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Revealing Transient Concentration of CO₂ in a Mixed Matrix Membrane by IR Microimaging and Molecular Modeling

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Abstract: Through IR microimaging the spatially and temporally resolved development of the CO₂ concentration in a ZIF-8@6FDA-DAM mixed matrix membrane was visualized during transient adsorption. By recording the evolution of the CO₂ concentration, it is observed that the CO₂ molecules propagate from the ZIF-8 filler, which acts as a transport “highway”, towards the surrounding polymer. A high-CO₂-concentration layer is formed at the MOF/polymer interface, which becomes more pronounced at higher CO₂ gas pressures. A microscopic explanation of the origins of this phenomenon is suggested by means of molecular modeling. By applying a computational methodology combining quantum and force-field based calculations, the formation of microvoids at the MOF/polymer interface is predicted. Grand Canonical Monte Carlo simulations further demonstrate that CO₂ tends to preferentially reside in these microvoids, which is expected to facilitate CO₂ accumulation at the interface.

Recent trends in mixed matrix membranes (MMMs) have led to remarkable progress on MMM fabrication techniques and a proliferation of new metal-organic framework (MOF)-based MMMs with enhanced separation performance overcoming the

limitation of pure polymeric membranes, namely the inevitable trade-off between guest molecule permeability and selectivity^[1]. Most of the applications of such composites are closely related/subject to the rate of molecular mass transfer between the internal pore system and their surrounding gas phase. Despite significant development of new MMM generations, relatively few fundamental studies dealing with the limiting steps of intrinsic mass transfer of guest molecules in MMMs and their quantitation have been published. As a consequence, casual factors associated with CO₂ uptake in the two different phases, i.e. fillers and polymer, within MMMs still remain speculative. A thorough investigation on the interfacial structures of MMMs and the individual and/or integrated effects of the two components on the overall uptake of guest molecules in the composites, which became possible recently along with molecular modeling^[2] and microimaging by infrared microscopy (IRM)^[3], is therefore considered as a prerequisite for a rational design of industrial-scale MMMs with optimum performance. To achieve optimum transport properties of MMMs, in particular, exploitation of the interfacial contact zone between fillers and polymer is very important^[4]. Depending on the interaction of fillers to surrounding polymer, (i) a nanometer-sized void phase, appearing as a gap, can be formed between the two components^[4-5] or (ii) structural modification of the polymer can occur in close proximity to the fillers, which is known as the “interfacial phase”^[6]. Among the numerous models in literature^[7], which are mostly derived or developed from Tafel equation^[8] to predict the permeability of MMMs, a rigorous modeling approach recently proposed by Petropoulos et al.^[6b] specifically takes into account the third phase, i.e., CO₂ adsorption on the fillers and polymer.

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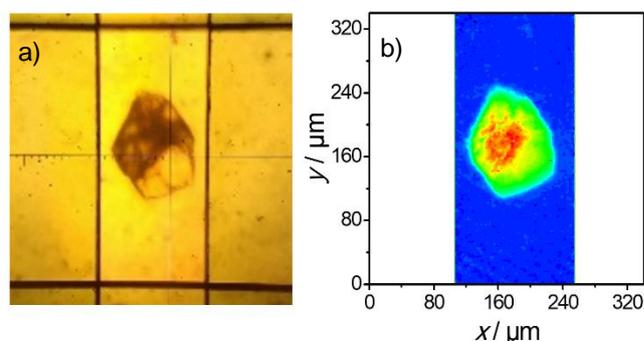


Figure 1. A big ZIF-8 crystal embedded in 150 μm -thick 6FDA-DAM polymer is placed in the measurement window (ca. 145 μm \times 340 μm size) which has been subject to microimaging via IR microscopy. a) The ZIF-8@6FDA-DAM MMM under the microscope in Viewing Mode. b) Color-filled contour map of ZIF-8 content in absence of CO₂. The increase of ZIF-8 content is indicated by the color change from blue to red.

polymer colored in blue in the map indicates that there are no small, powder-like ZIF-8 crystals present in the current measurement window. This observation was also confirmed by comparing the IR light absorbance spectra of different areas around the crystal (see Supporting Information and Figure S3). The red color at the center of the crystal illustrates that its center is thicker than its boundary.

In addition to Figures 1a and 1b, a Focused Ion Beam-Scanning Electron Microscopy (FIB-SEM) micrograph of the same type of the MMM (Figure S2) also shows no apparent empty gap between the fillers and the polymer. Although it is often used to assess the quality of the polymer-filler interface in MMMs, it does not provide us with a complete picture of the interfacial inhomogeneity and defects at the nanometer scale. To evaluate the nature of the polymer-filler interactions and their microscopic compatibility, molecular simulations and solid-state nuclear magnetic resonance will be employed later in the present study.

Figure 2 provides a series of time-resolved images of CO₂ concentration as captured by IR microimaging during the uptake of CO₂ in the ZIF-8@6FDA-DAM MMM (see Supporting Information). The filler ZIF-8 is clearly seen to reach equilibrium within 100 s (Figure 2b) since the commencement of the uptake, and its CO₂ concentration does not vary significantly until the end of the experiment. This is an expected behavior, considering the intracrystalline diffusivity of ZIF-8 of an order of 10⁻¹⁰ m² s⁻¹^[14] and its size. At equilibrium (Figure 2h), the polymer exhibits a higher CO₂ loading than the filler as expected from the CO₂ adsorption isotherms of the two components (Figure S4). It is also noticeable in Figure 2a–d that the CO₂ molecules propagate from the filler to the surrounding 6FDA-DAM polymer. The filler thus appears to act as a CO₂ mass transport, thereby accelerating the overall uptake or the permeance of CO₂ in the MMM. Such transport patterns were already predicted and reported in the literature^[15], but are here clearly visualized for the first time.

Furthermore, it should be noted that a high-CO₂-concentration layer (ca. 5 μm thick) is formed at the interface between ZIF-8 and 6FDA-DAM polymer during the transient adsorption, colored in red in Figure 2. At equilibrium, more CO₂ molecules tend to reside in the interfacial region, compared to the bulk polymer phase. This phenomenon was even more pronounced at higher CO₂ pressures in the surrounding gas phase. Figure 3 shows separate images of CO₂ concentration in the ZIF-8@6FDA-DAM MMM at different equilibrium pressures at 308 K (see Supporting Information). The increased CO₂ concentration at the interface was seen to become more prominent as we shifted to higher equilibrium pressures.

To shed light on the causes of the CO₂ accumulation at the interface, two sets of molecular simulations have been performed. First, the MOF/polymer interface was modeled by applying a recently developed methodology^[2a] that relies on density functional theory (DFT) and force-field based calculations. These simulations allowed us to obtain a microscopic description of the structural features that characterize the MOF/polymer interface. As a second step, the preferential location of adsorbed CO₂ in this MOF/polymer model was identified by means of Grand Canonical Monte Carlo (GCMC) simulations.

A previously DFT-optimized ZIF-8 [011] surface model^[2a] was combined with a polydisperse 6FDA-DAM model generated by an *in-silico* polymerization procedure^[16]. The polymer was modeled as a flexible collection of charged Lennard-Jones (LJ) sites with bonds, angles and dihedral energy potential parameters taken from the General Amber Force Field^[17], charges computed at the DFT-level and 12-6 LJ interatomic potential parameters taken from the TraPPE^[18] potential as already used for other polymers^[2a, 19]. The model, consisting of several chains ranging between 9 and 37 monomers, was validated by a very good agreement between simulated density and X-ray scattering pattern and the corresponding experimental data (see Supporting Information

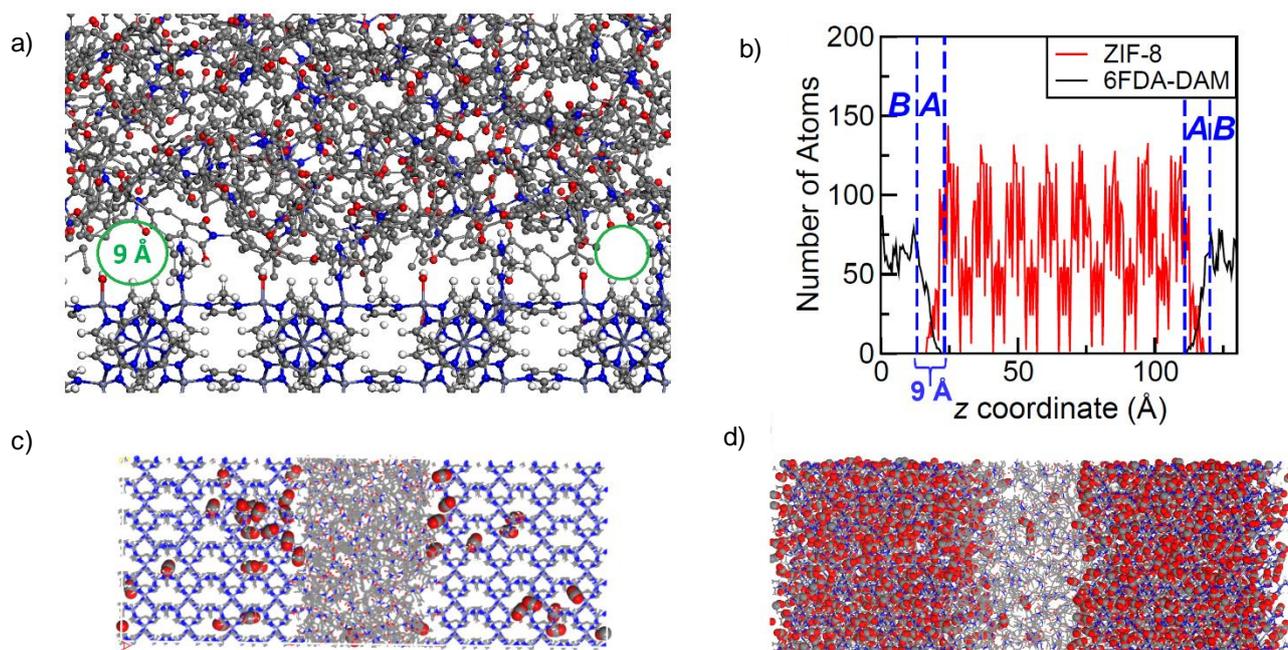


Figure 4. a) Representative snapshot of the interface where microvoids can be seen (C in grey, O in red, N in blue, H in white), b) Atomic density of ZIF-8 and 6FDA-DAM as a function of the coordinate perpendicular to the ZIF-8 surface, c, d) Representative configurations of the loaded MMM models at low and high pressure, respectively.

and Figure S6). This model was subsequently combined with that for the ZIF-8 surface model through a series of molecular dynamics (MD) simulations that included changes in temperature and pressure in order to allow the polymer to adapt its configuration to the external field imposed by the chemistry and morphology of the MOF surface^[2a]. Finally, structural data were collected from 10 statistically independent MD runs, spanning 10 ns each. The interface was found to be inhomogeneous at the nanometer scale, consisting of well-defined microvoids that are delimited by anchoring points resulting from weak interactions between the -NH and -OH terminations at the ZIF-8 surface and the -CH₃, -CF₃ and -CO groups of 6FDA-DAM (see Figure 4a, Figure S8 and Supporting Information). Figure 4b shows the atomic density of 6FDA-DAM as a function of the distance from the ZIF-8 surface along the z-direction (note that here the z-direction corresponds to the direction perpendicular to the MOF surface). In the closer proximity to the surface the atomic density of the polymer drops to zero (**region A**). This step-change which occurs along the first nanometer of the surface (9 ± 1 Å) is a consequence of the presence of the microvoids at the interface, of up to 9 Å diameter (see details in Supporting Information and Figure S7). These microvoids are large enough to accommodate CO₂ molecules, and might be the origin of the CO₂ injection from the MOF into the polymer, as discussed above. The prediction of the presence of microvoids is further supported by solid-state nuclear magnetic resonance (SSNMR) experiments (see Supporting Information). The ¹³C-¹H HETCOR (heteronuclear correlation) spectrum of the ZIF-8@6FDA-DAM MMM revealed the absence of strong interactions between the filler and the polymer, thereby implying poor compatibility of the two components (Figures S9-S11). Above a distance of 5 Å away from the last atom of the MOF surface, the atomic density of polymer fluctuates around more or less a constant value (**region B**), which still differs from that of the bulk polymer. This means that the polymer in **region B** still feels the impact of the MOF surface and a larger length along the z-direction would be required to mimic a bulk-like behavior at longer separating distances, as previously evidenced for the HKUST-1/PV OH^[2b] composite. **Regions A** and **B** describe the MOF/polymer interface and its first-neighbor environment, respectively, and consequently they only constitute a tiny part of the high CO₂ concentration region found at the border of the MOF nanoparticle (nanometers versus micrometers).

To confirm that the CO₂ molecules can reside in the microvoids, GCMC simulations were further performed to explore the preferential sittings of CO₂ into the atomistic composite model. Two different CO₂ pressures were explored: 0.15 and 30 bar to model the first adsorption stage and the saturation regime, respectively. The CO₂ molecule was described by a charged LJ 3-sites model^[20] while all atoms of the MOF model were treated with charged LJ sites with parameters taken from the UFF^[21] force field. The CO₂ molecules were found to be primarily located both in the ZIF-8 pores and in the microvoids present at the MOF/polymer interface (Figures 4c and 4d). These results thus provide microscopic insight into the structural features that give rise to the first stages of the generation of the high CO₂ concentration region at the ZIF-8/6FDA-DAM interface. It is important to remark that the latter region extends experimentally up to the micrometer scale, while the microvoids we describe are of sub-nanometric dimensions. We thus propose that the filling of the microvoids is only the first step in a mechanism that must also involve other transfer phenomena at the mesoscopic scale that

cannot be currently investigated with our atomistic-based models^[2b].

In summary, microimaging by IR microscopy has been applied to record the evolution of CO₂ concentration in the ZIF-8@6FDA-DAM MMM. To the best of our knowledge, such a type of concentration between the polymer and the filler has never been achieved so far. We have demonstrated from the time-resolved images that the CO₂ molecules propagate from the filler, which is the origin of CO₂ mass transport, to the surrounding polymer. We have also observed the enhancement of CO₂ concentration at the interface between the polymer and the filler at equilibrium. This phenomenon becomes even more pronounced at higher gas pressures. A microscopic explanation of the first stages of this phenomenon has been provided by means of atomic simulations, which have evidenced the presence of microvoids at the MOF/polymer interface. GCMC simulations have shown that the accumulation of CO₂ molecules is favored in these microvoids, which could constitute the first step in the mechanism of the formation of the high CO₂ concentration layer at the interface with the MOF and further support the importance of filler-polymer compatibility in MMM performance.

In future studies, the CO₂ transport diffusivity in the same MMM may propagate from an open edge of a surface-coated MMM towards its interior in which fillers are located. After calculating the diffusivity, the Maxwell model^[8], which is often considered as the most appropriate model to predict MMM behavior especially for MMMs with low volume fractions of filler^[4, 22], may be applied in order to study its validity in the present MMM.

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Keywords: IR spectroscopy, Adsorption, Mixed Matrix Membrane

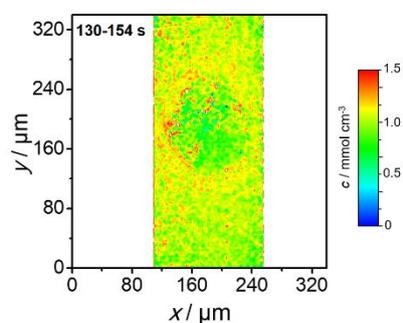
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Entry for the Table of Contents

COMMUNICATION

The evolution of the CO₂ concentration in ZIF-8@6FDA-DAM MMM during transient adsorption was visualized by means of IR microimaging technique. CO₂ molecules propagate from the ZIF-8 filler, which acts as a transport polymer. A high-CO₂-concentration layer is formed at the filler/polymer interface. A microscopic explanation of the first stages of this phenomenon is suggested via molecular modeling (see picture).



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