In situ high pressure study of ZIF-8 by FTIR spectroscopy†

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ZIF-8 as a promising storage material was investigated at high pressures up to ~39 GPa by in situ FTIR spectroscopy for the first time. Structural modifications are found to be reversible in a low-pressure region but irreversible in a high-pressure region. Overall, the ZIF-8 framework exhibits an unusual chemical stability even under extreme compression.

ZIFs, short for zeolitic imidazolate frameworks, are an emerging class of porous materials with extended 3D crystalline structures constructed from tetrahedral metal ions (Zn, Co, In, etc.) bridged by imidazolate (Im) units. Up to date, a large variety of ZIFs with rich structural and topological diversity have been made by virtue of the flexibility with which the metals and links can be varied.1,2 In the ZIF family, ZIF-8 [Zn(MeIm)2, MeIm = 2-methylimidazolate] has been widely studied due to its tunable pore size, chemical stability and thermal robustness, which make it a promising candidate for gas storage,3 molecular separation,4 catalysis5,6 and so on. The topology of ZIF-8 corresponds to the zeolite sodalite, which can be described as a space-filling packing of truncated octahedrons.7 In particular, it crystallizes in a cubic lattice (space group Ia3d) that contains cavities with a diameter of 11.6 Å connected via 6-ring apertures with a 3.5 Å window and 4-ring apertures (see Fig. 1).

In contrast to the extensive studies under ambient conditions and at different temperatures,7 ZIF-8 has only been studied under pressure in a very limited range.8–11 It is well known that pressure can influence the structures, physical and chemical properties and performance of nanoporous materials.12 Therefore, pressure provides a new approach to achieve structural modification which includes changes in pore size, opening and geometry, channel shape and internal surface area. Subsequently, these pressure-induced changes will affect the sorption selectivity, capacity and access to the binding sites of the porous materials.

Indeed, pressure has been used to tune the sorption properties of ZIF-8. For instance, Moggach et al. reported that ZIF-8 undergoes a reversible crystalline-to-crystalline phase transition at around 1.5 GPa in some pressure transmitting medium (PTM).11 The interaction between the PTM and ZIF-8 nanopore was believed to play an important role in the phase transition. This study demonstrated that pressure could be used to modify the pore size, shape and volume, eventually increasing the accessible surface area for gas storage materials. In parallel, Chapman et al. showed that compression of ZIF-8 at very low pressures (e.g., 0.34 GPa) resulted in an irreversible structural transition and amorphization upon recovery to ambient pressure.9 The amorphization behavior was found to be independent of whether a PTM was used or not. These different results not only involve guest–host interactions, but may be due to the intrinsic detailed intra-molecular chemical responses of ZIF-8 to compression. While X-ray diffraction provides information about structural evolution of the crystal lattice, vibrational spectroscopy allows the understanding of pressure effects on chemical bonding and especially local structures. Here we report the first in situ infrared (IR) absorption spectroscopic study of ZIF-8 under high pressures.

The ZIF-8 sample was synthesized according to the literature.13 Its identity and purity were checked by XRD, SEM and BET. A diamond anvil cell (DAC) equipped with type II diamonds with culet sizes of 400 and 600 μm was used to generate high pressures. The pure desolvated samples were loaded into the DAC without KBr or any other fluid PTM to rule out the possible guest–host interactions. The samples were 150–200 μm in diameter and ~30 μm thick. A few Rudy chips were inserted as the pressure calibrant. A customized IR micro-spectroscopy system with details described previously14 was used for all IR absorption measurements. Multiple runs were carried out for reproducibility and all measurements were performed under room temperature. During both compression...

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Fig. 1 Crystal structure of ZIF-8 viewed along the c-axis. The pink polyhedrons denote the ZnN₄ units, while the green and blue balls represent C and N atoms respectively. The yellow sphere indicates the space in the cage. Hydrogen atoms are omitted for clarity.
and decompression and in between runs, sufficiently long time was allowed for equilibrium to rule out any kinetic effect and no time dependent behavior was observed.

Fig. 2(a) shows the selected IR spectra of ZIF-8 on compression to 39.15 GPa and then decompression to ambient pressure. As a starting point, our ambient pressure IR measurement is in excellent agreement with that reported by Ordonez et al.\textsuperscript{15} The complete assignment of the observed IR bands is difficult due to the complex nature of the ZIF-8 framework. However, most of the absorption bands are associated with the vibrations of the imidazole units and thus can be described based on the origin of the bonds. For example, the bands at 3135 and 2929 cm\textsuperscript{-1} are attributed to the aromatic and the aliphatic C–H stretch of the imidazole, respectively. The peak at 1584 cm\textsuperscript{-1} can be assigned as the C–N stretch mode specifically,\textsuperscript{15} whereas the intense and convoluted bands at 1350–1500 cm\textsuperscript{-1} are associated with the entire ring stretching. The bands in the spectral region of 900–1350 cm\textsuperscript{-1} are for the in-plane bending of the ring while those below 800 cm\textsuperscript{-1} are assigned as out-of-plane bending. Due to the limitation of our IR apparatus (i.e., for mid-IR measurements only), the most interesting Zn–N stretch mode which is expected at 421 cm\textsuperscript{-1} was not observed.

Upon compression to 1.24 GPa, most of the IR absorption bands exhibited significant changes. For example, the aromatic C–H stretch mode at 3135 cm\textsuperscript{-1}, the C–N stretch mode at 1584 cm\textsuperscript{-1}, and an out-of-plane bending mode at 760 cm\textsuperscript{-1} were all broadened and split. Band splitting typically suggests enhanced intermolecular interactions, in this case, the ring–ring interaction of the ZIF-8 framework within the unit cell. Other changes include the significant enhancement of one of the ring stretch modes at 1420 cm\textsuperscript{-1} and the appearance of a new IR band at 1031 cm\textsuperscript{-1}. Further compression resulted in continuous broadening accompanied by mode merging. At the highest pressure of 39.15 GPa, the IR profile can be characterized by an extremely broadened pattern, indicating the transformation to disordered or amorphous structure, in accord with Chapman et al.’s observation above 0.3 GPa.\textsuperscript{9} Then the IR spectra of ZIF-8 were collected upon decompression all the way back to ambient pressure. The pressure evolutions were observed in the reverse sequence as expected. Upon complete decompression, however, the spectrum of the recovered sample only resembles that at around 4 GPa instead of the initial ambient-pressure spectrum before compression especially in the ring stretch region as well the C–N and the C–H stretch regions, indicating that the framework has been partially modified. Nonetheless, all other major IR bands of the recovered sample are still characteristic of the imidazole ring, indicating that the entire ZIF-8 framework has survived a compression pressure of 39.15 GPa without a permanent breakdown although the local structures might have been modified.

We then focused on a lower and narrower pressure region where the modification might be completely reversible. Fig. 2(b) shows the selected IR spectra of ZIF-8 on compression to a highest pressure of 1.60 GPa followed by decompression. In this pressure range, although pressure-induced band broadening was also observed, there was no significant change of the entire
IR profile in general, except that an out-of-plane bending mode (band 3) exhibited a splitting at 0.1 GPa. The recovered material exhibited a very similar profile to, but not exactly the same as the original sample, in strong contrast to that compressed to 39.15 GPa. In particular, the C=\(N\) stretch mode and both the aromatic and the aliphatic C–H stretch modes were clearly recovered. These observations suggest that the structural modifications of ZIF-8 were mostly reversible in the lower pressure region in which the crystallinity and framework structure are highly preserved, consistent with the structure and reversibility of the phase below 1.47 GPa reported by Moggach et al.\(^\text{11}\) using X-ray methods.

The above two runs established that different highest compression pressures resulted in different reversibilities. Thus we monitored the pressure dependence of IR modes of ZIF-8 in the respective two compression regions, i.e., 0–1.6 GPa and 2–14 GPa, as shown in Fig. 3. The pressure coefficients were analyzed by least-square fitting of the experimental data and are reported in Table S1 (ESI\(^\text{2}\)). In general, the pressure coefficient is typically extremely small in magnitude (\(\text{i.e.,} <5 \text{ cm}^{-1}/\text{GPa}\)), indicating that the bond strength is not very sensitive to compression in a broad pressure region. In the pressure region of \(>2 \text{ GPa}\), the IR modes exhibited regular pressure-induced blue shifts, consistent with that the bonds become stiffened upon compression. In contrast, some of the IR modes (e.g., bands 4, 5, 6 and 9) exhibited a significant red shift in the pressure region below 1.6 GPa. The soft behavior (\(\text{i.e.,} \) negative pressure coefficients) is typically associated with bond weakening processes that may ultimately lead to a phase transition. The largest negative pressure dependence of the C=\(N\) stretching mode as well as other soft in-plane ring bending modes most likely originates from the weakening of the \(\pi\) bonds, resulting from a slight ring distortion.

Finally, when combined with previous X-ray studies of high-pressure behavior, our results provide interesting implications about the stabilities of ZIF-8 and thus its potential applications. First of all, all the high-pressure studies so far suggest that the lattice stabilities were greatly reduced without a penetrating PTM. However, the chemical stability probed by the current IR study seems independent of the crystalline state and especially the surprising chemical stability probed by in situ IR spectroscopy provide new insight into the storage applications of ZIF-8.

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Notes and references