

Structural Characterization of D₂ in Cu₃(1,3,5-benzenetricarboxylate)₂ using Neutron Powder Diffraction

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Abstract. Sorption of ten different quantities of D₂ within the porous coordination metal framework Cu₃(1,3,5-benzenetricarboxylate)₂ were studied using neutron powder diffraction. D₂ sorption in the porous material reached saturation (at 25 K) at an amount equivalent to ~6.5 wt. % H₂. Rietveld analyses revealed that at saturation there are two saturated small pore and three saturated large pore sites, in addition to the primary site at the coordinatively unsaturated Cu. We reveal that the linked bimodal pore system provides up to nine distinct sites for D₂, at moderate D₂ concentrations up to saturation. Intermediate sites are attributed to local D₂-D₂ interaction within the confined pore spaces. Within the small and large pores one, and two, intermediate sites are identified, respectively. The population of D₂ at each site was found to affect the host lattice.

Introduction

The elucidation of the location of dihydrogen adsorbed within porous metal organic frameworks provides insight into the framework-dihydrogen interaction that may lead to the efficient solid state storage of hydrogen gas. The study of the structural characteristics of these materials upon dihydrogen sorption allows the delineation of the features that maximize hydrogen loading. Cu₃(BTC)₂, where BTC is 1,3,5-benzenetricarboxylate, is a three dimensional (*Fm-3m*) metal organic framework featuring dimeric Cu units in which the Cu atoms are coordinatively unsaturated and bridged by the carboxylate groups of four BTC linkers. A neutron powder diffraction study [1] of D₂ sorption in Cu₃(BTC)₂ revealed the location of six D₂ binding sites in Cu₃(BTC)₂ with 4.4 molecules of D₂ per Cu adsorbed. The most favored D₂ sorption site lies in close proximity to the open Cu sites. The largest pores in Cu₃BTC₂ are ~10 Å in diameter, and are formed from 12 dimeric Cu subunits. A second pore system of diameter ~5 Å, accessible from the larger pores *via* triangular ~3.5 Å windows, exists where four tetrahedrally arranged benzene rings constitute the inner surface. Previous work [1] demonstrated a competitive loading of the other D₂ sites, with a progressive filling of the smaller, then larger pores favoring sites closest to the framework over sites further towards the pore centers. The adsorption enthalpies of H₂ in Cu₃(BTC)₂ at the first three of these previously identified binding sites [1] were estimated using inelastic neutron scattering [2]. The strength of the interaction between the first adsorption site at the coordinatively unsaturated Cu and the H₂ was estimated to be between 6 and 10 kJ/mol. The second site is located within the small pore cage and has an estimated binding energy of 5 to 6 kJ/mol. The third site is located at the center of each of the tetrahedrally arranged windows of the small pore and has an estimated

adsorption enthalpy less than 5 kJ/mol. In this work we show that at 25 K more D₂ can be incorporated into the material, leading to a more complete filling of both the 5 Å and 9 Å pores. We show that some previously identified sites are intermediate to the final arrangement of D₂ in Cu₃(BTC)₂ at saturation and reveal new final and intermediate sites. The behavior of the Cu₃(BTC)₂ framework was found to be affected by D₂ population at the various sites.

Experimental

The Cu₃(BTC)₂ sample was dehydrated for 12 hours at 413 K and was transferred to a cylindrical vanadium can (equipped with a capillary gas line and a packless valve) in a helium-filled glovebox equipped with water and oxygen monitors, and sealed with an indium o-ring. The sample was mounted onto a sample stick equipped with a stainless-steel gas line with an additional valve for a top-loading closed-cycle helium refrigerator. The sample was further degassed in situ for over 20 min under vacuum ($\sim 1 \times 10^{-4}$ Pa) at room temperature. Neutron powder diffraction data were collected on the High Resolution Neutron Powder Diffractometer (BT-1) at the NIST Center for Neutron Research (NCNR) with a wavelength of 2.0787 Å and using 15 arc-minute in-pile collimation. Data were collected over scattering angles 3° to 167°. All measurements were performed on the 2.896 g sample at 3.5 K. Data were recorded as a function of D₂ loading for D₂:Cu ratios of 3.0, 4.5, 5.0, 5.5, and 6.5, which were loaded into the sample at temperatures of 55, 45, 40, and 40 K, respectively. In all cases, the final pressure reading in the system was zero at or before reaching 25 K.

Structural analyses were performed using Rietveld refinements using GSAS [3] as implemented in EXPGUI [4]. Rietveld refinement was performed using the previous structural model [1, 5] as the initial structure. A 16-term shifted Chebyshev background function and a pseudo-Voigt peak profile with asymmetry (CW Type III in GSAS) was used in the fitting. The refined model for the host material was used as the initial model for the D₂ adsorbed material with the D₂ locations derived using Fourier difference techniques. Deuterium molecules were treated as point scatters with double occupancy since they are expected to be rotationally averaged in the quantum ground state.

Results and Discussion

D₂ saturation at 25 K occurred at a D₂:Cu ratio of 6.5. Analyses of the Fourier-difference between the D₂ loaded and bare framework revealed the location of nine distinct D₂ sites within Cu₂BTC₃ (Table 1). The D₂ interaction at the bare Cu atoms and the location of D₂ at the two large pore sites, D₂(4) and D₂(6), was the same as in previous [1] work. A few minor differences were noted between the location of small pore sites in this and previous work [1].

Table 1: Approx. D₂ sites in Cu₃BTC₂.

Site	Mult.	x	y	z
D ₂ (1)	48	0.15	0.15	0
D ₂ (2)	48	0.25	0.25	~0.31
D ₂ (3)	32	0.14 - 0.16	0.14 - 0.16	0.14 - 0.16
D ₂ (4)	48	0	0.37	0.13
D ₂ (5)	32	0.21 - 0.20	0.21 - 0.20	0.21 - 0.20
D ₂ (6)	96	0	0.29 - 0.26	0.07 - 0.08
D ₂ (7)	96	0.05 - 0.06	0.21	0.05 - 0.06
D ₂ (8)	96	0	0.32 - 0.36	0.09 - 0.11
D ₂ (9)	32	0.08	0.42	0.08

D₂ site locations vary according to the quantity of D₂ adsorbed. We attribute these differences to D₂-D₂ interactions that were previously noted as D₂ molecules competitively rearrange themselves within the restricted small pore area. In comparison with the previous study [1], three new sites within the large pore were found, making five in total. D₂ is preferentially located at sites closer to the framework surface

rather than inside the pores, with the observation of a progressive filling of inner surface, then sites further in towards the pore center.

Table 2: Site Occupancy Factors (SOF) from Rietveld refined models (Fit to data shown as R_{wp}) of data for D_2 in $Cu_3(BTC)_2$ at the bare Cu atom (Cu), and in the small (SP) and large (LP) pores. Previous work [1] is marked *.

R_{wp} (%)	Meas.	Calc.	D ₂ (1)	D ₂ (2)	D ₂ (3)	D ₂ (4)	D ₂ (5)	D ₂ (6)	D ₂ (7)	D ₂ (8)	D ₂ (9)
	D ₂ :Cu	D ₂ :Cu	Cu	SP(I)	SP(II)	LP(I)	SP(III)	LP(II)	LP(III)	LP(IV)	LP(V)
3.17	0.5*	0.50(1)	0.94(2)	0.05(1)	-	-	-	-	-	-	-
3.51	1*	0.98(3)	1.80(2)	0.16(1)	-	-	-	-	-	-	-
3.58	2*	1.90(2)	2.02(2)	0.37(1)	2.11(3)	-	-	-	-	-	-
4.23	3	3.05(9)	1.95(2)	0.30(4)	1.87(3)	1.12(2)	0.59(6)	0.54(2)	-	-	-
3.77	4*	4.39(5)	1.99(2)	0.38(3)	2.12(4)	1.69(3)	0.78(5)	1.39(2)	-	-	-
4.04	4.5	4.6(1)	1.83(3)	0.31(4)	2.04(5)	1.01(7)	1.23(7)	0.87(4)	0.24(3)	0.82(5)	-
3.96	5	5.0(1)	1.55(3)	-	2.05(5)	0.45(6)	1.90(3)	0.48(4)	0.59(3)	1.57(4)	-
4.20	5.5	5.59(8)	1.73(3)	-	2.15(5)	-	1.89(3)	-	0.91(2)	2.12(3)	1.03(4)
3.78	6.5	6.60(8)	1.90(3)	-	2.08(5)	-	1.84(3)	-	1.68(2)	1.97(2)	2.08(4)

The models for Cu_2BTC_3 with moderate amounts of D_2 adsorbed to that at saturation are complex and include a larger number of intermediate D_2 sites, reflective of competitive D_2 - D_2 interaction in the sample. In the small pore, the previously observed $D_2(2)$ site, between the small pore center and window sites, is identified as being intermediate. In the large pore, D_2 re-arranges itself between site $D_2(4)$ and a newly observed site that lies in close proximity, $D_2(8)$; total occupancy of the $D_2(8)$ and $D_2(4)$ site is always less than full. The previously identified large pore site, $D_2(6)$, is observed also to be of an intermediate nature. At higher D_2 loads, the disordered and intermediate arrangements in the large pore give way to the appearance of sites further into the pore, including $D_2(9)$ and increasing population of $D_2(8)$.

At this dose, we see close to full site occupation for two small pore and three large pore sites. In the small pore, we see saturation of the small pore window site, $D_2(3)$, and close to site saturation at the central $D_2(5)$ site. At the highest loading we see site saturation for the most favorable large pore site, $D_2(4)$, which is located close to the inner surface, close to site saturation at the next large pore site, $D_2(7)$, and saturation of the innermost large pore site, $D_2(9)$. It is likely that the $D_2(5)$ and $D_2(7)$ sites would fully saturate under applied pressure or additional loading and cooling of the sample.

No major structural changes or re-arrangements of the framework were observed on D_2 loading. A similar lattice response to that previously noted occurs, where the lattice variation not only follows the quantity of D_2 adsorbed, but correlates with the population of the various sites (fig. 1). At D_2 :Cu loads below 1, the unit cell expands linearly with increasing D_2 adsorbed. When amounts of D_2 between 2 and 4.5 D_2 :Cu are adsorbed, the cell contracts slightly. This observation was previously noted to be associated with a subtle buckling of the BTC units and a concomitant decrease in the BTC bridged Cu-Cu distance from 8.07(1) Å to 8.03(1) Å. Here we note that at D_2 :Cu loadings of 5 D_2 :Cu and above the response of the unit cell becomes positive and more linear once again. A careful examination of the D_2 sites (Table 2) reveals that the unit cell response is consistent with the increasing population at specific D_2 guest sites. Most notably, population of the intermediate large pore site, $D_2(6)$, is associated with a significant reduction in the lattice parameter. This site is located in the large pore entrance, where four dimeric units form the corners of the large pore boundary. $D_2(6)$ is approximately 4.07 Å equidistant from the closest Cu atom of each dimer (fig. 2).

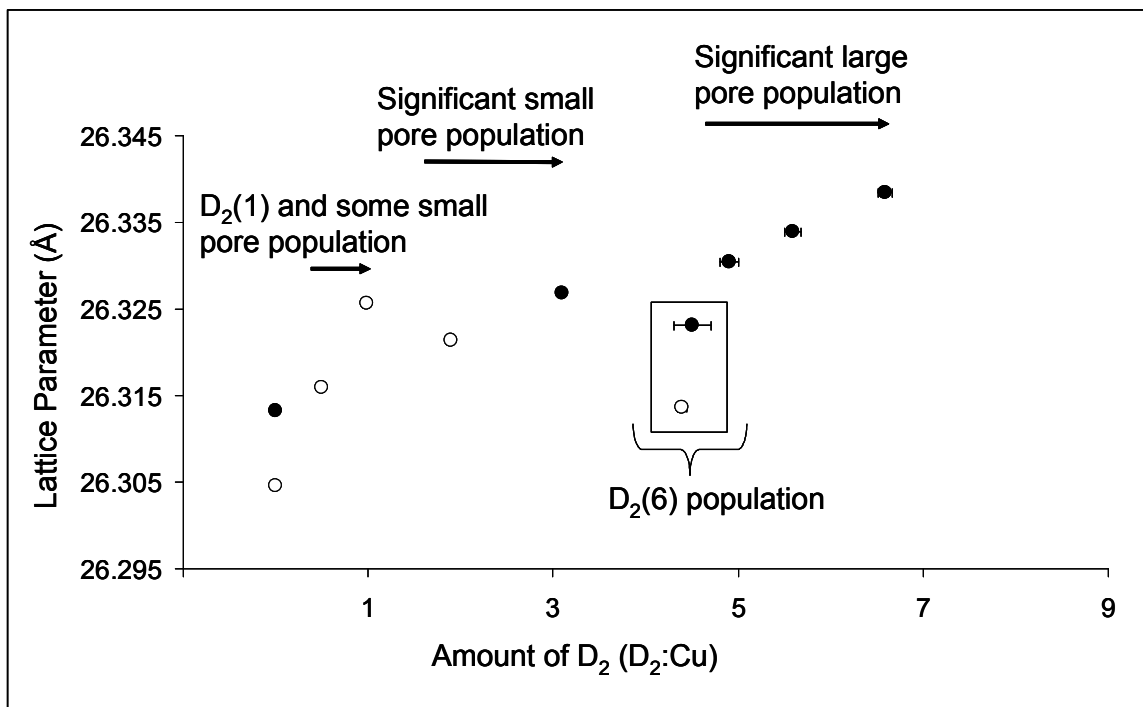


Figure 1: $\text{Cu}_3(\text{BTC})_2$ lattice response to D_2 sorption. Shown are these (closed circles) and previous (open circles, [1]) results. Error bars are shown or are smaller than the points.

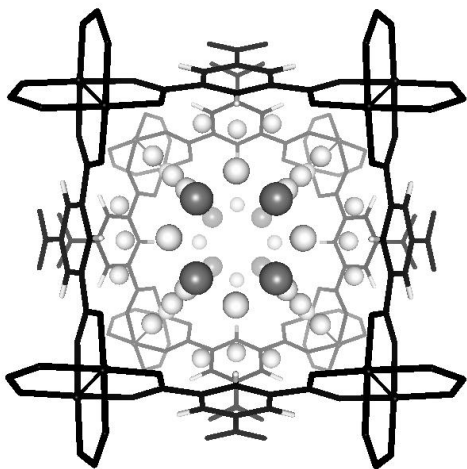


Figure 2: Large pore showing framework (black line) with D_2 (spheres) including $\text{D}_2(6)$ (larger grey spheres).

Conclusion

D_2 sorption in $\text{Cu}_3(\text{BTC})_2$ was studied using neutron powder diffraction. The material reached saturation at 25 K, adsorbing the equivalent of approximately 6.5 wt. % H_2 . Rietveld analyses revealed that at saturation there are two small pore and three large pore sites, in addition to the primary coordinatively unsaturated Cu site. We reveal the connected bimodal pore system provides up to nine distinct sites for D_2 at moderate D_2 concentrations to saturation. Sites intermediate to those occupied at saturation are attributed to local D_2 - D_2 interaction within the confined pore spaces. One small pore and two large pore intermediate sites were identified. The population of D_2 at each site was found to affect the lattice response.

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