Pressure-Induced Amorphization and Porosity Modification in a Metal−Organic Framework

Karena W. Chapman,*,[†] Gregory J. Halder,[‡] and Peter J. Chupas[†]

X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, and Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

Received October 2, 2009; E-mail: chapmank@aps.anl.gov

Porous materials are a cornerstone of modern chemical industry involved in storage, separations, and catalysis spanning petroleum cracking to waste sequestration.[1] Metal−organic frameworks (MOFs),[2] an emerging class of crystalline solid, hold promise as the next generation of porous materials. Their more diverse, expanded components allow unsurpassed porosities, internal surface areas, and structural and chemical versatility. These enhanced characteristics, which make nanoporous MOFs so apt for advanced applications, impact correlated physical properties that must be thoroughly understood before MOFs can supersede current materials technologies.

The highly porous (i.e., low density) MOF structures are extremely flexible/compressible,[3] with considerable sensitivity to applied force. Indeed pressurization of a simple expanded framework by just 0.5 GPa, a pressure routinely surpassed industrially, induces structural changes comparable to heating by 500 K.[4,5] With the functional properties of MOFs often being disproportionately responsive to subtle structural changes,[6] MOF functionalities are likely to be strongly pressure dependent. Pressure-induced changes in pore geometry will strongly affect sorption selectivity, sorption capacity, and access to binding sites. As such, exploring the pressure-dependence of MOF functionality is pivotal to the realization of new MOF-based technologies.

While a few recent studies[3,7] have probed the structure of MOFs at pressures beyond those readily accessible using compressed gas cylinders (<3000 psi ≈ 0.02 GPa), the influence of pressure-induced structural changes on the critically important sorption behavior of MOFs has yet to be explored.

Here we investigate the impact of modest, industrially accessible pressures (~ 1 GPa) on the structure and porosity of Zn(2-methylimidazole)$_2$ (ZIF-8),[8] an MOF now sold as a high-surface-area catalyst.[9] ZIF-8 is part of a broad family of MOFs with expanded zeolite topologies—zeolitic imidazolate frameworks—where the bidentate imidazolate-based ligand replicates the characteristic T−O−T angle of zeolites.[10] Impressive gas storage,[11] separations,[12] and catalytic[13] behaviors have been documented for these systems. The topology of ZIF-8, with imidazolate-bridged zinc tetrahedra, corresponds to the high symmetry zeolite sodalite.[8] The cubic framework ($I\bar{4}3m$, $a \sim 17.0$ Å) can be described by a space-filling packing of regular truncated octahedra. This defines 12.0 Å diameter pores connected *via* 3.5 Å diameter apertures (6-rings), with the 4-rings being too small to transmit guests.

The pressure-dependent structure of commercially available ZIF-8 was probed using synchrotron-based powder diffraction for the sample within a diamond anvil cell pressure apparatus. *In situ* X-ray diffraction data ($\lambda = 0.60511$ Å) were collected at the 1-BM beamline at the Advanced Photon Source, Argonne National Laboratory. High-pressure experiments often use fluids to uniformly transmit pressure (hydrostatic conditions). Sorption of small molecules from the pressure-transmitting fluid has previously been demonstrated in MOFs.[3] Here the sample was compressed without fluid (nonhydrostatic) or in large molecule, nonpenetrating fluid (Fluorinert) to focus on the intrinsic high-pressure behavior of ZIF-8 rather than any pressure-induced sorption. Sample pressures were precisely determined using an internal diffraction standard with known compressibility (NaCl).[14]
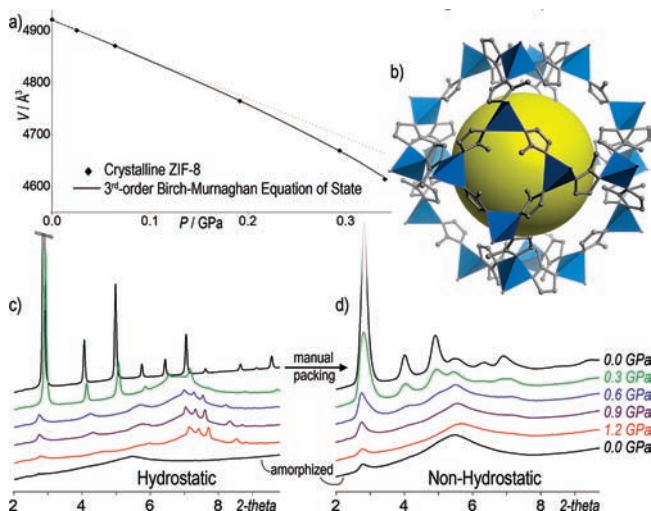
Figure 1. (a) Pressure-dependent lattice volume of crystalline ZIF-8, which is stable up to 0.34 GPa, and the corresponding equation of state. (b) The crystalline ZIF-8 consists of expanded sodalite cages (b) which define 12.0 Å pores. The diffraction data show irreversible amorphization of ZIF-8 under hydrostatic (c) and nonhydrostatic (d) compression.

Although among the most thermally stable MOFs, even manual packing of ZIF-8 produces a marked reduction in crystallinity and structural order (Figure 1). With additional nonhydrostatic compression the diffraction peaks broaden further and the sample eventually amorphizes. Under hydrostatic conditions, the framework compresses rapidly, by 5% over 0.3 GPa. The pressure-induced changes in lattice volume (0−0.34 GPa), from Le Bail analysis of the hydrostatic diffraction data, were best modeled by a third-order Birch−Murnaghan equation of state with a bulk modulus ($K = -V\, \partial P/\partial V$) of 6.52(35) GPa and $K' = -4.6(14)$. Pressurization beyond 0.34 GPa produced an irreversible structural transition and amorphization upon recovery to ambient pressure. Given the high structure−property correlation in MOFs, amorphized ZIF-8 is unlikely to retain the sorption and catalytic properties of the pristine, commercially available material.

To characterize the change in sorption behavior for pressure-treated and amorphized ZIF-8, bulk samples (~ 60 mg) were

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prepared using a hydraulic pellet press. This nonhydrostatic compression parallels processing used to increase packing density of dispersed or powdered solids and, thereby, optimize volumetric capacities. Samples were treated to equally spaced pressures up to 1.2 GPa (9 ton load, 10-mm-diameter die). Nitrogen gas sorption and desorption isotherms were measured at 77 K following rigorous evacuation of the pore network (see Supporting Information). For all samples the sorption was reproducible and fully reversible, without evidence of significant hysteresis.

The amorphized ZIF-8 remains porous, although the sorption characteristics are distinctly altered (Figure 2). Significant modifications are evident for all pressure-treated samples which show systematic decreases in total uptake and increases in the uptake at low pressure ($P/P_0 < 10^{-4}$) with increasing treatment pressure. Furthermore, the multistep features apparent in the pristine sample were progressively eliminated for the pressure-treated samples, suggesting a degree of homogenization of the pore and window/ aperture dimensions. The modifications of the nitrogen isotherms are likely to reflect far-reaching changes in the pore dimension and broader sorption properties, such as altering the relative affinity for different guests (i.e., selectivity).
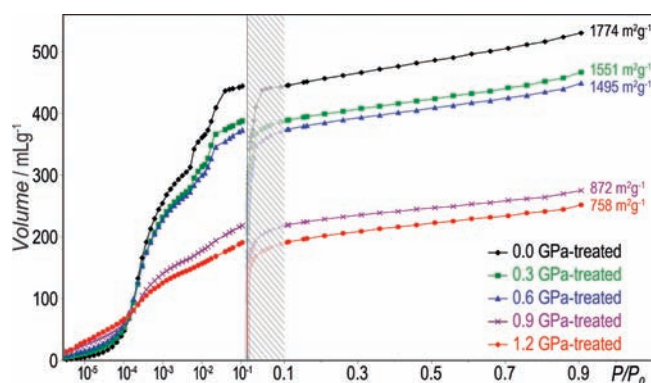
Figure 2. N$_2$ sorption isotherms for pressure-treated ZIF-8. A logarithm-scale expansion of the low pressure regime is given (left).

Compared to sodalite, ZIF-8 is a factor of 8 more compressible, with pressure amorphization induced at much lower pressures.[15,16] These differences can be attributed to increased structural degrees of freedom in the expanded framework, with molecular rather than single-atom bridges. Most zeolites are more compressible than sodalite, with amorphizations at lower pressures.[15] As such, it is expected that other ZIFs[10] will be even more compressible than ZIF-8, with transitions at lower pressures.

The negative value of K', the pressure dependence of the bulk modulus, indicates that the framework becomes more compressible with increasing pressure. Although anomalous for conventional solids, we propose that negative K' values may be relatively widespread in open framework solids,[5] where the volume reduction at moderate pressure is not sufficient to bring atoms into unfavorably close contact.

As in zeolites,[17] the pressure-induced amorphization of ZIF-8 is likely to involve disruption of long-range translational symmetry while retaining the local structure, framework connectivity, and, hence, porosity. In contrast other porous amorphous solids often rely on inefficient space filling by long, rigid components to generate porosity.[18] Pair distribution function studies, which probe local atomic structure irrespective of long-range symmetry, are in progress to investigate the amorphized structure, the amorphization

mechanism,[17] and guest-binding sites in the pristine and amorphized material.[19] It is further anticipated that these studies will provide unique insights into the amorphization mechanisms of zeolites.

We have demonstrated that ZIF-8 is highly compressible with an irreversible pressure-induced amorphization at extremely low pressures. This has been exploited to generate a new type of noncrystalline MOF system through amorphization of an existing crystalline MOF. Although crystalline diffraction has often been used as a benchmark for MOF stability, we have shown that the pressure-treated and amorphized MOFs exhibit nanoporosity and, therefore, retain some structural order. As such, pressure can provide a new route to systematically modify the structure and properties of MOFs, a nontraditional form of postsynthetic modification. Importantly, pressure modification of MOFs is effective at lower pressures than in zeolites and, consequently, is easily scalable and industrially relevant.

Supporting Information Available: Details of diffraction and sorption experiments and analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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