Deciphering the Relations between Pore Structure and Adsorption Behavior in Metal–Organic Frameworks: Unexpected Lessons from Argon Adsorption on Copper–Benzene-1,3,5-tricarboxylate

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Supporting Information

ABSTRACT: Consistent adsorption characterization of metal–organic frameworks (MOFs) is imperative for their wider adoption in industry and practical applications. Current approaches are based on the conventional intuitive representation of MOF pore space as a regular network of pore compartments (cages and channels), adsorption in which occurs independently according to their geometric dimensions. Here, we demonstrate that this conventional approach is unable to describe even qualitatively the shape of Ar adsorption isotherms on hydrated and dehydrated Cu-BTC structures, one of the most well-known MOF materials. A combination of geometric characterization of MOF crystallographic structure, molecular simulation, and virtual visualization of the adsorption process reveals that the filling of the adjacent pore compartments proceeds in parallel in a complex cooperative fashion. The proposed synergistic approach helps us to understand the relations between pore structure geometric and chemical features and adsorption behavior, laying down a foundation for improved methods for MOF characterization.

Metal–organic frameworks (MOFs) and related classes of porous crystals have dominated the literature on adsorption studies in the past 10 years.1−12 The promise these materials hold for various applications stems from their exceptional adsorption characteristics and wide range of textural properties. The important issue that needs to be addressed is consistent structural characterization of MOFs. Despite being crystalline materials in theory, real samples often deviate from the ideal structure due to residual solvent and reactants in the structure, missing linkers, and partially collapsed regions of the framework. The most instructive technique that is routinely used for MOF characterization is physical adsorption of nitrogen or argon at their normal boiling temperatures.13 Measured adsorption isotherms contain important information about the sample porosity, surface area, and pore sizes, provided a clear link exists between adsorption behavior and pore structure. It is assumed that, as the gas pressure increases, the adsorbate fills the pores in the order of their sizes, so that the pore size distribution (PSD) can be derived using a particular kernel of reference adsorption isotherms in model pores of different sizes.13

However, generic adsorption characterization methods rely on simplified pore structure models (independent cylindrical, spherical, or slit-shaped pores), which neglect real complex pore morphology of MOF crystals and produce, in some cases, PSDs inconsistent with the crystallographic parameters.14,15 Molecular simulations and computational structure characterization tools can be of immense help to remedy this situation, since in silico, unlike in experiments, one can investigate properties of an ideal, defect-free crystal, generate adsorption isotherms using well-developed force fields, and directly obtain information on the pore morphology. Superficially, one may think that, for the case of an idealized, perfect MOF, development of relations between structural characteristics and adsorption isotherms should be a straightforward task. However, application of this approach to a well-known Cu-BTC structure led to several challenges and unexpected lessons which we would like to share and explore in more detail, as they will be instrumental in further efforts to develop reliable characterization approaches.

Since its first reported synthesis in 1999 by Chui et al.,16 Cu-BTC (also known as HKUST-1) has been extensively investigated using both experimental and theoretical approaches. Notably, the first molecular simulation study of adsorption in MOFs was performed on Cu-BTC.17 The basic building block of Cu-BTC is formed by Cu atoms coordinated by benzene-1,3,5-tricarboxylate (BTC) ligands. Adsorption and catalytic properties are mainly determined by accessibility of unsaturated metal sites that might be easily hydrated or occupied by impurities or ligands. One of the goals of structural characterization is to distinguish between the samples with different levels of hydration.

In order to get a better understanding of the effects of hydration on structural and adsorption properties, we consider two reference Cu-BTC structures, one with fully saturated Cu sites (hydrated18) and another with unsaturated sites (dehydrated19). The cubic unit cell of Cu-BTC can be compartmentalized into three types of cages denoted here as S1, L2, and L3.20 The pore structure represents a 3D network of alternating larger spherical cages L2 and L3 with tetrahedral-shaped small S1 cages connected to L3 cages. In Figure 1A,C, we demonstrate the sizes of these cages by using probe spheres inscribed inside.
each cage, without overlapping with any framework atoms, and serving as yardsticks: purple for S1, green for L2, and orange for L3. For dehydrated structure, the defined cage diameters ($D$) are S1, 0.45 nm; L2, 1.05 nm; and L3, 1.29 nm; as such, S1 falls in the category of ultramicropores ($D < 0.7$ nm), while L2 and L3 are supramicropores ($0.7$ nm $D < 2$ nm).13

The hydrated structure, Figure 1C, has a more complex shape due to the presence of the extra 12 oxygen atoms protruding into the cage. These extra atoms significantly decrease the size of the sphere that can fit within the L3 cage (0.85 nm).

Several methods for geometric analysis were developed to calculate the pore volume, surface area, and PSD in model porous materials, both disordered (activated carbons, polymers) and crystalline (zeolites, MOFs, ZIFs, etc.).21−24 Here, we employ the Poreblazer code,24 described in detail in the Supporting Information (SI). It is based on the Connolly surface method25 originally described by Gelb and Gubbins in the context of model porous glasses.26 The algorithm assigns a point within the available pore space to a pore of a particular size with respect to the maximum diameter of a spherical probe, as shown in Figure 1B,D.

The geometric PSD analysis brings to light the striking effect of the hydration on the pore shape and connectivity. From the visual inspection of the pore structure compartmentalization presented in Figure 1A,C, one might expect to see three distinct peaks on the differential PSD corresponding to the three cage types. Indeed, this is what is observed for the PSD of the dehydrated structure (Figure 1E top). Each of these peaks corresponds to the pore spaces represented in Figure 1B by spheres of characteristic size and color (0.45 nm, purple; 1.0 nm, green; and 1.29 nm, orange). Similar distributions are found in the literature20,27 using the geometrical methods applied in RASPA19 and Poreblazer.24 The green spherical caps seen on top of the orange sphere represent the regions in the L3 cage not embraced by the largest fitted sphere due to not ideally spherical pore shape. Nevertheless, the volume of each cage type can be unambiguously determined from the geometrical PSD with the total pore volume distributed between S1 (15%), L2 (42.5%), and L3 (42.5%) cages.

In contrast, the PSD of the hydrated version (Figure 1E, bottom) has four, rather than three, pronounced peaks that should indicate the existence of four pore types of distinct sizes. This effect is a result of the protrusion of oxygen atoms into L3 cage, causing the geometric algorithm to interpret the shape of L3 cage as being comprised of smaller pores. Figure 1D illustrates the nature of this effect (additional schematics are provided in the SI). First, the maximum size of the fitted sphere in L3 cage reduces from 1.29 nm in dehydrated structure (orange in Figure 1B) to 0.85 nm (yellow in Figure 1D). Second, the remainder of L3 cage space is filled by additional blue (0.65 nm), and purple (0.45 nm) spheres. The shape of L2 cage becomes also more complex with the 1.01 nm cage in the center (green) and smaller peripheral compartments. The complex shape of the connected L2 and L3 cages is schematically presented in Figure 1F as a corrugated channel comprised of overlapping purple, yellow, blue, and green spheres. Notably, the blue spheres between the L2 and L3 cages correspond to the window spaces that were assigned to L3 cages in the dehydrated

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**Figure 1.** Geometrical characterization of the pore structure in the dehydrated and hydrated Cu-BTC crystals. The framework atoms are set in their crystallographic positions. (A, C) Compartmentalization of the unit cell into three types of cages shown by inserted spheres: S1 (purple), L2 (green), and L3 (orange). (B, D) Assignment of the pore diameters in geometric analysis by largest inserted spherical probes shown in different colors. (E) Geometric PSDs (differential and cumulative) of the dehydrated (top plot) and hydrated (bottom plot) structures. (F) Schematic representation of the pore space connecting L2 and L3 cages in the hydrated structure.
structure. Finally, smaller purple spheres represent not only S1 cages, but also the peripheral regions of L2 and L3 cages, making the correspondent peak bigger than the one seen in the PSD for the dehydrated sample.

The characteristic differences in the pore geometry should be reflected in the adsorption behavior, specifically by the characteristic steps and inflection points on the adsorption isotherms. Assuming the Cu-BTC structure as consisting of three cage types, one could expect a three-step adsorption isotherm for Ar at 87 K, with the first step at low pressures corresponding to the filling of ultramicropores (S1) and two subsequent distinct steps corresponding to the filling of supramicropores L2 and L3. Such three-step isotherm would correspond to the geometrical PSD with three distinct peaks such as the one for the dehydrated structure. On the other side, the PSD distribution with four peaks found for the hydrated Cu-BTC makes one expect a four-step adsorption isotherm reflecting the subsequent filling of four groups of pores.

Surprisingly, the adsorption isotherms obtained using grand canonical Monte Carlo (GCMC) simulations (computational details are given in the SI) do not conform to any of these expected scenarios (Figure 2A). Aside from the filling of the ultramicropore cages S1 at 10^{-5} to 10^{-3} P/P_0, the dehydrated sample features essentially one step in the region between 10^{-3} P/P_0 and 10^{-2} P/P_0. This step is initially very sharp, followed by a gradual increase before reaching saturation levels. On the other

Figure 2. Molecular simulations of adsorption. (A) Adsorption isotherms of Ar at 87.3 K. (B, C) Adsorption potential maps with isosurfaces at −11 (red), −8 (light green), and −4 (purple) kJ/mol.

Figure 3. Simulated adsorption isotherms of Ar at 87.3 K in (A) dehydrated and (E) hydrated structures of Cu-BTC and respective snapshots at the pressure points 4 × 10^{-4} (B, F), 3.2 × 10^{-3} (C, G), 1 × 10^{-1} (D, H). Framework atoms shown: C, gray; O, red; Cu, tan. To distinguish the distribution of adsorbate in different cages, Ar molecules are shown in purple within S1, green within L2, and orange within L3. (B, F) Complete filling of S1; (C, G) complete filling of L2 and partial filling of L3; (D, H) complete filling.
hand, in the hydrated sample in the same pressure range there are two very distinct steps. Additional insight is brought by the adsorption potential maps (Figure 2B, C) with isosurfaces for three characteristic potential energies: −11 (red), −8 (light green), and −4 (purple) kJ/mol. A side-by-side comparison of the isosurfaces shows the differences of the key adsorption sites in the structures considered. The first isosurface, with energy of −11 kJ/mol (shown in red), is larger for the hydrated structure, which explains the higher adsorption in micropores, which includes S1 cages, at pressures below 10^−3 P/P_0. The second isosurface (−8 kJ/mol, light-green) is also larger for the hydrated structure, which is, most likely, the cause of slightly earlier Ar condensation in L2 cages. Lastly, the third isosurface (−4 kJ/mol, purple) is smaller for the hydrated structure, which could explain delayed condensation in L3 pores in the hydrated structure in contrast to the dehydrated one.

To understand the adsorption mechanisms in these structures, it is instructive to visualize the distributions of molecules along the isotherms. Snapshots in Figure 3 show that although the geometric PSD analysis interprets L3 cage as a system of smaller pores in the hydrated sample (even smaller than L2), the sequence of complete pore filling in both structures is the same: S1, then L2, then L3 (detailed description of Figure 3 is in the SI). The significant difference is the fact that, in the dehydrated sample, the steps associated with condensation of argon in L2 and L3 are not distinct. While the step associated with the filling L2 cages is quite sharp, filling of the L3 cages proceeds gradually due to relatively large windows between these cages. From this perspective, the supramicropore structure of the dehydrated sample can be thought of as a network of corrugated channels rather than a network of distinct cages (L2 and L3) connected by narrower windows. For the hydrated sample, apparently, the adsorption in the windows between L2 and L3 cages is delayed and, despite the geometrical size of L3 cage is smaller due to the protruding oxygen atoms, filling of L3 cage is reflected as a separate step on the isotherm.

In conclusion, a synergistic combination of geometrical characterization of the pore structure, Monte Carlo simulation of adsorption isotherms, and molecular visualizations is needed to elucidate adsorption mechanisms and to establish nontrivial relationships between geometrical and chemical features of a MOF and specifics of adsorption behavior. Our results give impetus to developing a novel approach to MOF characterization based on the comparison of the experimental isotherms with their in silico simulated counterparts to reveal the similarity and the difference between the real samples and the ideal crystals. This will allow us to identify the fraction of MOF crystals in the sample, the degree of hydration, and possible crystal defects due to residual solvents and other imperfections.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b00906.

Poreblazer details, Monte Carlo simulation details, and details of visualization of adsorption behavior (PDF)

Computational files: adsorption isotherms, geometrical pore size distributions, and potential maps, including input-output files and codes (ZIP)

**REFERENCES**


