Molecular Diffusion in a Flexible Mesoporous Metal-Organic Framework over the Course of Structural Contraction

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ABSTRACT. In situ $^1$H pulsed field gradient (PFG) NMR was used to investigate molecular diffusion of $n$-butane at 298 K during the negative gas adsorption (NGA) transition caused by contraction of the flexible metal-organic framework DUT-49(Cu). Supported by molecular dynamics simulations, it provided crucial insight to confined diffusion within a highly-flexible pore environment. The self-diffusion coefficients were derived from the experiment and compared with simulations, capturing the diffusion during $n$-butane adsorption and desorption. This complementary approach has yielded experimental characterization of molecular diffusion mechanisms during the unique process of NGA. This includes the observation of a 4-fold decrease of diffusivity within a less than 2 kPa gas pressure variation, corresponding to the NGA transition point.

**KEYWORDS:** flexible MOFs, DUT-49(Cu), diffusion, molecular dynamics, in situ PFG NMR.
Metal-organic frameworks (MOFs) are a class of crystalline porous materials, designed by a modular building principle connecting inorganic nodes, such as metal ion or clusters, with organic multidentate ligands to form a broad variety of the open framework structures. Owing to their unique porosity characteristics, MOFs are poised for a variety of applications typical for porous solids such as gas storage, gas separation, catalysis, sensor applications and adsorptive heat transformations. In contrast to conventional nanoporous materials, such as zeolites, silicas or carbons, which generally exhibit rigid pore systems, some MOFs feature pronounced framework dynamics, reflected in porosity changes. These dynamics can be induced by external stimuli such as guest molecules or electromagnetic irradiation.\textsuperscript{1,2} Flexible MOFs have demonstrated extremely high selectivity for gas separation.\textsuperscript{3–8} However, the understanding of framework dynamics and its implication on guest mobility is in its infancy. For kinetic gas separations, a better understanding of molecular dynamics in such systems is of great importance. Moreover, the role of molecular dynamics and its influence on framework responsivity has rarely been studied.

Negative gas adsorption (NGA) is a unique counterintuitive phenomenon recently discovered in the micro-mesoporous framework DUT-49(Cu).\textsuperscript{9} NGA can be described as spontaneous release of adsorbed molecules, accompanied by the structural transition from an open pore (\textit{op}) to contracted pore (\textit{cp}) phase. It is observed upon adsorption of subcritical fluids close to their standard boiling points. The structure of the framework in the \textit{op} state contains three distinct pore types - metal-organic polyhedron cages (10 Å diameter, “\textit{cub.”}), which are interconnected to form tetrahedral- (17 Å diameter, “\textit{tet.”}) and octahedral (24 Å diameter, “\textit{oct.”}) cages (Figure 1). The transition from the \textit{op} to \textit{cp} phase has a strong influence on the pore system of DUT-49.
The smallest *cub*.-cage remains unaltered, whereas *tet*.- and *oct*.-pores contract into micropores with a wider distribution in the range (5-11) Å due to the irregular pore shape after contraction.

**Figure 1.** Crystal structure of the DUT-49(Cu) showing unit cells and pore types in the open pore (op, blue) and contracted pore (cp, red) phases.

The diffusion of fluids in the pores of MOFs can be evaluated by experimental and theoretical approaches.\(^{10-26}\) Amongst these, the combination of pulsed field gradient (PFG) NMR and molecular dynamics (MD) simulations represents a powerful complimentary approach to enable the exploration of diffusion at time- and length scales differing by orders of magnitude.\(^ {14,27,28}\) MD simulations can track molecular mobility within a single pore of ideal structures, while the PFG NMR is capable of direct probing of molecular displacements ranging from hundreds of nanometers to microns, i.e. being potentially relevant for applications. Previously, Snurr et al.\(^ {22}\) investigated diffusion of methane, ethane, propane and *n*-butane as pure components and in mixtures in DUT-49(Co) by MD simulations. The diffusivity of *n*-butane, using a rigid framework model, revealed type IV dependence (or \(\cap\)-type) according to Kärger and Pfeifer classification,\(^{29}\) however, no further experimental observations or analysis was reported with respect to structural transitions.
In the present contribution, we provide first experimental demonstration of a step-like change of a sorbate diffusion mechanism triggered by the NGA phenomenon. The self-diffusion of \( n \)-butane in DUT-49(Cu) framework at 298 K in the pressure range from 0.7 to 101 kPa was probed in situ using PFG NMR and complete atomistic analysis by MD simulations for a range of loadings, from near-zero to almost full pores saturation. The combination of these two techniques allowed tracing diffusion at length scales of several \( \mu \)m (by NMR) and several nm (by MD) highlighting the complex loading- and framework phase dependent diffusion of gas inside this flexible porous material.

A batch of DUT-49(Cu), with average crystallite size of 14 \( \mu \)m, was synthesized using established protocols (for details see sections 1 and 2.2 of the ESI), in order to minimize the influence of interparticle diffusion. After solvent removal using supercritical CO\(_2\), initial analysis using powder X-Ray diffraction (PXRD), digestion \(^1\)H and \(^{13}\)C NMR and elemental analysis confirmed synthesis of highly crystalline DUT-49(Cu). Adsorption of \( n \)-butane at 298 K confirmed the expected phase transitions between the \( op \) and \( cp \) phases at 30 kPa, accompanied by the NGA (Figure 2).
A flexible model of DUT-49 was employed using the MOF-FF forcefield, and the TraPPE forcefield for n-butane. Simulations were performed for op and cp phases of DUT-49 in the absence of structural transitions. Detailed description of the simulation methodology can be found in the section 3 of the ESI. It is worth noting that the simulations reveal changes by less than 1% for the cell- and pores volume during adsorption within the op phase.

The loading dependences of the self-diffusion coefficient obtained by MD simulations for n-butane in the op and cp phases are presented in Figure 3a. Upon adsorption in the op phase, the
entire loading dependence revealed type IV dependence according to ref.\textsuperscript{29} and showed excellent agreement with data of ref.\textsuperscript{22} A monotonic increase of diffusivity with increasing loading below 100 mol./u.c. is associated with preferable residence of molecules in the smaller $\textit{cub.}$-pores. These pores possess sites with higher adsorption energies, occupation of which reduces mobility. Similar effects have been observed in other experimental studies (see, e.g., refs.\textsuperscript{30-32}) showing monotonic diffusivity increase at low loadings. Thus, the changes observed for $n$-butane diffusion for the $\textit{op}$ phase were found to be directly related to the preferable pore filling at a given loading. Snapshots of each simulation were used to locate $n$-butane molecules with respect to the pore structure. This analysis employed a Monte Carlo (MC) approach to sample the pore space and categorizes the pore system according to the three different pore environments and determines the relative occupancy.
Figure 3. (a) – Self-diffusion coefficients of n-butane simulated for op and cp phases of DUT-49(Cu) at 298 K. (b) – Simulated loading of each individual pore type in the op phase as a function of the total loading. The inset represents snapshots of the complete unit cell saturation.

The pore site analysis highlights the loading-dependent occupancy of each pore within the structure. Surveying changes in loading in each pore type, Figure 3b, at low loading n-butane preferentially fills the smallest pore with few molecules in the larger pores. The loading dependence of diffusivity in the cp phase reveal moderate variations although being always lower than in the op phase due to reduced sizes of the tet.- and oct.-pores and thus stronger confinement effect. It is worth noting that at the lowest loading of 0.1 mol./u.c. used in MD...
simulations, diffusivity in the *op* phase is ~2-fold higher than that in the *cp* phase. Since the molecule-pore surface interaction potential is the same for both phases, this observation may result from the modified confinement of *tet.*- and *oct.*-pores. In the *cp* phase, molecules interact with the surface of these pores more frequently compared to the *op* phase leading to the observed difference of the self-diffusion coefficients. At higher loadings, this difference further increases due to higher population of the *tet.*- and *oct.*-pores by *n*-butane thus leading to their higher impact into the diffusivity. It is evidently seen at loadings >100 mol./u.c., where in both phases *cub.*-pores are fully saturated (see Figure 3b). Thus, only diffusion in *tet.*- and *oct.*-pores is distinctive for the different *cp* and *op* phases, due to pore size variation, producing the observed difference in diffusivity of ~(5-9)-fold.

PFG NMR is capable of providing high accuracy diffusion experimental measurement during the sorbate-induced framework transition in situ. Selected NMR signal attenuations are presented in Figure 4a and the full set of attenuation curves is provided in section 4 of the ESI. Generally, the curves exhibit a poly-exponential shape characterized by three or more *n*-butane diffusivities. This is a result of the several possible diffusion regimes that NMR is sensitive to, including, e.g., diffusion through the gas phase between the crystals, film diffusion on the outer crystal surface, diffusion upon exchange between the intra- and inter-crystalline spaces. In such case, a complete analysis of attenuation curves and assignment of diffusivities would be rather speculative. Thus, we focus solely on the analysis of the high-gradient region, resulting in the lowest observable diffusivity. It corresponds to the intra-crystalline diffusion, i.e., within the pore space of an individual MOF-crystal, for which the lowest value of diffusivity amongst other mechanisms is expected. These values are presented in Figure 4b as a function of *n*-butane pressure and in Figure 4c, in which the x-axis is transformed to loadings using a measured sorption isotherm.
Figure 4. A set of selected diffusion attenuation curves for n-butane adsorbed in DUT-49(Cu) at 298 K (a). The self-diffusion coefficients obtained using the analysis of a high-gradient part of
the attenuation curves and plotted as a function of (b) pressure and (c) loading per unit cell. Using letters “A-F” and the corresponding color-coding, the respective self-diffusion coefficients obtained from the data set (a) are highlighted in (b) and (c).

Diffusivities are measured throughout the adsorption process from 0.7 kPa to 100 kPa. The characteristic inflection points on the adsorption branch of the loading dependence are indicated by letters alphabetically from “A” to “F”. Upon adsorption from “A” to “B”, a monotonic increase of diffusivity is observed revealing a qualitative agreement with diffusivity increase seen by MD simulations in the range (0-100) mol./u.c. This increase is attributed to preferable occupation of cub.-pores and surface diffusion in the tet.- and oct.-pores with hopping between different surface adsorption sites with pronounced energetic heterogeneity. Based on in situ neutron powder diffraction study at defined methane loadings in DUT-48, -49 and -50 at 111 K and corresponding GCMC simulations, the preferable adsorption sites in the cub.-pores are triangular pore windows and open copper sites, while in the tet.- and oct.-cavities these are their linker backbones.

A plateau between the points “B” and “C” (130-169 mol./u.c.) followed by an increase until “D” (i.e., 169-211 mol./u.c.) is reached at loadings of a near-complete saturation of the cub.-pores and progressive filling of larger ones. In this range, several diffusion mechanisms are expected resulting in a complex dependence for diffusivity. In addition to configurational diffusion in the cub.-pores there is the possibility of diffusion of condensed n-butane on the crystal surface and diffusion through the gas-like phase in the partially filled tet.- and oct.-pores. The intrinsic flexibility of the framework and its response to the formation of condensed phase may also affect diffusion in this loading range. For further clarification and deeper understanding
of involved diffusion mechanisms, the synthesis of MOFs isoreticular to DUT-49, but with notably lower framework flexibility is currently in progress.

The most remarkable observation of this study occurs at approximately 36 kPa or 211 mol./u.c., which according to \(n\)-butane sorption studies corresponds to the pressure of the NGA step (see Figure 2a). The NGA step between points “D” and “E” is accompanied by a large change of the total specific pore volume (from 2.9 to 1.1 cm\(^3\)g\(^{-1}\)). Here, the self-diffusion coefficient undergoes a dramatic \(\sim\)4-fold decrease within a narrow window of only 2 kPa pressure change, i.e. the self-diffusion coefficient drops from \(4 \cdot 10^{-9}\) m\(^2\)s\(^{-1}\) to \(1 \cdot 10^{-9}\) m\(^2\)s\(^{-1}\). Notably, this precisely coincides with the value predicted in MD simulations (\(\sim 1.1 \cdot 10^{-9}\) m\(^2\)s\(^{-1}\)) for the same loading of 162 mol./u.c. This is due to an abrupt shrinking of \(tet\.-\) and \(oct\.-\)pores upon framework transition from the hierarchical micro-mesoporous DUT-49\(op\) into the purely microporous DUT-49\(cp\). This transformation strongly enhances the impact of the nanopore confinement on the \(n\)-butane diffusion within MOF crystal. Further increase of a pressure to 100 kPa led to only slight decrease of diffusivity due to increased “crowding” within micropores and thus more often inter-molecular collisions.

Subsequent desorption from 100 kPa to 30 kPa reveals slight increase of diffusivity as the pores become less filled. Finally, from 30 kPa to 0.3 kPa there is a decrease observed owing to adsorption on the strongest adsorption sites. However, an additional possible influence on this decrease originating from the progressive contraction of the framework upon desorption in the \(cp\) phase cannot be excluded and thus requires further investigation. It is worth mentioning that diffusivities obtained by MD simulations of the \(cp\) phase and PFG NMR of the desorption branch showed an excellent quantitative agreement. This suggests that prepared MOF crystals are nearly-ideal possessing negligibly small amount of structural defects hindering sorbate
diffusion. Such defects typically lead to higher diffusivities obtained by MD simulations compared to the measured ones in PFG NMR experiments. On the adsorption branch, moderate difference between simulated and experimental diffusivities might originate from the framework flexibility of entire MOF crystals. This cooperative effect cannot be accounted in the MD simulations using periodic boundary conditions.

In summary, the presented study demonstrates high capability of the PFG NMR for an in situ investigation of sorbate diffusion in highly-flexible MOF structures, which to the best of our knowledge has not been reported until now. The combination of PFG NMR with MD simulations has revealed the distinctive diffusion behavior of $n$-butane in the DUT-49(Cu) during adsorption and desorption at 298 K. In the range of investigated pressures and loadings, the self-diffusion coefficients of the $op$ phase are always higher than the $cp$ phase in both simulations and NMR experiments. This is due to more pronounced confinement effect originating from the $tet.$- and $oct.$-pores changing their size from 17 Å and 24 Å, respectively, to (5-11) Å. At loadings up to a saturation of $cub.$-pores as seen by our adsorption site analysis, diffusion is mostly determined by interaction of $n$-butane with strong adsorption sites – copper metals of $cub.$-pores and linkers framing $tet.$- and $oct.$-pores. As a result, the diffusivity increases with loading due to preferable occupation of these sites by sorbate molecules and thus lowering their accessibility at higher loadings. After saturation of $cub.$-pores, and progressive filling of larger $tet.$- and $oct.$-pores, the diffusivity drops by 4-fold within pressure change from 35.7 kPa to 37.4 kPa. This corresponds to the range of NGA-step of (31-37) kPa observed in volumetric sorption experiments at the same temperature. As a result, this large change in diffusivity is attributed to the colossal structure transition triggered by the gas sorption. Further pressure increase until 100 kPa showed only slight decrease in diffusivity due to continued “crowding” within the contracted
pore space. The results of our study also suggest that when complimentarily supported by MD and MC simulations, the PFG NMR provides essential experimental understanding of molecular diffusion mechanisms in a variable pore structure. Besides the fundamental interest, deeper understanding of molecular diffusion mechanisms in flexible MOFs is also of crucial importance for rationalizing their selective pore dynamics in the MOF-based separation applications.
ASSOCIATED CONTENT

**Supporting Information.** The Supporting Information is available free of charge at https://pubs.acs.org/doi/XXXXXXX. Details of the NMR experimental procedures and MD simulations, including additional information about textural, structural and sorption properties of DUT-49 (PDF).

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**Notes**

The authors declare no competing financial interests.

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