Supporting Information

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1 Interference Microscopy

Interference microscopy has recently been introduced to diffusion studies on microporous materials \(^1,^2\) and a schematic representation of its instrumentation can be seen in Figure 1. The technique is able to monitor transient intracrystalline concentration profiles with a spatial resolution of 0.5 µm x 0.5 µm in short time intervals (presently 10 s, but with no fundamental limitations towards shorter values). Since it is a microscopic technique, it focuses on an individual crystallite and, therefore, information about the intracrystalline process can be directly deduced. Furthermore, interference microscopy has the unique capability to pinpoint irregularities in the interior (and on the surface) of the studied crystal, which were unknown until now \(^3,^4\). Quite often, though, these irregularities dominate the rate of the diffusion process and, in this case, their disclosure is of major importance.

Prior to the measurements, the sample with the crystals is kept under vacuum and activated (heated up in order to remove residual molecules from the pore system). Afterwards, the nanoporous “host” is equilibrated with an appropriately chosen atmosphere of the desired guest molecules. Eventually, molecular uptake or release is initiated by a corresponding variation of the surrounding atmosphere of guest molecules. The camera on top of the microscope records the interference pattern of the crystal under study every 10 s and transfers the pictures to the computer where the evaluation of the experimental data with the help of ad hoc software takes place after the end of the experiment.

The technique is based on the analysis of the interference pattern generated by the superposition of two light beams, one passing through the nanoporous crystal and the other passing through the surrounding atmosphere. Since the optical density depends on the concentration of the guest molecules, changes in local concentration appear directly as corresponding changes in the interference patterns. Therefore, it is possible to deduce the concentration profiles from the measured changes in the interference pattern \(^5,^6\). The quantity directly accessible is the integral over the intracrystalline concentration in the observation direction with a spatial resolution of...
If, due to a corresponding blockage of the relevant crystal faces or because of the architecture of the pore system, diffusion in the $x$-direction is prohibited, there will be no variation of concentration in that direction. In this case, interference microscopy directly yields the local concentrations $c(y,z)$. Otherwise, a more complex analysis must be used for studying the mass transfer.  

\[ \Delta(\Delta \varphi(t)) \propto \Delta \int n(t, x, y, z) \, dx \propto \Delta \int c(t, x, y, z) \, dx \]

Figure 1: Schematics of the measurement of guest diffusion in nanoporous hosts by interference microscopy.  
(a) A schematical representation of the vacuum system to which the cell with the sample is attached;  
(b) The interference microscope on top of which the camera is placed;  
(c) The computer which is directly connected to the camera;  
(d) Schematic representation of the principle of the technique: changes in the intracrystalline concentration during diffusion of guest molecules will affect the refractive index of the crystal ($n_1$) and hence the phase difference $\Delta \varphi$ of the two beams. The correlation of those variables is reflected by the mathematical relation of the figure. Having measured the difference of the optical path length we can evaluate the difference of the intracrystalline concentration;  
(e) Enlarged view of the cell containing the crystal under study.
2 Infrared micro-imaging

The concentration in nanoporous crystals can also be recorded by using the molecular feature of absorbing infrared light with a special wave length. The technique of analysing the wave length (or the wave number, i.e. the inverse wave length) is based on Fourier transformation (FT). Detailed information about the FTIR principle may be found in the literature \(^8\)\(^{-10}\). The used FTIR microscope (Bruker Hyperion 3000) consists of a spectrometer (Bruker Vertex 80v) and a microscope with a Focal Plane Array (FPA) detector (Figure 2) \(^10\),\(^11\). The novel FPA detector consists of an array of 128 × 128 single detectors with a size of 40 µm × 40 µm each. By means of a 15x objective, a resolution of 2.7 µm × 2.7 µm is gained in the focal plane, where the crystals are placed.

![IR micro-imaging device](image)

**Figure 2:** IR micro-imaging device *Bruker Hyperion 3000* consisting of a spectrometer and the microscope with optics and detectors. The main part of the spectrometer is a Michelson interferometer.

Each single element of the FPA detector records the IR signal. The intensity of the IR light as a function of the wavelength, i.e. the transmission spectrum, is determined by means of the spectrometer using Fourier transformation. So, the characteristic absorption bands of molecules which perform vibrations that change the electric dipole moment \(^8\),\(^9\) can be recorded. As a consequence of Lambert-Beer’s law, the concentration of molecules is proportional to the
intensity of the absorption band (Figure 3). Consequently, a two-dimensional concentration profile with a resolution of up to 2.7 µm can be recorded by this IR micro-imaging device.

Figure 3: IR absorption spectra of deuterated propane in MOF Zn(tbip). The absorption band of the C-D valence vibrations is clearly distinguished from the band of the C-H valence vibrations of the crystal framework. The absorption spectrum is the negative logarithm of the ratio of the transmission spectrum of the sample and of the background.

Examples of thus recorded concentration profiles, which evolve during uptake/release or self-exchange experiments, are shown by Figure 4 and Figure 5. This technique provides the unprecedented option to directly determine, from the transient concentration profiles during tracer exchange, self-diffusivities and surface permeabilities, including the potentials of recording the concentration profiles during multi-component mass transfer. Conventional IR microscopy\textsuperscript{12-15}, by contrast, has to imply assumptions on the limiting process during the mass transfer.

Figure 4: Two-dimensional profile of the C-D absorption band recorded by IR micro-imaging. The gray scale displays the intensity of the C-D band (from 0 to 3 a.u.). The crystal is equilibrated with a surrounding atmosphere of 60 mbar of deuterated propane. The bright bar represents the region which yields the profiles displayed in Figure 5. The scattering on the left side of the picture is caused by a “corrupt” illumination of the detector caused by its large size.
Figure 5: Transient concentration profiles of deuterated propane in MOF Zn(tbip) during tracer exchange with the undeuterated isotope at an overall pressure of 60 mbar. The thin lines represent the best fits of the analytical solution (with constant diffusivity and permeability) to the experimental data.
3  Zeolite ferrierite

Silica-ferrierite is a cation-free zeolite with two perpendicular channel systems which intersect each other\textsuperscript{17}. One channel system is adjusted along \( y \)-direction and is framed by an 8-membered ring, this means the rings are formed by 8 oxygen and 8 silicon atoms. The other channel system is along \( z \)-direction and is formed by 10-membered ring channels (Figure 6). The outer geometry is like a cuboid with its long-side lengths in \( y \)- and \( z \)-direction \((l_y = 25 \ \mu m \ and \ l_z = 100 \ \mu m; \ l \) denotes the half edge length) and a short-side length in \( x \)-direction \((l_x \approx 10 \ \mu m)\). On both big side faces of the crystal (parallel to \( y-z \)) there are small roof-like parts (Figure 6). The ferrierite crystals were activated under high vacuum at a temperature of 673 K for 12 h\textsuperscript{4}. Due to large transport resistances at the entrances to the pores along \( z \)-direction, the mass transport proceeds mainly along \( y \textsuperscript{4} \). The adsorption isotherm may be found in ref.\textsuperscript{10}.

![Figure 6: Ferrierite crystal with a two-dimensional pore structure. The scheme shows the channels in \( z \)- and \( y \)-direction.](image)
4 MOF Zn(tbip)

Zn(tbip) (H$_2$tbip = 5-tert-butyl isophthalic acid) $^{18,19}$ is a highly stable representative of the family of metal-organic frameworks (MOFs). The crystals are elongated, hexagonal prisms with lengths of hundreds and diameters of tens of micrometers. Zn(tbip) is traversed by an array of parallel chains of channel segments in the direction of longitudinal crystal extension (Figure 7). The resulting one-dimensionality of diffusion and the structural stability make MOFs of type Zn(tbip) excellent candidates for a systematic investigation of mass transfer in nanoporous materials. Prior to measurement, the sample was activated for 1.5 h under evacuation at 393 K. The adsorption isotherm was determined by IR microscopy and Configurational-Bias Monte Carlo simulations $^{18}$.

Figure 7: Schematics of the investigated Zn(tbip) crystal. The structure of the one-dimensional channel with a loading of 1 propane molecule per segment is also shown (adopted from $^{18}$). The side pockets are ordered like two three-leafed clovers separated by windows of a diameter of 0.45 nm.
5 References


