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Characteristic features of molecular transport in MOF ZIF-8 as revealed by IR microimaging

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ABSTRACT

In this study differences in the diffusion characteristics of several small molecules in MOF ZIF-8 were examined. The diffusion data were obtained using the technique of IR microscopy by investigating individual crystals. Most of the primary data were already published separately but are revisited here, complemented with new data and discussed together as a mini-review on the diffusion characteristics. The range of the reported diffusivities covers six orders of magnitude. This study was only possible owing to the particularly wide range of crystal sizes, from 20 up to 300 μm, available for the diffusion experiments. Different features in the loading dependencies are identified. They reflect a large variety of mechanisms which dominate the mass transfer within the pores, including window blocking effects and molecular clustering. It is demonstrated that the diffusion characteristics may change significantly if a small molecule like methane diffuses in a mixture with other guests. However, this is not a general feature of the system as for larger molecules like ethane and ethene no difference in the mixture was found compared to the single compound. Hence, predictions solely based on single-component data like membrane separation factors may differ notably from the real performance. On the basis of diffusivity measurements with small alcohols the validity of the Darken relation is demonstrated and found to provide a quantitative tool to correlate transport and self-diffusivity in this host system. Besides all details of the underlying transport mechanisms this study provides a broad basis of reference data for the diffusivity in one of the most prominent representatives among the ZIF MOFs.

1. Introduction

Over the last fifteen years the new class of metal-organic frameworks (MOFs), which is also known as porous coordination polymers (PCPs), attained great attention as MOFs may be easily tailored to the particular demands in technical applications [1–9]. A subgroup among the MOFs is built by the zeolitic-imidazolate frameworks (ZIFs) [10–14]. They are based on framework types that are known from zeolites. The ZIF framework is obtained by replacing the T-atoms of the aluminosilicates by transition metals (e.g. Zn, Co, Cu etc.) and the oxygen bridges by imidazolate-type linkers. Reticular chemical synthesis yields a series of homologous ZIF structures with various topologies known from zeolites.

One of the most frequently studied and most stable representative of this group is MOF ZIF-8. For MOF ZIF-8 a variety of experimental and simulation studies were published with a number of striking findings. In the following, just a few of them shall be mentioned. Thus, molecules with critical diameter substantially exceeding the XRD window size of ZIF-8 (3.4 Å) were found to be adsorbed [15–20]. This is attributed to the flexibility of the ZIF-8 structure. Furthermore, a structural transition by reorientation of the linker molecules (“gate-opening”) was reported upon guest adsorption [16,21,22]. The first separating ZIF membranes were synthesized with ZIF-8 [23]. The experimental studies were accompanied by a variety of molecular simulations to provide insight into the underlying mechanism on the atomistic scale [16,24–31].

Concerning the diffusion of guest molecules and their mixtures, only data for selected systems was reported so far [29,32–37]. This study is a combination of a mini-review based on own data which is already published and new results. In the discussion new aspects are highlighted and are presented as systematic investigation of the diffusion characteristics of different small compounds. Differences in the loading dependence of the diffusivity are reported and traced back to different guest–guest and host–guest interactions.

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2. Material and experimental

2.1. Synthesis and ZIF-8 structure

The synthesis of the crystals used in the current study was done by the group of J. Caro (Hannover) within a joint project on MOFs. For specific details it is referred to literature [34,36]. In short, the crystals were obtained in a solvothermal synthesis at 140 °C using methanol as solvent. A diffusion mediated mixing of the salts led to a growth of particularly large crystals of ZIF-8 with sizes up to 300 µm (see Fig. 1a). In addition, smaller crystals obtained in a conventional synthesis with mixed components [23,34,36] were used for further diffusion measurements with propane. For all other data presented, crystals from the diffusion-mediated synthesis batch were taken.

The ZIF-8 structure is equivalent to the zeolitic sodalite structure. It consists of larger cages (ca. 11.6 Å) in cubic arrangement, which are octahedrally connected by narrow windows (XRD size 3.4 Å). In Fig. 1b the structure of one cage is shown (H-atoms are hidden). The C-Atoms near the 6-ring window in the front are marked in black. The structure data were taken from Ref. [21]. Please note, that one unit cell contains two cages.

2.2. IR microscopy (IRM)

The details of IR microscopy and IR microimaging (IRM) are described elsewhere in detail [34,39,40]. Here, only a brief summary will be given.

For the experiments, a few dozens to a hundred of crystals were introduced into an optical cell and activated at 120 °C under vacuum for at least 15 h. For the measurement one individual crystal was selected in the visible mode of the IRM. Crystals with sizes between 20 and 300 µm were selected for the measurements with the different molecules and chosen to adjust the uptake times in a detectable range. While the fastest uptake was finished after about 5 s in the largest crystals, it took several hours for the slowest adsorbate to fill the smallest crystals.

Transport diffusion experiments are initiated by step-changes in the gas phase surrounding the crystals. Alternatively, the gas phase might be quickly evacuated and replaced by the fully deuterated compound at the same initial pressure. Then, the tracer exchange of the guest molecules can be followed separately by means of their different IR vibration frequencies to obtain self-diffusivities.

The intensity of characteristic vibrations of the guest molecules is recorded in a time-resolved manner. According to the Beer-Lambert-law, the intensity of these bands can be considered as proportional to the guest concentration within the investigated crystal. From the equilibrium data adsorption isotherms can be constructed. Other experimental data from literature were used to calibrate the IRM isotherms, i.e. to determine the conversion factor from the a.u.-units of the IR signal into absolute concentrations. After calibration, in all cases the initial slope (Henry regime) and the maximum loading at high pressures were in good agreement with the reference data. The IRM mixture data were calibrated based on the single-component data and compared to predictions from ideal adsorbed solution theory (IAST).

2.3. Data analysis

The mathematical structure for transport diffusion and self-diffusion by tracer exchange is very similar in the notation of Fick's 1st law [41]:

$$j_x = -D_T \frac{\partial c}{\partial x} \quad \text{and} \quad j_x^* = -D_s \frac{\partial c^*}{\partial x} \tag{1}$$

with the flux density j, the concentration c and D_T and D_s as transport and self-diffusivity, respectively. The asterisk denotes labelled particles with identical diffusion properties as the unlabeled species (e.g. a fully deuterated compound). By fitting the integral uptake curves or transient concentration profiles the transport parameters can be obtained. Here, the solution of Fick's second law for spherical particles was employed [41,42]:

$$\frac{c(t)}{c_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \pi^2 \frac{D_T}{r^2} t \right) \tag{2}$$

were r is an effective radius defined as the radius of the equivalent sphere with the same surface-to-volume ratio as the ZIF-8 crystal under study. For crystals with the shape of rhombic dodecahedra it follows from the edge length of the rhombic faces a via $r = \sqrt{2/3}a$. The tracer exchange curves were fitted with the same formula to obtain D_S.

An alternative approach to diffusion was formulated by Einstein, Stefan and Maxwell, using the gradient of the chemical potential as the thermodynamic driving force. By comparison with the Fickian model an equation is found which correlates the transport (Fickian) diffusivities D_T and corrected diffusivites D_0 via the thermodynamic factor $d\ln p/d\ln c$:

$$D_0 = D_T \frac{d \ln c}{d \ln p} = D_T \frac{dc/dp}{c/p} \tag{3}$$

The thermodynamic factor can be directly obtained from the adsorption isotherms. For single-component systems the corrected diffusivity D_0 is identical to the Maxwell–Stefan diffusivity $Đ_\mathrm{MS}$. In systems with negligible correlations for the elementary diffusion steps corrected and self-diffusivity equal each other. Eq. (3) is then referred to as the Darken relation [41].

The description of mixture diffusion is complicated by the fact that in general the components may interact and influence each

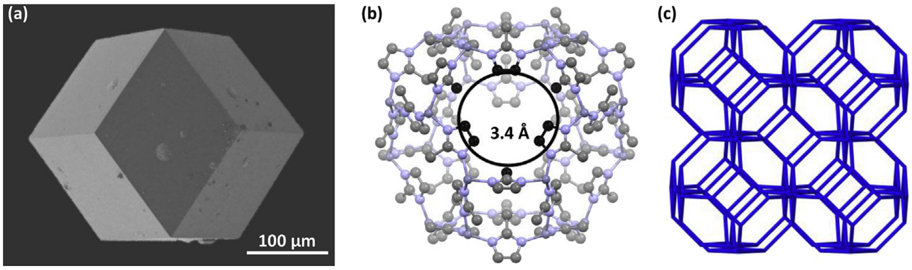

Fig. 1. **(a)** SEM image of a giant ZIF-8 crystal obtained by the synthesis described in Refs. [23,34,36] (courtesy of J. Caro). **(b)** Structure of a ZIF-8 cage (H-atoms hidden). The C-atoms near the narrow 6-ring window in the front are highlighted in black. The structure data were taken from Ref. [21]. **(c)** SOD topology know from zeolites [38].