

CORRELATIONS BETWEEN STRUCTURE AND GAS-ADSORPTION / SEPARATION PROPERTIES OF METAL-ORGANIC FRAMEWORKS

Wendy L. Queen* and Jason Lee

Molecular Foundry, Lawrence Berkeley National Lab, 1 Cyclotron Road, Berkeley CA, 94720

Miguel Gonzalez, Stephen J. Geier, Jarad A. Mason, and Jeffrey R. Long
Department of Chemistry, University of California, Berkeley CA, 94720

Craig M. Brown

Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg MD, 20899

Department of Chemical Engineering, University of Delaware, Newark, DE 19716

Matthew R. Hudson

Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg MD, 20899

Simon J. Teat

The Advanced Light Source, Lawrence Berkeley National Lab, 1 Cyclotron Road, Berkeley CA, 94720

ABSTRACT

To help reduce industrial CO₂ emissions, better materials are required to lower the parasitic energy associated with current carbon capture and sequestration (CCS) technologies. As a result, much emphasis has been placed on the design of new porous materials that can selectively bind and store CO₂ and other gases associated with various CCS technologies. Metal-organic frameworks (MOFs) are promising candidates for initial carbon capture from industrial flue gas streams due to their high porosity, high internal surface areas, facile chemical tenability, and easy regeneration. To gain a better understanding of the mechanism of gas adsorption in these porous materials, we are carrying out *in-situ* structural characterization. This transaction outlines CO₂ adsorption in a well-known MOF, Co₂(dobdc) (dobdc⁴⁻ = 2,5-dioxido-1,4-benzenedicarboxylate), and its *in-situ* structural characterization using both single crystal X-ray diffraction and powder neutron diffraction experiments.

1. INTRODUCTION

The prospect of global warming has directed much attention towards the mitigation and sequestration of atmospheric CO₂. Since the 1970's, global CO₂ emissions have increased by over 80%, a direct result of the combustion of fossil fuels.[1] While carbon capture from air is difficult, that of large point sources, such as coal-fired power plants, could be realized. As a result, materials that can selectively bind CO₂ and offer easy regeneration could serve as a future

* Corresponding author: wlqueen@lbl.gov

** Commercial materials and equipment are identified in this paper only to specify adequately the experimental procedure. In no case does such identification imply recommendation by NIST nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

means to this end. One such class of materials, Metal organic frameworks, are highly porous, 3-dimensional network solids that consist of metal-ions or metal-ion clusters linked together by organic molecules. Through judicious selection of building block combinations that control pore size/shape and surface interactions with guest species, their properties can be tuned for targeted functions, such as gas adsorption/separation, and catalysis.

The crystalline nature of MOFs gives rise to a nonhomogeneous van der Waals potential on the framework surface that dictates how bound guest species are arranged. As a result, X-ray and neutron diffraction can provide a molecular level view of how gases bind to framework surfaces. Throughout our studies we have used *in-situ* structural characterization to elucidate vital information about the adsorption properties of metal-organic frameworks. Using neutron and X-ray powder diffraction, we have demonstrated the ability to discern the location and orientation of static guest molecules, relative differences in binding energies between adsorption sites, the nature of binding interactions, pertinent information about reactions occurring on the framework surface, and the framework response to various stimuli such as pressure and temperature.[2-5] Due to the fact that structure dictates function, *in-situ* structural characterization of frameworks with adsorbed gas species will help improve understanding of the structural properties necessary to optimize frameworks for carbon capture purposes. Further, structural studies used as a means to validate and aid theoretical efforts focused on structure and property prediction, will allow the vast phase space of these highly diverse materials to be narrowed in the search for the “Dreamium” material that will solve the problem of carbon dioxide emissions.

2. SINGLE CRYSTAL X-RAY AND POWDER NEUTRON DIFFRACTION

To carry out the single crystal diffraction studies, a Bruker D8 Advance** single crystal X-ray diffractometer located at the Molecular Foundry at Lawrence Berkeley National Laboratory, was used to assess procedures necessary to achieve complete solvent removal in single crystals of Co₂(dobdc). The samples were placed in glass capillaries that were first heated under dynamic vacuum which were subsequently flame sealed. Once solvent removal procedures were identified, single crystals were mounted on a loop with epoxy and sealed inside of a custom made gas loading cell, Figure 1, for data collection on the chemical crystallography beamline, 11.3.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory. Before data collection was carried out, single crystals were outgassed at 200 °C under dynamic vacuum for 2 hrs., cooled to room temperature, dosed with CO₂, and then further cooled to 150 K.

Powder neutron diffraction experiments were carried out using the high-resolution powder neutron diffractometer BT-1 located at NIST Center for Neutron Research. A 1.0 gram sample of Co₂(dobdc) was first activated under dynamic vacuum at 200 °C and then transferred into a vanadium sample can equipped with a gas loading lid and sealed with an indium o-ring inside of a He purged glove box. The sample can was then mounted on the bottom of a closed-cycle refrigerator and diffraction data was collected on the bare sample at 10 K. The sample was warmed to room temperature before the delivery of a known amount of CO₂ and then subsequently cooled to 10 K at a rate of approximately 2 K/min.

** Commercial materials and equipment are identified in this paper only to specify adequately the experimental procedure. In no case does such identification imply recommendation by NIST nor does it imply that the material or equipment identified is necessarily the best available for this purpose.



Figure 1. *In-situ* single crystal X-ray diffraction cell used for gas dosing experiments of $\text{Co}_2(\text{dobdc})$

3. AN ISOSTRUCTURAL SERIES OF MOFS

$\text{M}_2(\text{dobdc})$, alternatively known as M-MOF-74 or M-CPO-27, is an extensive family of metal-organic frameworks (M=Mg, Mn, Fe, Co, Ni, or Zn) with 1-D honeycomb-like channels made of metal-oxide chains interlinked by dicarboxylate ligands, Figure 1.[6-11] This framework is quite unique to MOF chemistry in that upon solvent removal it exhibits the highest known density of open-metal sites, a structural feature known to improve binding strength, increase surface packing density of adsorbates, induce selectivity for gas separations, and provide a means for charge transfer between the framework and bound molecular species.[4-5,12] Further, the framework can undergo chemical substitution with a wide variety of first-row transition metals, thereby creating a rare opportunity to perform structure/property correlations and providing a means to chemically tune the material for specific functions. For all of the aforementioned reasons, the $\text{M}_2(\text{dobdc})$ series are some of the most well studied in the field, making it the prime candidate for *in-situ* structural studies.

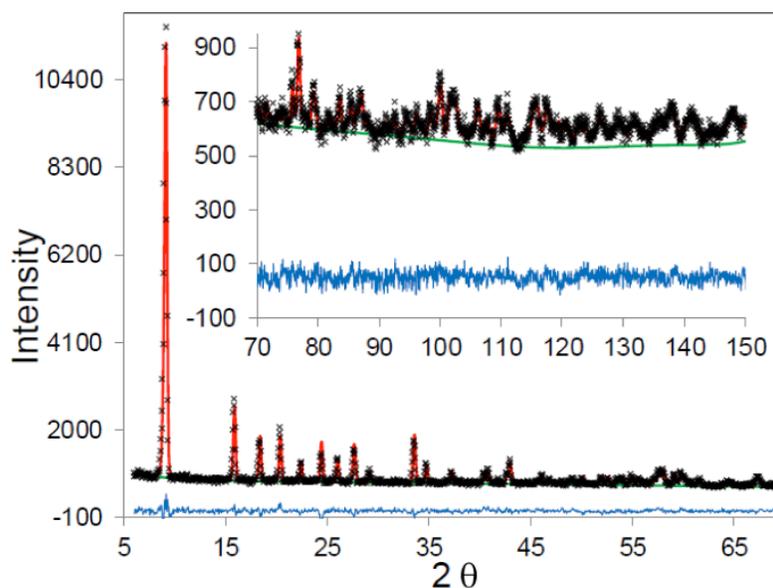


Figure 2. Neutron powder diffraction data for bare $\text{Co}_2(\text{dobdc})$. The green line, crosses, and red line represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns.

4. STRUCTURAL CHARACTERIZATION OF CO₂-FRAMEWORK INTERACTIONS

Rietveld refinement of the structural model of the host framework was carried out and compared to the neutron powder diffraction data obtained from the activated Co₂(dobdc) sample, Figure 2. Fourier difference analysis revealed no excess nuclear scattering density in the channels indicating that the sample was sufficiently activated. Further, the data is well described using a structural model (Table 1) similar to what has been previously published.[13]

Unit Cell Parameters, Unit Cell Volume, CO ₂ Occupancies, and Selected Bond Distances and Angles obtained from Neutron Powder and Single Crystal X-ray Diffraction of Co ₂ (dobdc), (Trigonal, R-3)						
CO ₂ Occupancy	Temp. (K)	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	M-CO ₂ (Å)	< CO ₂ (°)
0	10	25.907(1)	6.8548(5)	3984.3(3)	----	----
0.65(2) (site I)	10	25.898(1)	6.8461(5)	3976.6(4)	2.24(4)	173(4)
0.73(2) (site I)	10	25.874(1)	6.8486(4)	3970.5(4)	2.31(4)	176(3)
0.78(2) (site II)						173(4)
0.85(3) (site I)	150	25.993(7)	6.813(2)	3986(2)	2.260(9)	171(7)
0.62(2) (site II)						

To assess the structural response of the framework to CO₂ adsorption, the sample was dosed with ≈ 0.5 CO₂ per Co²⁺ and then slowly cooled to 10 K to achieve complete adsorption. Fourier difference analysis followed by Rietveld refinement allowed the elucidation of CO₂ site positions and occupancies. The analysis indicates that the CO₂ occupies a single position located at the open-coordination site of the metal with a M-CO₂ distance of approximately 2.24(4) Å. This distance is short indicating a strong electrostatic type interaction that results from the highly polarizing nature of the metal. The distance, while comparable to those observed for both Mg and Ni analogs, is unexpectedly short considering the much lower initial isosteric heat of adsorption of 34.5 for Co, as compared to 42 and 38.7 for Mg and Ni, respectively.[14-16] Similar experiments, carried out to assess the structural properties of this framework family upon H₂ adsorption, have revealed a negative correlation between the distances of the H₂ from the open-metals and experimentally determined isosteric heats of adsorption.[17] However, it should be noted that the diffraction data is collected at 10 K while the isosteric heats of CO₂ adsorption are calculated from isotherms collected at temperatures above 278 K. The difference in experimental conditions could result in significant variations in the local framework environment around CO₂ adsorption sites.

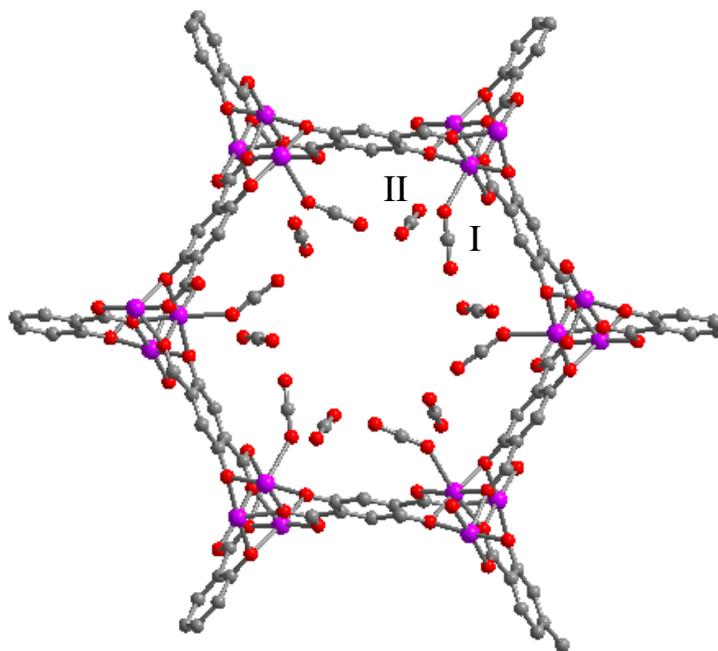


Figure 3. Ball and stick model showing two CO₂ adsorption sites within the Co₂(dobdc) framework. Purple, grey, and red spheres represent Co, C, and O, respectively. The site I CO₂ is shown bound at the open-metal coordination site. The secondary adsorption site is found angled between two site I molecules on the framework wall.

The site I CO₂ is found angled with respect to the framework surface, with a M-C-O angle of 118(2)° due to the presence of secondary, weak van der Waals interactions with the framework surface, Figure 3. Further, the intramolecular CO₂ angle deviates significantly from the expected linear geometry with a value of 173(4)°, which is thought to result of a misinterpretation of the position averaged powder data due to the presence of static disorder in the bound CO₂. In an attempt to more accurately assess this angle we collected single crystal X-ray diffraction data on the CO₂ adsorbed Co₂(dobdc) using a newly designed gas loading cell at the Advanced Light Source at Lawrence Berkley National Laboratory, Figure 1. The expectation was that higher resolution single crystal data could lead to a more reasonable CO₂ angle. However, the X-ray data, collected at 150 K, indicates a M-CO₂ distance of 2.261(9) and an angle of 171(5)° showing consistency with the previously observed values from powder neutron diffraction. It should be noted that the higher temperature used for single crystal data collection could further induce dynamic disorder that is eliminated in the 10 K neutron diffraction data likely causing issues with the average position and accuracy of the CO₂ angle.

Upon increasing the CO₂ loading to ≈ 1.5 CO₂ per open Co²⁺ site, there is observation of a second adsorption site that is angled between two site I CO₂ molecules on the framework wall, Figure 3. The site II CO₂-framework distances, ≈ 3.0 to 3.4 Å, are indicative of weak van der Waals type interactions with the framework surface. Although the exact intermolecular distances are susceptible to error, due to some disorder of the secondary adsorption site, II, the long distances indicate that the binding enthalpy associated with II is significantly lower than that for I. Additionally, the intermolecular CO₂ distances and site II CO₂/framework distances are all comparable to the sum of the van der Waals radii for C (1.70 Å) and O (1.52 Å), indicating that the strength of the interactions between site II CO₂ and nearest neighbor gas molecules are

similar to those between the site II CO₂ and framework surface.

5. CONCLUSIONS

We have performed a detailed structural analysis of CO₂(dobdc) while systematically varying the amount of adsorbed CO₂. We have observed structural evidence of the population of two adsorption sites from both powder neutron and single crystal X-ray diffraction. We have further shown that the open-metal site is responsible for the high, initial isosteric heat of adsorption. Like several previous reports we see significant deviations from the expected linear geometry of the bound CO₂ and speculate that this extreme bending is likely a misinterpretation of the structural data due to the presence of static and or dynamic disorder of the surface bound CO₂ molecule and a lack of high quality crystallinity of the powder sample. High-resolution single crystal data was collected to resolve these issues; however, the lowest achievable temperatures of 150 K from the N₂ cryostream is not adequate to eliminate dynamic disorder resulting from lattice vibrations. As such, it will be beneficial to carry out future measurements again upon installation of a He cryostream at temperatures below 20 K.

ACKNOWLEDGEMENTS

Part of this research was funded through the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award no. DE-SC0001015. J. L. was supported as part of the Nanoporous Materials Genome Center by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-FY12-SC0008688. We thank the Camille and Henry Dreyfus Foundation Postdoctoral Program in Environmental Chemistry and NSERC for support of S. J. G., the National Science Foundation for fellowship support of J. A. M, and support M. R. H. from the NIST/NRC Fellowship Program. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

REFERENCES

- [1] A. Najam, A.A. Rahman, S. Huq and Y. Sokona, *Clim. Policy*, 3 (2003), S9.
- [2] W. L. Queen, M. R. Hudson, C. M. Brown and J. R. Long, *Chem. Sci.*, 4 (2013), 2054.
- [3] T.-H. Bae, M. R. Hudson, J. A. Mason, W. L. Queen, J. J. Dutton, K. Sumida, K. J. Micklash, S. S. Kaye, C. M. Brown and J. R. Long, *Energy Environ. Sci.*, 6 (2013), 128.
- [4] E.D. Bloch, W. L. Queen, R. Krishna, J. M. Zadronzny, C. M. Brown and J. R. Long, *Science*, 335 (2012), 1606.
- [5] E.D. Bloch, L.J. Murray, W.L. Queen, S. Chavan, S. N. Maximoff, J. P. Bigi, R. Krishna, V.K. Peterson, F. Grandjean, G.J. Long, B. Smit, S. Bordiga, C.M. Brown and J.R. Long, *J. Am. Chem. Soc.*, 133 (2011), 14814.
- [6] N.L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O’Keeffe and O.M. Yaghi, *J. Am. Chem. Soc.*, 127 (2005), 1504.
- [7] P.D.C. Dietzel, Y. Morita, R. Blom and H. Fjellvåg, *Angew. Chem., Int. Ed.*, 44 (2005), 6354.

- [8] P.D.C. Dietzel, B. Panella, M. Hirscher, R. Blom, and H. Fjellvåg, *Chem. Commun.* (2006), 959.
- [9] S. R. Caskey, A. G. Wong- Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 130 (2008), 10870.
- [10] W. Zhou, H. Wu and T. Yildirim, *J. Am. Chem. Soc.*, 130 (2008), 15268.
- [11] P. D. C. Dietzel, R. E. Johnsen, R. Blom and H. Fjellvåg, *Chem.–Eur. J.*, 14 (2008), 2389.
- [12] Y. Liu, H. Kabbour, C.M. Brown, D.A. Neumann, and C.C. Ahn, *Langmuir*, 24 (2008) 4772.
- [13] P.D.C. Dietzel, Y. Morita, R. Blom and H. Fjellvåg, *Angew. Chem., Int. Ed.*, 44 (2005), 6354.
- [14] D. Yu, A.O. Yazaydin, J.R. Lane, P.D.C. Dietzel and R.Q. Snurr, *Chem. Sci.*, 4 (2013), 3544.
- [15] W.L. Queen, C.M. Brown, D.K. Britt, M.R. Hudson, P. Zajdel and O.M. Yaghi, *J. Phys. Chem. C.*, 115 (2011), 24915.
- [16] P.D.C. Dietzel, R.E. Johnsen, H. Fjellvåg, S. Bordiga, E. Groppo, S. Chavan and R. Blom, *Chem. Commun.* (2008), 5125.
- [17] W.L. Queen, E.D. Bloch, C.M. Brown, M.R. Hudson, J.A. Mason, L.J. Murray, A.J. Ramirez-Cuesta, V.K. Peterson and J.R. Long, *Dalton Trans.*, 41 (2012), 4180.