

Evidence of Pressure Enhanced CO₂ Storage in ZIF-8 Probed by FTIR Spectroscopy

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S Supporting Information

ABSTRACT: Due to the large porosity and unique framework stability, ZIF-8, a representative zeolitic imidazolate based member of metal–organic framework (MOF) family exhibited excellent adsorption capacities for a wide range of gases, including greenhouse gases. Using in situ FTIR spectroscopy, ZIF-8 framework was investigated when loaded with CO₂ in a diamond anvil cell at high pressures far beyond the conventional gas adsorption pressure. The IR profile of CO₂ as well as the ZIF-8 shows direct evidence of the interactions between CO₂ and ZIF-8, indicating enhanced storage of CO₂ in the framework. In addition, the storage behavior was found to be strongly pressure dependent, and the interaction mechanism was explored. These findings demonstrated great potential in the greenhouse gases storage applications using MOF based materials.

Zeolitic imidazolate frameworks (ZIFs) are an emerging class of metal–organic framework (MOF) materials that could serve as an effective platform for the capture and storage of CO₂ due to their ordered structures, high thermal stability, very high porosity, and adjustable chemical functionality.^{1–4} In the large ZIF family, ZIF-8 [Zn(MeIm)₂, MeIm = 2-methylimidazolate] is one of the most studied ZIFs featuring a cubic lattice (space group *I*43m) and sodalite (SOD) topology that contains cavities with a diameter of 11.6 Å connected via 6-ring apertures with a 3.4 Å window and 4-ring apertures.³ Adsorption studies of various gases (e.g., CO₂, CH₄ and N₂) in ZIF-8 have been documented both experimentally and theoretically.^{5–9}

Among these studies, it is suggested that the framework stability and flexibility play an important role in the mechanism and performance of gas adsorptions. Application of high external pressure (e.g., in the gigapascal range) on the framework far beyond the practical gas adsorption pressure (e.g., up to 100 bar) may significantly alter the framework topology and thus the adsorption properties.^{10–14} For instance, Chapman et al.¹⁰ showed that compression of ZIF-8 to 0.34 GPa either in nonpenetrating fluid or without pressure transmitting medium (PTM) resulted in an irreversible structural transition and amorphization. Using in situ high-pressure single crystal X-ray diffraction, however, Moggach et al.¹¹ observed a reversible crystalline-to-crystalline phase transition at around 1.5 GPa in some penetrating PTM. Thus the interaction between the PTM and ZIF-8 framework was

believed to play an important role in the phase transition and have a significant influence on the framework stability. While X-ray diffraction was extensively used in these studies to provide the information about structural evolution of crystal lattice with pressure, vibrational spectroscopy allows the understanding of local structures, chemical bonding, and thus the nature of host–guest interaction between the adsorbed molecules and the framework. Given the facts that kinetic diameter of CO₂ (3.3 Å) is slightly smaller than the size of the hexagonal channels of ZIF-8 (3.4 Å) and that the ZIF-8 framework has relatively high stability, it should be possible to insert more CO₂ into the framework at pressures of gigapascal range to substantially enhance the storage capacity. So far no study has addressed the CO₂ storage capacity and CO₂-ZIF-8 interaction at the above-mentioned pressure range, despite extensive adsorption studies and simulations at lower pressures. Here, using in situ FTIR spectroscopy, we investigate the CO₂ adsorptive performance of ZIF-8 and provide the first evidence of the enhanced CO₂-framework interactions at high external pressures.

The ZIF-8 sample was synthesized according to the literature.¹⁵ A diamond anvil cell (DAC) equipped with type II diamonds with culet sizes of 600 μm was used to generate high pressures. The pure desolvated ZIF-8 powder samples were loaded into the DAC together with solid CO₂ in a cryogenic bath of liquid nitrogen at a temperature below the melting point of dry ice (i.e., < -78 °C) by introducing the pure gaseous CO₂. Then the cell was carefully sealed with minimal possible pressure (e.g., 0.5 GPa) at low temperature before warming up to room temperature. A customized IR microspectroscopic system with details described previously¹⁶ was used for all mid-IR absorption measurements. Far-infrared measurements were performed at the U2A beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). Figure 1b shows the optical image of the loaded sample where transparent areas are mainly solid CO₂ outside the ZIF-8 framework. From top to bottom, representative IR absorption spectra of pure CO₂, ZIF-8 loaded with CO₂ and pure ZIF-8 collected at a similar pressure (~0.8–1 GPa) are shown in Figure 1a. The IR spectrum of pure ZIF-8 is consistent with that previously reported in the literature.¹³ The two strong absorption bands at 671 and 2325 cm⁻¹ in the pure CO₂ spectrum are attributed to the bending mode (ν_2) and asymmetric stretching mode (ν_3), respectively. In addition, two high-frequency bands were observed at around 3600 and

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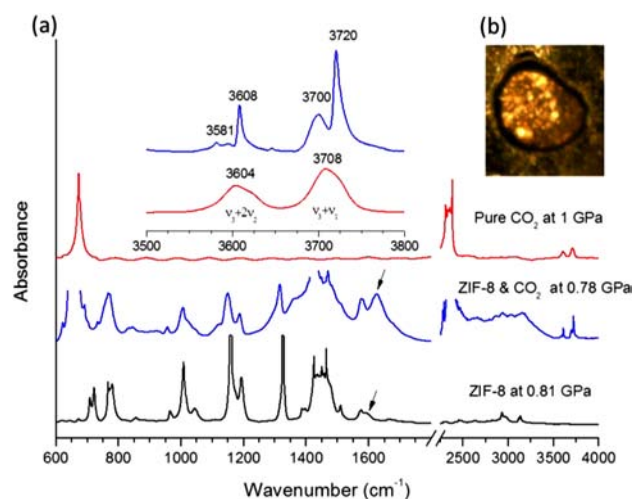


Figure 1. (a) IR spectrum of ZIF-8 loaded with CO₂ (middle) compared with that of pure CO₂ (top) and that of pure ZIF-8 (bottom) at similar pressures. Inset shows the zoomed spectral region for the combination modes of ZIF-8 loaded with CO₂ (top) and pure CO₂ (bottom). (b) Photograph of ZIF-8 loaded with CO₂ taken under an optical microscope. Arrows indicate the positions of the C=C stretching mode of the imidazole ring (see text).

3700 cm⁻¹, which are well understood as the CO₂ combination modes of $\nu_3 + 2\nu_2$ and $\nu_3 + \nu_1$, respectively due to the strong Fermi resonance effect.

The IR spectrum of ZIF-8 loaded with CO₂ not only indicates the successful CO₂ loading but also provides strong evidence for guest–host interactions between ZIF-8 framework and CO₂. First, the IR spectrum exhibits a composite characteristic profile that comprises the contributions from individual pure CO₂ and pure ZIF-8 framework with some modifications (discussed later). Due to the extremely intense IR absorptions of ν_2 and ν_3 modes of CO₂, their behavior is difficult to monitor directly. A previous work demonstrated that the CO₂ overtone/combination bands can be used to follow the insertion of CO₂ into the pores of zeolites.²⁰ In the present case, the most striking observation is the drastically different absorption profile of the overtone/combination bands as shown in Figure 1 inset. Each of these two bands splits into a doublet: the $\nu_3 + \nu_1$ band originally at 3708 cm⁻¹ displays a doublet at 3700 and 3720 cm⁻¹, while the $\nu_3 + 2\nu_2$ band also splits into two peaks. For each doublet, the low-frequency component resembles the original profile of pure CO₂, and slightly lower frequency suggest that the portion of loaded CO₂ with this characteristic is residing outside the framework as the excessive pressure medium. The higher-frequency component can be interpreted as a substantial portion of CO₂ molecules being inserted into the ZIF-8 framework under the current pressure–temperature conditions. The sharper and narrower band shape is due to the fact that an isotropic pore topology provides homogeneous chemical surroundings for CO₂ molecules residing inside the pore, in contrast to those outside the framework as medium. The different pressure dependences (see Table S1) of the two components of the $\nu_3 + \nu_1$ doublet further confirmed that the CO₂ molecules with

different environments give rise to different pressure responses. The overtone of $\nu_3 + \nu_1$ at 3720 cm⁻¹ observed at 0.78 GPa, if extrapolated to ambient pressure, would yield a frequency of 3718 cm⁻¹ (see Table S1), a frequency that is even higher than that in gas phase (i.e., 3714.8 cm⁻¹).²¹ It is well established that upon solidification, all vibrational frequencies of CO₂ exhibit significant red shifts, including this overtone (e.g., at 3709 cm⁻¹ for solid CO₂).¹⁸ In addition, in a previous IR study of CO₂ trapped in solid N₂ matrix, a similar splitting behavior for the $\nu_3 + \nu_1$ combination mode was reported by McCluskey and Zhuravlev.²² These observations provide strong evidence that CO₂ is trapped and constrained in the SOD cages of ZIF-8 crystal lattice experiencing the same highly ordered local environment.

Furthermore, we found that the insertion and extrusion of CO₂ with respect to the framework can be mediated by external pressure. Figure 2 shows the IR absorption spectra of the two

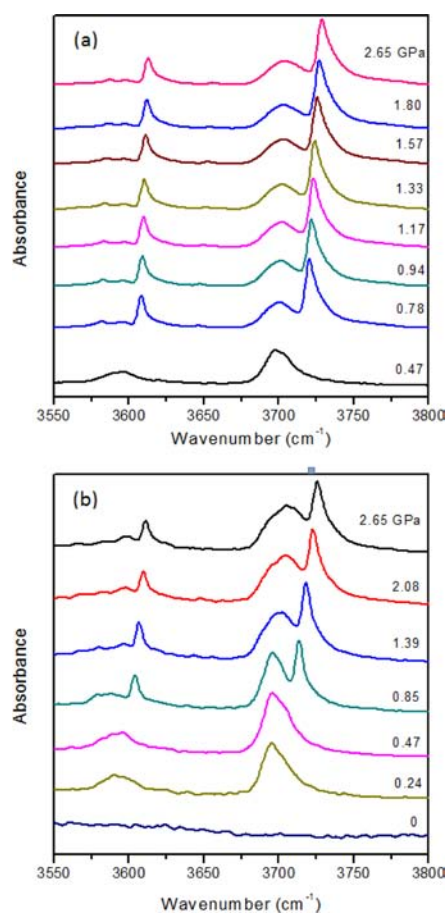


Figure 2. IR spectra of ZIF-8 loaded with CO₂ in the spectral region of the combination modes collected on compression (a) and decompression (b) at room temperature.

combination modes of CO₂ loaded with ZIF-8 upon compression and decompression. When initially loaded at 0.47 GPa, the IR spectrum shows a regular profile of pure CO₂. When compressed to above 0.78 GPa, a new band associated with CO₂ trapped inside the framework was observed. Continuously compressing to higher pressures (e.g., 2.65 GPa or higher) resulted in the blue shift of all modes (Figures 2a and S1). Upon releasing the pressure, the doublet starts to merge into a singlet at 0.47 GPa (Figure 2b), indicating that the

CO₂ molecules migrate out of the framework. When the pressure is completely released, the CO₂ molecules inside the framework have escaped from the cages completely (see the bottom spectrum in Figure 2b). The compression–decompression cycles can be repeated several times reversibly with very little hysteresis, and the splitting always occurs at 0.4–0.8 GPa. In addition, based on the absorption intensity of the two components of the $\nu_3 + \nu_1$ mode, we estimated that up to ~68% of the loaded CO₂ was inserted in the framework upon compression (Figure 2a) and at least 45% CO₂ remains trapped upon decompression to above the extrusion threshold pressure (Figure 2b). These results indicate an interesting reversible, pressure-mediated CO₂ storage behavior in the ZIF-8 framework.

The nature of the interaction between CO₂ and ZIF-8 framework as well as the migration mechanism is of great interest, which may be understood from previous studies. For instance, Lee et al.²³ observed a similar reversible insertion behavior of CO₂ into a small-pore zeolite natrolite under a pressure of 1.5 GPa, which results in the expansion of unit cell volume of the host framework. However, the insertion must be triggered at elevated temperatures, in contrast to the room-temperature behavior of ZIF-8 observed here. The work by Haines et al.²⁴ and Coasne et al.²⁵ showed that at room temperature, CO₂ can be incorporated into the framework of completely siliceous zeolite ZSM-5 (silicalite-1) with a pore size slightly larger than that of natrolite and that the presence of CO₂ in the pore stabilizes the zeolitic framework.²⁴ The pore size of ZIF-8 is in between natrolite and silicalite-1. Other contributing factors that must be considered to fully understand the insertion mechanism of CO₂ into the framework at high pressures include: (1) The pressure for insertion/extrusion of CO₂ with respect to the ZIF-8 framework is relatively low (<0.8 GPa at room temperature) compared to that for natrolite (1.5 GPa at high temperature), suggesting that CO₂ must be in superfluid state for effective diffusion under stressed conditions;²³ and (2) the unique pressure characteristics of ZIF-8 in terms of framework flexibility and pressure-induced enlargement of pore opening and volume play an important role in the facilitation of CO₂ insertion at high pressures. At high pressures, Moggach et al.¹¹ observed a new phase with the same space group symmetry as the ambient ZIF-8 but with a twisted conformation of the imidazolate linkers, resulting in total opening of the six-member ring window. And thus methanol molecules as the PTM can be reversibly inserted into the pores even at 1.5 GPa, leading to the expansion of the unit cell volume as well. Using molecular dynamics simulations, Pantatosaki et al.⁹ investigated the mobility of the imidazolate ligands of ZIF-8 framework together with diffusivity of CO₂ in comparison with experimental data. Their results further confirmed that the flexibility of the imidazolate linkers plays a critical role in the guest transportation dynamics. More recently, the framework flexibility of ZIF-8 was found to facilitate the N₂ adsorption⁷ by adopting the high-pressure structure via the swing effect of the imidazolate linker^{7,8} even though the loading pressure is substantially lower than the gigapascal level. Based on these studies, our IR spectroscopic data consistently suggest that pore opening, framework flexibility, and diffusivity of CO₂ all play an important role in the migration of CO₂ with respect to the ZIF-8 framework.

The interaction between CO₂ and the framework is further evidenced by the different IR features of ZIF-8 loaded with CO₂ compared to that of empty framework (Figure 1a). The

most prominent difference, for example, is the appearance of an intense absorption band at around 1620 cm⁻¹ in the spectrum of the ZIF-8 loaded with CO₂, which can be assigned to the C=C stretching mode of the imidazole ring. The enhancement of this mode, which is otherwise lacking in the pure ZIF-8, strongly suggests the interaction between CO₂ and the framework on the specific site of the imidazole ring. The adsorption site of gaseous CO₂ in the ZIF framework has been extensively investigated both by experiments and simulations. Most studies established that preferential adsorption sites are located in specific regions close to the organic imidazolate linkers rather than the zinc atoms.^{6,9,26} Thus our spectroscopic observations are consistent with previous interpretations that the major interaction sites of ZIF-8 framework for CO₂ are the organic linkers. In situ X-ray diffraction measurements at high pressure on the ZIF-8 and CO₂ system would be helpful to elucidate the exact interaction mechanism between CO₂ and the framework.

Being guest molecules, CO₂ can, in turn, influence the stability of ZIF-8 under high pressure substantially. Using synchrotron far-IR spectroscopy, the structural stability of the empty ZIF-8 framework was examined in the lattice region (Figure S2). Pressure-induced distortion of [ZnN₄] tetrahedral as well as irreversible amorphization was observed as evidenced by the splitting and broadening of the Zn–N stretching and bending modes and the depletion of the lattice modes. In addition, our previous mid-IR measurements on empty ZIF-8 framework showed that the C=N stretching mode at 1584 cm⁻¹ was very sensitive to compression, first by exhibiting a significant red shift in the pressure region below 1.6 GPa¹³ and subsequently being weakened at higher pressures, indicating the distortion of imidazolate ring. When ZIF-8 and CO₂ mixture was compressed to higher pressures (e.g., 2.65 GPa, Figure S3), however, no obvious change in the IR bands of the framework was observed (see Figure S4 and Table S2), in strong contrast to the pressure behavior of the pure empty ZIF-8 framework (Figure S3). Furthermore, the near zero pressure dependence of the C=N mode (see Table S2) was observed for the ZIF-8 loaded with CO₂, and its constant IR intensity (Figure S3) indicates that when CO₂ is inserted into the framework, the imidazolate rings are much less distorted, and thus the rigidity of the entire framework is substantially enhanced. Overall, the chemical and mechanical robustness of the framework formed by the relatively stiffer metal centered tetrahedrons as joints but with flexible linkers makes ZIF-8 an interesting and promising agent for the storage of CO₂ (and perhaps other gases) at high-pressure conditions.

In summary, we demonstrated that CO₂ can be inserted into the ZIF-8 framework at high pressures around 0.8 GPa as observed using in situ FTIR spectroscopy. Two types of CO₂ molecules (inside the framework and outside as bulk medium) can be differentiated by the combination IR bands of CO₂ unambiguously. Pressure can play a regulating role in the insertion and extrusion of CO₂ with respect to the framework, even at room temperature. The strong interactions between CO₂ and framework are apparent from the IR features of the framework in the C=C stretching region, providing consistent information about the possible interaction site. As guest molecules, CO₂ can substantially influence the structural stability of the ZIF-8 framework. The enhanced CO₂ storage capacity of ZIF-8 at high pressure provides new insight into the gas capture and storage applications of ZIFs.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures and data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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