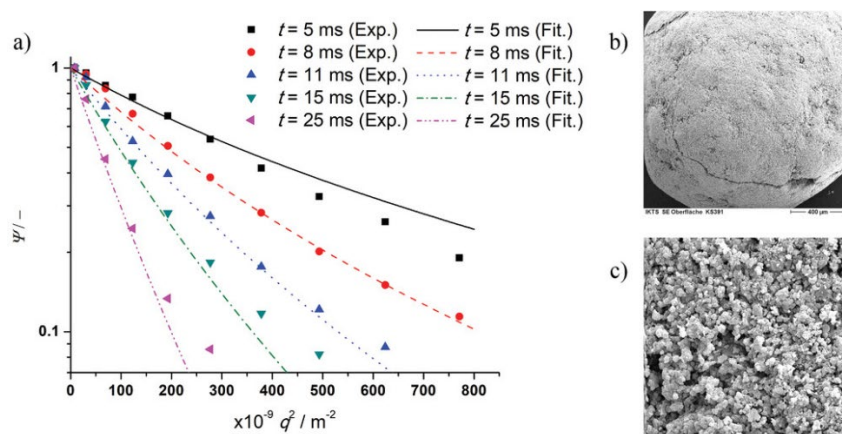


Fig. 2. Consistency check of the applicability of the “two-region model” for quantitating mass transfer in hierarchically structured nanoporous materials [8], using binderless granules of zeolite NaY (right) as a model system. PFG NMR attenuation curves as a finger print of internal dynamics of *n*-hexane (left, experimental points) are found to be in reasonable agreement with the predictions of the two-region model (left, lines [7]).

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