Site-Specific CO₂ Adsorption and Zero Thermal Expansion in an Anisotropic Pore Network

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Supporting Information

ABSTRACT: Detailed neutron powder diffraction (NPD) experiments were carried out on the parent and CO₂ adsorbed Mg-MOF-74 (MOF: metal—organic framework). Data collected at low temperature revealed two CO₂ adsorption sites on the pore surface and multiple changes in the framework as a function of CO₂ loading. Upon heating the samples to room temperature, the data revealed minimal changes in expansivity upon adsorption of up to 0.94 CO₂/Mg (≈ 25% mass fraction). Further, temperature-dependent data collected on the bare framework reveals net zero thermal expansion between 10 and 475 K.

INTRODUCTION

Separation of CO₂ from flue gas streams and other point sources is an important component in the mitigation of atmospheric CO₂. While methods exist to separate CO₂ from the other components of a postcombustion stream (primarily scrubbing with liquid amine solutions), their wide implementation on an industrial scale has not been possible due to the massive energy requirement of such processes. Efficient methods for effecting such a separation are urgently sought. Metal—organic frameworks (MOFs) are a versatile class of compounds with a nearly infinite number of building block combinations. Their high internal surface areas coupled with chemical tunability make them particularly attractive for the selective capture of CO₂. Recent work has shown that the incorporation of coordinatively unsaturated metal centers (UMCs) into the frameworks provide enhanced binding energy and an increase in surface packing density of adsorbates due to the highly reactive, electron deficient nature of the sites. While UMCs provide strong interactions allowing CO₂ adsorption close to room temperature and slightly above, these interactions are weak relative to the formation of chemical bonds also providing facile CO₂ release during regeneration processes.

The activated MOF-74 series of compounds are candidates for selective adsorption of CO₂, having unsaturated 5-coordinate metal ions decorating the inside of one-dimensional hexagonal channels. Of these, the Mg-MOF-74 material was recently found to exhibit an exceptionally high CO₂ uptake at low pressure (<0.1 bar) and room temperature and easy, reversible adsorption/desorption of CO₂. In order to obtain a better understanding of how structure dictates function during adsorption/desorption processes, we have performed detailed neutron diffraction experiments, allowing us to probe structural changes in the framework as well as the exact positions, occupancy, and site affinity of the gas as it is adsorbed. These studies have for the first time allowed the identification of a secondary CO₂ adsorption site. Comparisons between the bare and CO₂-adsorbed phase reveal no significant change in the unit cell volume for room temperature CO₂ adsorption, a property that might be of particular interest for the future implementation of adsorbent materials in separation/storage applications. Further, temperature-dependent studies performed on the bare framework have revealed a net zero thermal expansion (ZTE) over a wide range of temperatures, a phenomenon that to the best of our knowledge has not before been reported in a highly porous MOF system.
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Table 1. Unit Cell Parameters, CO$_2$ Occupancies, and Selected Bond Distances and Angles of Mg-MOF-74 (Trigonal, R-3).$^a$

<table>
<thead>
<tr>
<th>CO$_2$ per Mg site</th>
<th>temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Mg–O(2b)</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>O(2a)–C(2a)</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>O(2b)–C(2a)</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>O(3a)–C(3a)</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>O(3b)–C(3a)</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>C(2a)–O(2)</td>
<td>3.10(8)</td>
</tr>
<tr>
<td>C(2a)–C(3)</td>
<td>3.07(9)</td>
</tr>
<tr>
<td>C(3a)–O(2)</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>C(3a)–O(3)</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>angles ($^\circ$)</td>
<td>O(2a)–C(2a)–O(2b)</td>
</tr>
<tr>
<td></td>
<td>O(2a)–O(2)–C(2a)</td>
</tr>
<tr>
<td></td>
<td>O(3a)–C(3a)–O(3a)</td>
</tr>
</tbody>
</table>

unit cell parameters

| a (Å)  | 25.921(2) | 25.895(2) | 25.867(1) | 25.847(2) | 25.824(1) | 25.767(1) |
| c (Å)  | 6.8625(8) | 6.8705(6) | 6.8768(7) | 6.8788(6) | 6.8904(5) | 6.9145(5) |
| volume (Å$^3$) | 3993.5(5) | 3989.7(5) | 3984.8(4) | 3979.8(5) | 3979.4(3) | 3975.8(3) |

occupancy of CO$_2$

| site | 0 | 0.24(1) | 0.60(1) | 0.89(1) | 0.88(1) | 0.99(1) |
| site II | 0 | 0 | 0 | 0 | 0.24(1) | 0.86(2) |

$^a$The values in parentheses represent one standard deviation.

RESULTS AND DISCUSSION

Rietveld refinement$^{21}$ of the neutron powder diffraction (NPD) data obtained from bare Mg-MOF-74 is well described using a structural model similar to that published.$^{22}$ After structural refinement of the host material, Fourier difference maps allowed subsequent elucidation of CO$_2$ site positions that were further refined along with their occupancies as a function of loading. Development of a suitable structural model permitted nearly unconstrained Rietveld refinements (see Supporting Information).

The lowest loading, at 0.25 CO$_2$/Mg, reveals that the CO$_2$ only populates a single site, I, located at the UMC. As shown in Table 1, the refined site I occupancy is in good agreement with this initial CO$_2$ loading. The Mg–O(2b)–C(2a) interaction exhibits a highly angular orientation, 125(7)$^\circ$, with two short lateral interactions, approximately 3.1 Å, between the electron deficient C(2a) of the CO$_2$ molecule, and the framework atoms, O(2) and C(3) (Figure 1, left). The gas molecule exhibits an “end on” coordination (Figure 1, right), similar to that reported in an X-ray analysis of CO$_2$ in Ni-MOF-74.$^{23}$ The Mg–O(2b) distance is relatively short at 2.39(6) Å, consistent with the reported high initial isosteric heat of adsorption ($\sim$47 kJ/mol) and $-39$ kJ/mol. As observed previously,$^{24}$ the interaction between the framework and CO$_2$ and the local potential that it sits in gives rise to an unexpected nonlinear geometry of the gas molecule with a refined intramolecular angle of significantly less than 180$^\circ$. The next closest CO$_2$/framework distance ($\sim$2.9 Å) is found between O(2b) and O(2), which is equatorially coordinated to the Mg$^{2+}$ ion. This distance, only slightly shorter than the sum of the van der Waals radii for two O atoms, is likely a limiting factor in the approach of the CO$_2$ molecule to the framework surface as electrostatic repulsion would begin to destabilize the CO$_2$ adsorption. The observed atomic displacement parameters (ADP) for C(2a) and O(2a) ($0.06(2)$ Å$^2$ and $0.12(2)$ Å$^2$, respectively) are rather large compared to those of the framework atoms and the Mg bound O(2b). One interpretation is that the large binding energy present between Mg and O(2b) leads to a strong localization on the position of the binding oxygen, whereas the remaining CO$_2$ atoms have weaker interaction with the framework and are less constrained, creating a distribution of positions and an “apparent” bending that is likely static in nature. This argument is further supported by density functional theory (DFT) calculations, which show the lowest energy rotational/vibrational mode for CO$_2$ adsorbed in Mg-MOF-74 to be $\sim$4.3 meV.$^{26}$ This mode is only likely to be thermally populated at the 10% level for our lowest measurement temperature of 20 K.

As the loading level is increased, the refinements progress in a systematic fashion; however, at 1.0 CO$_2$/Mg the first sign of population of the second site, II, occurs. Increasing the loading to 1.75 CO$_2$/Mg leads to an even greater increase in site II occupancy (0.86(2)) and large ADPs for the oxygen associated with this additional molecule. Both oxygen atoms were refined anisotropically, improving the refinement, and the resulting displacement ellipsoids appear to be elongated (Figure 1, right). Although it is unclear as to whether the origin of the elongation is static or dynamic in nature, it is more likely that at 20 K, it is due to slight differences in CO$_2$ orientation within the channel rather than thermal motion of the molecules. The weak van der Waals interaction between the CO$_2$ and framework could lead to a rather flat local potential and a lack in orientation preference upon adsorption. Attempts to model the site II CO$_2$ as two discrete molecular units with slightly rotated orientations are possible, but require a highly constrained molecular structure, leading us to prefer the anisotropic ADP description. Our observation of population at site II contradicts the assertions made by Wu et al.$^{25}$
who assumed that secondary adsorption sites would not be associated with the framework surface due to the packing density of site I; however, recent adsorption studies have indicated population of this site is likely to occur at room temperature and even at low-pressure.27

The CO2 orientation in II is not parallel with that of I, but instead is canted between two site I molecules allowing full surface coverage. Although the exact intermolecular distances are susceptible to uncertainties in site II, due to disordered O(3a,b), there is an average intermolecular distance of approximately 3 Å. Further, there appears to be strong interactions along the pore-channel direction, allowing multiple site II/framework interactions (Figure 1, left). These distances, which range from ∼3 Å to 3.25 Å, indicate that the binding enthalpy associated with II is significantly lower than that for I. Additionally, observed similarities between intermolecular distances and site II CO2/framework distances, all of which are comparable to the sum of the van der Waals radii for C (1.70 Å) and O (1.52 Å), indicate that the site II CO2 has a similar strength of interactions with nearest neighbor gas molecules as with the framework.

Systematic increases in the amount of loaded gas reveals several trends in the structural response to CO2 adsorption in Mg-MOF-74 (Table 1). First, the Mg–O(2b) distance decreases over the entire loading range from ∼2.39 Å to ∼2.24 Å. These distances are comparable to what has been observed in the previously reported study of the Ni-MOF-74 analogue at 2.29(2) Å.23 Additionally, despite the fact that NPD data has been collected on CO2-loaded Mg-MOF-74 previously, the report lacks further structural information, and the loading dependence was unevaluated.26 The second structural response to CO2 loading is an overall decrease in the unit cell volumes. Despite a slight expansion in the c axis at higher CO2 loadings, the volume reduction stems from a significant reduction along the a- and b-axes (Figure 2). Our results are contrary to a recent report by Valenzano et al., who use theoretical calculations to estimate structural features of the Mg-MOF-74 framework upon CO2 adsorption.24 Their study shows a slight lengthening of the average Mg–O distances in the MgO5 moiety and a 1% increase in unit cell volume, both of which they assert is due to a slight displacement of the Mg cation from the framework. Our observed volume reduction can be rationalized when looking at the O(1,2,3)–Mg–O(2b) angles (Figure 1, left). Upon increasing the loading level, these angles show a gradual increase from an average value of 87.8° at 0.25 to 90.6° at 1.75 CO2/Mg. This implies that increased repulsive interactions between the electronegative O atoms as the Mg and CO2 molecule become closer induce a compression of the a- and b-axes, creating an overall decrease in the unit cell volumes from 3993.4(5) Å3 for the parent material to...
3975.9(4) Å$^3$ for the 1.75 CO$_2$/Mg loading, a change of $-0.44\%$.

It should be noted that the observed changes in the Mg—O (1,2,3)–O(2b) angles allow preservation of O(2b)–O(1,2,3) distances, which range from 3.04 to 3.08 Å, throughout our five loadings. The third trend involves a steady increase in the Mg—O(2b)–C(2a) angle, which ranges from $125(7)^\circ$ to $129(2)^\circ$ until there is significant occupancy of site II, after which it jumps to $144(2)^\circ$. This trend is presumably related to slight changes in packing energetics of CO$_2$ in the pore. As Mg—O(2b) and intermolecular CO$_2$–CO$_2$ interactions increase, there is a subsequent decrease in van der Waals site I CO$_2$/framework interactions, which is substantiated by a lengthening of the C(2a)–O (2) distance from $\sim3.1–3.2$ Å for 0.25–0.75 loadings to $\sim3.35$ Å and 3.46 Å for the 1.0 and 1.75 loadings, respectively.

It has been noted in several studies that CO$_2$ coordination at the UMC in MOF-74 derivatives leads to the unexpected non-linear geometry of the adsorbed molecule. When taking into account the strong Mg–CO$_2$ interaction, indicated by short Mg—O(2b) distances and large enhalphy for adsorption, it is therefore expected at low-temperatures that angles $\lesssim 170^\circ$ must have some contribution from static disorder resulting in a misinterpretation of the actual bond angle from re

Further, much of the NTE reported in MOFs thus far has been observed for Mg-MOF-74. We have observed the first structural evidence for deviations of up to $10^\circ$ (less than 25 meV/molecule) from the normal linear geometry of a free CO$_2$ molecule. When quenching CO$_2$ in Mg-MOF-74, the refined models show bond angles of 160$^\circ$ with unphysical ADPs that necessitate restraining their values to being equal and positive. The data we show here, however, result in excellent goodness-of-fit parameters with unstrained model refinement that lead to more reasonable intramolecular angles and ADPs that get progressively larger on traversing the CO$_2$ atoms away from the Mg$^{2+}$ ion. However, even in the case of the lowest loading at 20 K, the adsorption is so rapid it is effectively quenched, and we observe a much smaller intramolecular angle similar to that previously published.

The intrinsic limitations of Fourier difference techniques and atom-based Rietveld analysis, we additionally turned to the maximum entropy method (MEM) to reconstruct the scattering densities (Figure S3–S7, Supporting Information), removing model-bias from our approach and further confirming the shape of the adsorbed CO$_2$ molecule. While conventional diffraction studies are based on an atomistic model, and thermal motion or static disorder are usually accounted for in terms of split positions and/or anisotropic ADPs, MEM can offer increased freedom from the atomic approximation. In the case of Mg-MOF-74, MEM was applied in visualizing the scattering density of adsorbed CO$_2$ molecules for two data sets with nominal 0.5 and 1.75 CO$_2$/Mg loadings (data measured at 20 K). Even though the atom positions are much more evident from the extracted nuclear densities compared to Fourier techniques (Supporting Information), we conclude that there is no improvement in describing the data when applying an MEM approach compared to Rietveld analysis, and that Mg-MOF-74 is adequately described using the atomic model.

After collecting 20 K NPD data on the sample loaded with 0.5 and 1.75 CO$_2$/Mg, the temperature was increased to 300 K, and the data was collected again. The 0.5 loading showed no significant change in the site I CO$_2$ occupancy ($0.63(2)$) upon heating, while for the 1.75 loading, site II was completely evacuated, and site I maintained a relatively high CO$_2$ occupancy equal to 0.94(3). These results again reiterate that the high initial isosteric heat of adsorption for Mg-MOF-74 is directly related to the UMC. The physisorptive nature of this interaction is further evidenced by the lengthening of the Mg—O(2b) bond with increased temperature: 2.48(5) Å and 2.58(5) Å for the 0.5 and 1.75 (300 K), respectively. The unit cell volumes of the 0.5 and 1.5 loadings at 300 K (3992.3(5) Å$^3$ and 3992.0(5) Å$^3$, respectively) are comparable to the volume of the bare material, indicating that occupancy of site I at room temperature has little effect on the overall unit cell volume. In fact, the volume is constant from the bare to loaded phase within $\pm 0.06\%$ error ($\pm 1.5$ Å$^3$). Despite the lack of volume change, the room temperature data still shows a similar compression of $a/b$ and simultaneous expansion of $c$ with higher loading as observed for the framework at 20 K data.

For further comparison, temperature-dependent NPD studies were carried out on the bare framework. Rietveld refinement of the data revealed unusual thermal behavior. While most materials undergo thermal expansion in all three-dimensions upon heating, Mg-MOF-74 instead undergoes compression along the $a/b$ axes and a simultaneous expansion along $c$. This structural response leads to an approximate ZTE over a fairly wide range of temperatures, 20–475 K (Figure 2), quite different from the usual negative thermal expansion (NTE) seen in cyanides, MOF-5, HKUST-1, and COF-102, although ZTE has been observed in cubic cyanides. The current NPD data does not allow a clear determination of the mechanism for the observed thermal properties, as the changes in the overall unit cell are minimal. Further, much of the NTE reported in MOFs thus far has been attributed to dynamic properties related to low-energy vibrational modes of various rigid units found within the framework, but similar efforts have not yet been made for MOF-74.

**CONCLUSION**

We have performed a detailed structural analysis of Mg-MOF-74 while systematically increasing temperature and the amount of adsorbed CO$_2$. We have observed the first structural evidence of population of a second CO$_2$ adsorption site associated with the framework and speculate that even further CO$_2$ adsorption would be forced to form a second layer, as current intermolecular distances will not permit any further adsorption directly onto the framework surface. In contrast to other published data that report larger deviations from the normal linear geometry, a careful experimental approach and application of bias-free MEM analysis provides confidence in a model resulting in a more realistic bond angle of approximately 170$^\circ$ in all cases.
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ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures, neutron powder diffraction patterns, additional structural images, and crystallographic information are provided as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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