Universal Gas-Uptake Behavior of a Zeolitic Imidazolate Framework ZIF-8 at High Pressure

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ABSTRACT: We report the pressure-induced insertion (PII) of gases in a zeolitic imidazolate framework (ZIF) at high pressure. ZIF-8 crystals were compressed in the presence of nonpolar CO2 and SF6 as well as polar CHClF2 (aka R22) up to 4.07, 0.81, and 2.06 GPa, respectively, in a diamond anvil cell, and their X-ray powder diffraction data were analyzed by Rietveld methods. ZIF-8 showed pressure-induced amorphization in SF6 but maintained its crystallinity in the presence of other gases. In general, the unit cell volume of ZIF-8 expanded via PII of CO2 or R22 up to ca. 0.5 GPa and contracted linearly after completion of the PII processes. The total volumes of the inserted guest molecules, which were estimated from the residual electron densities, indicated that the inserted guest molecules fully occupy the pores of ZIF-8. The relationship between the total occupied volumes by guests and applied pressures was best represented with an asymptotic logarithmic curve regardless of the type of molecules. These results reveal the universal gas-uptake behavior of ZIF-8 at high pressure, which requires only the penetration of molecules into the pores of the framework of ZIF-8.

Introduction

The most versatile property of porous materials is their gas adsorption capability, which is invaluable for gas separation and storage applications, usually conducted at about 1 bar up to ca. 100 bar.12 Zeolitic imidazolate frameworks (ZIFs) are crystalline porous materials having zeolite-like structures.3 Among known ZIFs, ZIF-8 (Zn(mIm)2, mIm = 2-methylimidazolate), which has a framework of fused sodalite cages (Figure 1a), has attracted a lot of attention due to its water stability.3 For example, recent research on the repeated intrusion and extrusion of water demonstrated that ZIF-8 does not suffer framework degradation up to 56 MPa (0.056 GPa);6 at such a high pressure, water molecules are inserted into the pores of ZIF-8. In particular, ZIF-8 is known to have a high framework stability at high pressure in various pressure-transmitting media (PTM). Until reaching a hydrostatic pressure of 0.34 GPa in a nonpenetrating PTM (Fluorinert), ZIF-8 can maintain its long-range order and permanent porosity.7 In penetrating PTMs, although the stability of ZIFs is known to be dependent on particle sizes,8 IR studies show that ZIF-8 reversibly stores CO2 at 0.4–0.8 GPa and its imidazolate rings are almost intact even at 2.65 GPa while those of empty ZIF-8 are distorted above 1.6 GPa.9

The structure and porosity changes of ZIF-8 under high pressure have been investigated mainly using a diamond anvil cell (DAC) and X-ray diffraction methods.10–12 ZIF-8 has a void space of ca. 2500 Å3 per unit cell when calculated with a probe radius of 1.2 Å. Six-membered rings (6MRs) in a sodalite cage have 3.4 Å windows through which molecules with kinetic diameters smaller than ca. 7.6 Å can pass at 50 °C; indeed, the diffusion of larger molecules is extremely slow.13 ZIF-8 can store 41 MeOH molecules per unit cell at 1.47 GPa and room temperature.10 At high pressure and ambient temperature, the mIm ligands of four-membered rings (4MRs) rotate, giving rise to an increase in the torsion angle (θ) from ca. 64 to 90°; the angle is defined by an imidazolate plane and the plane of four Zn atoms in a 4MR sitting on a crystallographic (100) plane.11,12 This torsion of ligand is called the “swing-effect” or “gate-opening”, previously reported under various other conditions such as under adsorption of...
ZIF-8 sample was loaded with CO$_2$, R22, or SF$_6$ in its CCl$_4$, studied by 1H NMR spectroscopy suggested that the chlorodi and CH$_4$ PTMs, respectively (Figure 2b). Interestingly, the gate-opening at 0.75, 0.75, 0.21, and 0.70 GPa in Ar, O$_2$, N$_2$, and SF$_6$, respectively. For example, the adsorption kinetics and host-guest interactions of large molecules, namely CS$_2$, CDCl$_3$ and CCl$_4$, studied by 1H NMR spectroscopy suggested that the larger molecules showed a slower diffusion rate through the channel and a lower degree of the swing-effect. Monte Carlo simulations also suggest that the increase in the torsion angle leads to enhanced gas storage. For instance, the rotation of mIm ligands allows N$_2$ molecules to be inserted in the newly formed 4MR sites (Figure 1b) and also induces a rearrangement of the gas molecules in sodalite cavities toward a more efficient packing. Indeed, the threshold pressures for such structural changes are dependent on the type of gases. That is, at ambient temperature, ZIF-8 shows structural changes or gate-opening at 0.75, 0.75, 0.21, and 0.70 GPa in Ar, O$_2$, N$_2$, and CH$_4$ PTMs, respectively (Figure 2b). Interestingly, the guest-insertion profiles seem to mimic conventional gas adsorption isotherms as shown in the intrusion experiments of H$_2$O, EtOH, or MeOH PTMs pressurized respectively up to 2.1, 3.6, and 4.0 GPa. Here, we report the high-pressure X-ray powder diffraction (XRPD) studies on the insertion of greenhouse gases into ZIF-8. The used gases are CO$_2$, chlorodifluoromethane (CHCIF$_2$, aka the R22 refrigerant), and SF$_6$, having kinetic diameters of 3.30, 4.25, and 5.50 Å, respectively.

**METHODS**

**Synthesis of ZIF-8.** ZIF-8 was prepared according to the literature method with a slight modification. Zinc nitrate hexahydrate, Zn(NO$_3$)$_2$·6H$_2$O (0.146 g, 0.49 mmol), was dissolved in methanol (10 mL). Separately, 2-methylimidazole (0.325 g, 3.96 mmol) was also dissolved in methanol (10 mL). The two solutions were mixed and gently stirred at room temperature for 2 h. The collected white solid was washed with neat methanol (25 mL) three times and dried at 50 °C in a convection oven for 2 days. Finally, the product was evacuated at 100 °C under vacuum for 10 h.

**High-Pressure X-ray Powder Diffraction Study.** The ZIF-8 sample was loaded with CO$_2$, R22, or SF$_6$ in its cryogenic liquid state in a specific sample chamber inside a diamond anvil cell (DAC). Subsequently, the sample chamber was compressed at room temperature in pressure increments of ca. 0.5 GPa up to 4.07, 2.06, and 0.81 GPa, respectively, for CO$_2$, R22, and SF$_6$, and their XRPD patterns were obtained (Figure S1) for crystal structure refinement using Rietveld methods. X-ray powder diffraction experiments using diamond anvil cells were conducted at the beamline 6D at the Pohang Light Source II (PLS II) in the Pohang Accelerator Laboratory (PAL). We used X-rays from a bending magnet source, which was monochromatized to give a wavelength of 0.6530(1) Å. A MAR345 image plate was employed as a detector, and the first 10 Debye-Scherrer rings from SRM 660c (LaB$_6$) were used for the calibration of the detector. The residual electron densities in the pores of ZIF-8 at different pressures were obtained from difference Fourier syntheses using Rietveld refinement in the GSAS suite of programs. The residual electron densities in pore spaces were assigned to oxygen atoms, and their positions, thermal parameters, and site occupancy factors were refined. The background was fitted by a Chebyshev polynomial with 36 coefficients. The peak shapes were fitted using the Voigt-plot function.
We used a piston-cylinder-type diamond anvil cell (DAC), which was manufactured with a design modified from the original one as reported by Jenei et al. (2013). Two brilliant-cut type-IA diamonds with culet diameters of 700 μm were aligned to have their culets face each other. Each anvil was attached to a tungsten-carbide seat with an epoxy resin fixture. The cylinder part of the DAC had a hole elongated along one direction to allow a maximum 20° angle of ca. 45°. The microcrystalline ZIF-8 sample was loaded into a cylinder-shaped sample chamber with ca. 350 μm diameter and ca. 120 μm height. The sample chamber was made by drilling the center of the hexagonal dent of a pre-engraved stainless-steel foil gasket of 250 μm thickness. Pressure determination was achieved by observing the shift of the ruby R1 emission patterns measured at and above 0.73 GPa CO2 pressure. The intensities of the solidi...

**RESULTS AND DISCUSSION**

**Structural Changes of ZIF-8 upon Pressure-Induced Insertion (PII) of Greenhouse Gases.** The unit cell parameters and volume of the evacuated ZIF-8 were determined to be $a = 17.004(1)$ Å and $V = 4916.8(7)$ Å³ in a cubic $I4_13m$ space group (Figure S2a). The unit cell volume of the CO2-loaded ZIF-8 expanded slightly at 0.41 GPa and then decreased gradually up to 1.02 GPa (Figure 2a). Upon increasing the pressure, the solidification of CO2 to the cubic phase-I was detected on the XRPD pattern at 0.73 GPa (Figure S2c). Then, to enhance the mobility during the pressure-induced insertion (PII) of CO2, the sample was annealed at 100 °C for an hour, leading to a secondary volume expansion between 1.02 and 1.11 GPa. The expansion at 1.11 GPa was accompanied by an increase in the torsion angle $\theta$ to 84.4°, which is in accordance with the values observed in the high-pressure structure, ZIF-8HP (Figures 1 and 2b). This structural change was accompanied by the additional insertion of CO2, giving rise to an increase in electron densities on the 4MR sites, similar to the N2 adsorption behavior mentioned above (Figures 1, 3, and S6). The unit cell volume gradually decreased with the pressure increasing up to 4.07 GPa, with little change in the amount of inserted CO2 molecules (Figure S5). The ratios of Cl and Zn were averaged using a linear fit in Origin2019 provided by OriginLab Corp.

**X-ray Fluorescence Spectroscopy.** The elemental distribution of the pressure-recovered samples was measured using a Bruker M4 Tornado X-ray fluorescence spectrometer. A rhodium Kα X-ray beam focused down to a diameter of 20 μm illuminated 49 points of the sample for 1 min, from which 41 points that were not disturbed by the stainless-steel gasket surrounding the sample were adopted and used for analysis (Figure S5). The ratios of Cl and Zn were averaged using a linear fit in Origin2019 provided by OriginLab Corp.

**Framework Refinement.** We used the ambient ZIF-8 structure reported by Moggach et al. as a starting point of structure refinement. A total of 32 interatomic distances in the framework were softly constrained. The ZIF-8 structure at ambient pressure was successfully refined without any meaningful indication of residual electron density within pore spaces. The structural model at ambient pressure was then used as a starting model to refine structures at higher pressures.

**Electron Density Refinement Using Dummy Atoms.** We employed dummy atoms to account for the electron density distribution within pore spaces. Difference Fourier calculations were performed to locate high-density points (Q-sites), which were then fitted with oxygen dummy atoms in the order of high-density values. The site occupancy factor of each dummy atom was refined. In the final stage, we refined all refinable variables simultaneously, except for the site occupancy factors of the framework atoms. Every atom was assumed to be thermally isotropic, and the atoms of the same kind in an equivalent environment were constrained to have the same $U_{iso}$ values to reduce the number of variables and their correlations. We observed the reflections originating from solidified CO2 (space group Pa3 no. 205) in the XRPD patterns measured at and above 0.73 GPa CO2 pressure. The intensities of the solidified CO2 were accounted by profile fitting using the Le Bail method. The refinement was completed when the variables from the dummy atoms were converged to certain values with a negligible change (<1%).

**Calculation of Void Spaces and the Torsion Angle ($\theta$).** The void volumes of the ZIF-8 structures in this work were calculated using the Mercury (CSD 3.10.3) program. After loading the CIF files generated from the models of which structure refinements are completed, the oxygen dummy atoms were removed to produce empty pore structures. The void volumes were obtained by calculating contact surfaces, instead of solvent-accessible surfaces, employing a probe radius of 0.20, 1.20, 1.25, or 1.70 Å, with a grid spacing of 0.25 Å. The resulting void volumes calculated in a probe radius of 1.20 Å are presented in Table S1. It should be noted that the probe radius of 1.20 Å may not be suitable for the estimation of dead volumes such as the 4MR sites when guest molecules are significantly larger than the sites as seen in the R22 case in the main text. Therefore, to calculate the effective void volume for R22 in a possible ZIF-8HP structure, we used CO2 molecules in the 4MR site to remove the potentially dead volume using the BIOVIA Materials Studio 2019 software. The resulting model structure was saved as a CIF file for further calculations using Mercury. The torsion angles were calculated using the “mpln” instructions in Olex2 (v1.2) software. The CIF files were loaded, and the asymmetric units were expanded using a “grow” command to build a structure encompassing the 4MR moieties. A mean plane for an mIm ligand was defined by selecting five atoms in an imidazole ring, while another plane was defined by four Zn atoms in a 4MR unit. Between the two mean planes, the torsion angles were measured.
showed no electron densities on the 4MR sites (Figure S6). In structures including the structure at 2.06 GPa (the ZIF-8 structure at 1.11 GPa CO$_2$, the centroid distance of two facing imidazole rings of 4MRs is 6.2 Å, and thus, even a CO$_2$ molecule can be tightly bound to the 4MR site, considering the van der Waals radii. Although R22 may also be able to induce a similar HP structure, for example, the ZIF-8 structure at 1.11 GPa CO$_2$ ($\theta = 84.4^\circ$), R22 molecules cannot access the 4MR space due to their much greater molecular size compared to that of CO$_2$. Subsequently, the practically available void space for R22 becomes reduced significantly from 2579 Å$^3$ at 0.83 GPa to 2428 Å$^3$ at 2.06 GPa (Table S2, Figure 3d). Because of the unfavorable dead volume, the R22 insertion seems to be unfavorable to induce a ZIF-8HP-like structure.

The diffraction peaks of ZIF-8 became broad under compression in SF$_6$ at 0.28 GPa, and pressure-induced amorphization occurred at 0.81 GPa (Figure S1c). Our diffraction data reveal that at 0.28 GPa no diffraction peaks above a $2\theta$ of 8° are observed, clearly indicating that the long-range order has been destroyed. A more detailed analysis would require extracting the pair-distribution function from the scattering data. Due to the limited q-range, we did not pursue this analysis. This amorphization is attributed to the size of SF$_6$ molecules. Usually, this phenomenon happens in nonpenetrating PTM such as silicone oil$^{24}$ or Fluorinert.$^{10}$ However, since some large molecules with kinetic diameters greater than 5.5 Å can access the pores despite slow diffusion,$^{14}$ there is a possibility of partial insertion of SF$_6$ in the amorphized ZIF-8, similar to I$_2$-trapping in ZIF-8 by pressure-induced amorphization.$^{10}$ We did not continue further structural analyses due to the broadened XRPD patterns.

**Universal Gas-Uptake Behavior of ZIF-8 under a Kilobar Pressure Regime.** The residual electron counts of the CO$_2$- and R22-inserted ZIF-8 are almost twice those obtained from the PII of water, methanol, and ethanol in our previous investigation (Figure 4).$^{24}$ With increasing pressure, the PII process continued until the number of the electrons converged to maximum values, giving rise to curves similar to gas adsorption isotherms. The electron counts in the pores were then converted to the number of the inserted guest molecules, using the number of electrons in each molecule: H$_2$O (10), MeOH (18), EtOH (26), CO$_2$ (22), and R22 (42). The numbers of the maximum inserted molecules were then compared to those calculated from the adsorption isotherms measured at subatmospheric pressures. We used the values for H$_2$O, MeOH, and EtOH from the literature,$^{41,42}$ while those for CO$_2$ and R22 were from our measurements (Figure 5a). In detail, ca. 53 CO$_2$ and 26 R22 molecules per unit cell are incorporated in ZIF-8 by PII processes whereas only ca. 2.0 CO$_2$ and 11.3 R22 molecules can be stored at 1 bar (Figure S8).

When the total volumes occupied by inserted guest molecules in ZIF-8 are plotted against applied pressures, the traces for all guest molecules could be best represented as an asymptotic curve (Figure 5b), where the numbers of guest molecules are simply converted from the total electron counts within the pores, and the molecular volumes of each molecule are estimated from their densest liquid states: namely 29.9, 46.8, 67.0, 96.4, and 97.0 Å$^3$ for H$_2$O, CO$_2$, MeOH, R22, and EtOH, respectively. This simple plot unveils the inherent porosity of ZIF-8 at high pressures. As a host material, ZIF-8 behaves universally at high pressure regardless of the type of guests. At gigapascal pressures, the total volume of the inserted guest molecules per unit cell increases in a logarithmic manner until full saturation of the ZIF-8 pores is achieved, irrespective
of the penetrating guest molecules. This observation indicates that the physical properties of guest molecules such as sizes, shapes, or polarities are not critical factors affecting the pressure-loading capacity of ZIF-8 as long as the guest molecules can access the pores. Indeed, in the common gas adsorption at subatmospheric pressures, the physical properties affect the weak interactions between guest molecules and framework surfaces during physisorption.

**CONCLUSIONS**

In this study, we revealed the universal gas-uptake behavior of ZIF-8 at kilobar pressures. Using DAC and XRPD methods, the amounts of inserted CO\(_2\) and chlorodifluoromethane (R22) molecules in ZIF-8 were calculated. These amounts were plotted against the applied pressures to give an asymptotic logarithmic curve, representing the relationship between applied pressures and the total molecular volumes of the inserted gases. The relationship indicates that in the kilobar regime, ZIF-8 can fully take up adsorbates regardless of the type of molecules, and the inserted molecules occupy almost the entire available space in the pores. In addition, in contrast to CO\(_2\) and other small gases, R22 did not induce a ZIF-8HP structure until 2.06 GPa due to its large molecular size, which has not been observed in the known high-pressure experiments on ZIF-8 thus far. Lastly, the uptake of SF\(_6\) results in pressure-induced amorphization and calls for further modeling studies.

**REFERENCES**

6. Sun, Y.; Lib, Y.; Tan, J.-C. Framework flexibility of ZIF-8 under liquid intrusion: discovering time-dependent mechanical response and...