JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
pubs.acs.org/JACS

Trapping Guests within a Nanoporous Metal−Organic Framework through Pressure-Induced Amorphization

Karena W. Chapman,*,† Dorina F. Sava,‡ Gregory J. Halder,† Peter J. Chupas,† and Tina M. Nenoff*,‡

†X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, United States
‡Sandia National Laboratories, Surface and Interface Sciences, Albuquerque, New Mexico 87185, United States

S Supporting Information

ABSTRACT: The release of guest species from within a nanoporous metal−organic framework (MOF) has been inhibited by amorphization of the guest-loaded framework structure under applied pressure. Thermogravimetric analyses have shown that by amorphizing ZIF-8 following sorption of molecular I_2, a hazardous radiological byproduct of nuclear energy production, the pore apertures in the framework are sufficiently distorted to kinetically trap I_2 and improve I_2 retention. Pair distribution function (PDF) analysis indicates that the local structure of the captive I_2 remains essentially unchanged upon amorphization of the framework, with the amorphization occurring under the same conditions for the vacant and guest-loaded framework. The low, accessible pressure range needed to effect this change in desorption is much lower than in tradition sorbents such as zeolites, opening the possibility for new molecular capture, interim storage, or controlled release applications.

The structural versatility and flexibility of metal−organic frameworks (MOFs) affords opportunities for applications distinct from those of established nanoporous sorbents.[1,2] The unparalleled sorption selectivity that can be achieved in MOFs, through the initial synthesis or postsynthetic chemical modification of the framework, pore geometry, and surface functionality, is well established.[3] Recently, it has been recognized that the expanded structures of MOFs are extremely flexible, such that the associated pore geometries can be modified mechanically, through the application of pressure.[4−6] Notably, for ZIF-8, an archetypal MOF with an expanded zeolite topology, application of pressure induces an irreversible structural transition to an amorphous phase—a pressure-induced amorphization or PIA—which alters the pore structure and sorption characteristics without collapsing it.[5] Because of the flexibility of the expanded MOF structure, this amorphization occurs at low, easily accessible pressures; pressures an order of magnitude lower than for traditional nanoporous sorbents like zeolites.[7] Consequently, for MOFs, the amorphization can be achieved on a bulk, industrial scale, for example, through pressing pellets, mechanical grinding, ball milling, sonication, and so forth, providing opportunities for unique applications.

Here, we demonstrate the possibility to exploit pressure-induced changes to the MOF structure and sorption−desorption characteristics for new molecular capture applications. By pressure-amorphizing ZIF-8 following I_2 capture,[8] subsequent release of this volatile species, which is formed as a radioactive byproduct of nuclear energy production, is minimized. Detailed analysis of the local structure of the I_2 guests, using the PDF method which can probe both crystalline and amorphous materials,[9,10] indicates that this remains unaffected by the framework amorphization. In contrast to chemical postsynthetic modification of MOFs, this mechanical modification through pressure can be applied at an intermediate point in a sorption or sequestration process, rather than simply being used to generate the initial sorbent and sorption characteristics. Consequently, when employed *after* guest-sorption, mechanical modification has the potential to alter desorption properties, for example, to physically trap guests. This approach decouples guest sorption and changes to porosity, providing unique opportunities, distinct from the guest-triggered switching of pore structure reported in some framework materials (e.g., MIL-53) and molecular systems.[11,12] This is the first study to quantify the effect of pressure amorphization of MOFs for gas retention and storage, and show that this is pertinent to a wide range of molecular capture and interim storage applications including for volatile fission gases from nuclear fuel reprocessing,[8,13] such as I_2, Kr, and other species relevant to clean energy production (e.g., CO_2, and H_2).

ZIF-8, Zn(2-methylimidazole)$_2$, is part of a broad family of MOFs with expanded zeolite topologies—zeolitic imidazolate frameworks (ZIFs)—where the Zn−imidazolate−Zn link replicates the characteristic T-O-T angle of zeolites.[14] The sodalite-type topology of the cubic ZIF-8 framework (I-43m, $a \sim 17.0$ Å) defines 12.0 Å diameter pores connected via 3.5 Å diameter apertures (6-rings). The unmatched I_2 sorption capacity, retention, and selectivity of the ZIF-8 pore network benefits from the close correspondence of these 6-ring apertures to the I_2 molecular dimensions (3.5 cf. 3.35 Å).[8]

Activated ZIF-8 (∼1.5 g, Sigma-Aldrich) was loaded with iodine at ∼75 °C to different final concentrations (20, 40, 60, 80, 100, and 120 wt % I_2). A portion of each sample was annealed at 125 °C for 6 h to remove I_2 from the external surface. While the as-loaded samples were brown, with the color intensity increasing for higher loadings, all samples faded to a pale brown or tan shade upon annealing, independent of I_2 loading. This suggests that the color of the bulk sample is correlated to external surface-sorbed I_2.

Variable pressure X-ray diffraction measurements, for a 40 wt % I_2 sample, indicate that the I_2-containing sample can be amorphized at the same pressure as the vacant framework (∼0.34 GPa, see Supporting Information). Bulk powders of I_2-loaded ZIF-8

Received: September 8, 2011
Published: October 24, 2011

dx.doi.org/10.1021/ja2085096 | *J. Am. Chem. Soc.* 2011, 133, 18583–18585

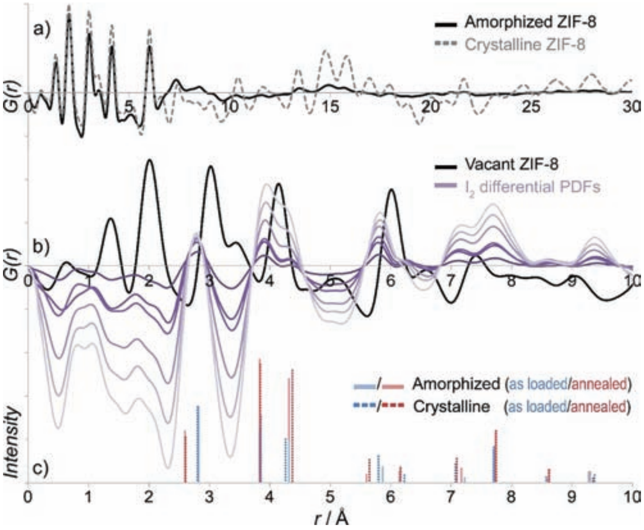

Figure 1. Representative PDFs, $G(r)$, for the crystalline and amorphous materials (a), and differential PDFs (b) corresponding to I−I and I−framework interactions in the pressure-amorphized as-loaded series (120 wt % loading). The intensity and position of features in differential PDFs for crystalline and amorphous, and as-loaded and annealed samples are compared (c).

(as-loaded and annealed) were amorphized within a pellet press (9 ton, 10-mm-diameter die, ∼1.2 GPa average pressure), and redispersed as powders for subsequent analysis. The structure of the crystalline and amorphized materials were compared using PDF analysis of high energy X-ray scattering data collected at beamline 11-ID-B at the Advanced Photon Source at Argonne National Laboratory. The PDF provides local structure information, independent of crystallinity, as a weighted histogram of all atom−atom distances within a material.[9] Not only can the PDF provide insight into the structural features that are retained in the amorphous ZIF-8 framework, but using a differential approach, and subtracting the contribution associated with the framework, the local I−I and I−framework interactions in the crystalline and amorphized materials can be directly compared.[10]

The well-defined long-range correlations, evident in PDFs for the crystalline materials, are eliminated for the amorphized ZIF-8 systems (Figure 1). However, the shorter range features, including those up to 6 Å, which correspond to the Zn−imidazolate−Zn links, are entirely preserved in the amorphous materials. The combined retention of guests, porosity,[5] and the $\mathrm{Zn}\cdots\mathrm{Zn}'$ connectivity in the pressure-amorphized materials suggests that the sodalite topology of ZIF-8 is preserved, despite the local structural changes that destroy the long-range order, that is, the crystallinity. These structural changes are likely to involve symmetry-reducing distortions of the 6-ring apertures, eliminating the well-defined features in the PDF beyond ∼6 Å and impeding diffusion of guest molecules through the framework. This displacive amorphization contrasts with the reconstructive transition to a dense amorphous phase induced thermally in ZIFs containing unsubstituted imidazole.[15]

While the long-range framework order is eliminated upon amorphization, the short-range I−I and I−framework interactions remain unchanged. Indeed, a larger change in local structure is associated with the annealing and surface-desorption compared to the amorphization itself (Figure 1). Specifically, the nearest neighbor I−I peak shifts from 2.8 to 2.6 Å while simultaneously narrowing, indicating less disorder (dynamic or static).[16] This is accompanied by an increase in the relative intensity of the second and third peaks at 3.85 and 4.3−4.4 Å, associated with intermolecular interactions within pores. These changes may reflect a refinement of the I_2 arrangement within the pores upon annealing.

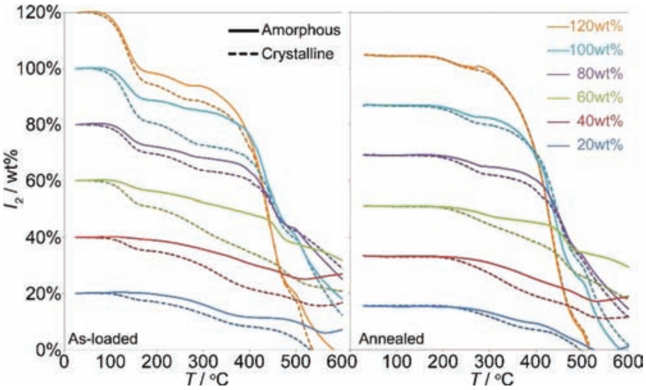

Figure 2. The mass loss associated with I_2 release from the crystalline and amorphized ZIF-8 based on TGA of the as-loaded (left) and annealed (right) samples. The mass losses for the vacant ZIF-8 materials have been subtracted.

The retention of I_2 is enhanced in the amorphized relative to the crystalline ZIF-8, as evidenced from thermogravimetric analysis (TGA). The mass losses upon heating (10 °C min^{-1}, N_2 flow, Figure 2) were shifted to higher temperatures for the amorphized materials, by up to 150°. These gains were most pronounced for the intermediate I_2 loadings. At the highest loadings, there appeared to be some destabilization of the framework, with a greater overall mass loss for the I_2-containing framework than for the vacant ZIF-8. This is consistent with the reduced crystallinity observed at high loadings. For the as-loaded samples, the TGA showed mass loss associated with surface desorption starting at 100−120 °C, with a further loss at 170−240 °C associated with release of I_2 from within the pores. For the surface-desorbed samples, the mass loss occurred at 170−240 °C, starting at lower temperatures for higher loadings.

The improvement in I_2 retention was quantified by comparing the I_2 mass loss from ZIF-8 samples (annealed 80 wt %) at constant temperature in the TGA apparatus (200 °C, N_2 flow, see ESI). The I_2 loss is retarded by a factor of approximately 12 in the amorphized ZIF-8.

The enhanced guest retention of the amorphized material is associated with a kinetic trapping mechanism,[17] rather than a change in binding energy, with identical host−guest interactions in the crystalline and amorphous materials. Leach testing, which evaluates the long-term durability of a final waste form, by heating in deionized water for 7 days at 90 °C,[18] showed minor differences in I_2 retention upon amorphization. As such, the amorphized pellets are most suitable for applications as an interim waste-form. Initial tests suggest that these can be successfully incorporated into core−shell structured final waste forms[19] that combine excellent long-term stability with potentially unmatched I_2 densities.

The present study shows that independent of guest molecules loaded into pores of ZIF-8, the framework can be amorphized at the same mild pressure and temperature conditions as empty ZIF-8. This is particularly striking considering the extremely high I_2 loading (up to ∼6 I_2 molecules per sodalite cage). This is generally consistent with the relative independence of certain MOFs' compressibility to different guest loadings.[4] The structural changes to the framework associated with this amorphization improve the I_2 retention upon heating, by up to 150°, retaining the local structure of the captive I_2 despite the changes to the framework crystallinity.

An efficient radioactive waste capture process, in reprocessing nuclear fuel or cleanup following inadvertent environmental release, is perhaps one of the highest impact (in terms of cost savings per unit quantity) potential sorption applications for MOFs.[20] In this field, there are overwhelming economic drivers that dictate that contamination, and accordingly, processing steps and materials, must be minimized, with the same storage requirements applied to any component used as part of the waste capture as for the waste itself. The amorphization of I_2-loaded ZIF-8 provides for secure interim storage before incorporation into a long-term waste form, ensuring noncontamination of the environment. The unmatched I_2 uptake capacity for ZIF-8, relative to existing zeolite getters, and the possibility to minimize subsequent release through amorphization, makes this a promising I_2 capture method. Furthermore, the invariance of the host−guest interactions to pressure treatment, demonstrated here, answers an important question in materials for radioactive waste storage. Here, the preferred technology to densify radioactive waste to a monolithic form that is suitable for transport is hot isostatic pressing (HIPping).[21] Not only does the present work provide a route to an interim waste form based on amorphized ZIF-8, but more generally, it provides insight into the behavior of other I_2 containing MOFs under HIPping conditions, showing that the pore structure can retain iodine under pressure.

More generally, in contrast to chemical postsynthetic modification of MOF structure and sorption−desorption behaviors which must be applied before guest-loading, this mechanical modification through pressure can be applied at any point in a sorption-sequestration process. Consequently, pressure-induced structural changes can be used as a macroscale handle with which to control the nanoscale sorption properties. Specifically, they can be used for increasing hysteresis in the sorption−desorption kinetics, at will, to kinetically trap I_2. Potential applications, beyond the capture of radioisotopes, include the controlled release of agrochemicals.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Details about sample preparation, variable-pressure diffraction measurements, PDF measurements, thermogravimetric analysis and leach testing. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

chapmank@aps.anl.gov; tmnenof@sandia.gov

■ ACKNOWLEDGMENT

Work done at Argonne and use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. DOE Office of Science by Argonne National Laboratory, were supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. Work done at Sandia was supported by the US DOE/NE/FCRD-SWG and DOE/NE-NEAMS. Sandia National Laboratories is a multiprogram lab operated by Sandia Corp., a wholly owned subsidiary of Lockheed Martin company, for the US DOE's NNSA under contract DE-AC04-94AL85000.

■ REFERENCES

(1) *Themed issue: Metal-Organic Frameworks*; Long, J. R.; Yaghi, O. M., Eds.; *Chem. Soc. Rev.*, **2009**; Vol. *38*, Issue 5.

(2) *Handbook of Zeolite Science and Technology*; Auerbach, S. M., Carrado, K. A., Dutta, P. K., Eds.; Marcel Dekker, Inc.: New York, 2003.

(3) Wang, Z. Q.; Cohen, S. M. *Chem. Soc. Rev.* **2009**, *38*, 1315.

(4) Chapman, K. W.; Halder, G. J.; Chupas, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 10524.

(5) Chapman, K. W.; Halder, G. J.; Chupas, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 17546.

(6) (a) Spencer, E. C.; Angel, R. J.; Ross, N. L.; Hanson, B. E.; Howard, J. A. K. *J. Am. Chem. Soc.* **2009**, *131*, 4022. (b) Moggach, S. A.; Bennett, T. D.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2009**, *48*, 7087.

(7) (a) Hazen, R. M.; Sharp, Z. D. *Am. Mineral.* **1988**, *73*, 1120. (b) Huang, Y. M. *J. Mater. Chem.* **1998**, *8*, 1067.

(8) Sava, D. F.; Rodriguez, M. A.; Chapman, K. W.; Chupas, P. J.; Greathouse, J. A.; Crozier, P. S.; Nenoff, T. M. *J. Am. Chem. Soc.* **2011**, *133*, 12398.

(9) Egami, T.; Billinge, S. J. L. *Underneath the Bragg Peaks: Structure Analysis of Complex Materials*; Cahn, R., Ed.: Oxford/Pergamon Press: New York, 2004.

(10) Chapman, K. W.; Chupas, P. J.; Kepert, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 11232.

(11) (a) Serre, C.; Millange, F.; Thouvenot, C.; Nogues, M.; Marsolier, G.; Louer, D.; Ferey, G. *J. Am. Chem. Soc.* **2002**, *124*, 13519. (b) Barthelet, K.; Marrot, J.; Riou, D.; Férey, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 281.

(12) (a) Jones, J. T. A.; Holden, D.; Mitra, T.; Hasell, T.; Adams, D. J.; Jelfs, K. E.; Trewin, A.; Willock, D. J.; Day, G. M.; Bacsa, J.; Steiner, A.; Cooper, A. I. *Angew. Chem., Int. Ed.* **2011**, *50*, 749. (b) Mobian, P.; Huguenard, C.; Henry, M. *Chem. Commun.* **2011**, *47*, 9630.

(13) Thallapally, P. K.; Grate, J. W.; Motkuri, R. K.*Chem. Commun.* DOI: 10.1039/C1CC14685H.

(14) (a) Park, K. S.; Ni, Z.; Cote, A. P.; Choi, J. Y.; Huang, R. D.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10186. (b) Huang, X. C.; Lin, Y. Y.; Zhang, J. P.; Chen, X. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1557.

(15) (a) Bennett, T. D.; Goodwin, A. L.; Dove, M. T.; Keen, D. A.; Tucker, M. G.; Barney, E. R.; Soper, A. K.; Bithell, E. G.; Tan, J. C.; Cheetham, A. K. *Phys. Rev. Lett.* **2010**, 104. (b) Bennett, T. D. B. T. D.; Keen, D. A.; Tan, J. C.; Barney, E. R.; Goodwin, A. L.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2011**, *50*, 3067.

(16) A similarly contracted I−I distance has been observed for I_2 in a cationic state and intercalated in C_{60}. See, for example:(a) Nandana, W. A. S.; Passmore, J.; White, P. S.; Wong, C.-M. *J. Chem. Soc., Chem. Commun.* **1982**, 1098. (b) Zhu, Q.; Cox, D. E.; Fischer, J. E.; Kniaz, K.; McGhie, A. R.; Zhou, O. *Nature* **1992**, *355*, 712.

(17) (a) Yang, S. H.; Lin, X.; Blake, A. J.; Walker, G. S.; Hubberstey, P.; Champness, N. R.; Schroder, M. *Nat. Chem.* **2009**, *1*, 487. (b) Mitra, T.; Wu, X.; Clowes, R.; Jones, J. T. A.; Jelfs, K. E.; Adams, D. J.; Trewin, A.; Bacsa, J.; Steiner, A.; Cooper, A. I. *Chem.−Eur. J.* **2011**, *17*, 10235.

(18) ASTM International. *Standard Test Methods for Determining Chemical Durability of Nuclear Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT)*, Designation: C 1285-02. ASTM International: West Conshohocken, PA, 2008.

(19) Garino, T. J.; Nenoff, T. M.; Krumhansl, J. L.; Rademacher, D. X. *J. Am. Ceram. Soc.* **2011**, *94*, 2412.

(20) (a) Ewing, R. C.; von Hippel, F. N. *Science* **2009**, *325*, 151. (b) Weber, W. J.; Navrotsky, A.; Stefanovsky, S.; Vance, E. R.; Vernaz, E. *MRS Bull.* **2009**, *34*, 46.

(21) *Waste Forms: Technology and Performance*; National Research Council, National Academy of Sciences, National Academy Press: Washington, D.C., 2011.