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Amorphization of metal-organic framework MOF-5 at unusually low applied pressure

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So far, amorphization of solid materials at ambient temperature required a high pressure (several gigapascal). This raises an important question: is it possible to induce amorphization of solid materials by a low pressure at ambient temperature? Herein, our x-ray diffraction measurements demonstrated that $Zn_4O(BDC)_3$ metal-organic framework (MOF-5) can be irreversibly amorphized at ambient temperature by employing a low compressing pressure of 3.5 MPa, which is 100 times lower than that required for amorphization of other solids. This was further supported by the collapse of pores. Furthermore, the Raman spectra indicated that the irreversible pressure-induced amorphization (PIA) was due to the destroying of some carboxylate groups. One can conclude that the availability of thousands of MOFs can allow ones to reveal relationships between structures and PIA at a low pressure.

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I. INTRODUCTION

Identifying structural relationships between crystalline and noncrystalline states is of fundamental interest in materials research. Pressure-induced transitions from crystalline to noncrystalline have been the focus of intense study,[1–9] particularly since the discovery of amorphization of H_2O ice under ultrahigh pressure.[2] Furthermore, recently, the pressure-induced amorphization (PIA) of zeolites at ambient temperature attracted special attention.[8,9] Zeolites are crystal frameworks (forming micropores) with a general formula $A^{n+}_{x/n}Al_xSi_{1-x}O_2$, where A is a charge-compensating cation. Such a framework crystal structure should be much more sensitive to pressure than the dense crystal structure of solid materials. However, amorphization of framework-structured zeolites at ambient temperature still requires an ultrahigh pressure of several gigapascal (GPa).[8–12] Along with the progress of inorganic porous solids, the innovation for the synthesis of hybrid porous materials emerged at the beginning of the 1990s with the self-assembly of inorganic metal cations with organic linkers to form a network in the appropriate topology.[13–22] Such metal-organic frameworks (MOF) are attracting much attention due to their unusual structures and properties as well as their potential applications.[17–22] Clearly the microporous crystal structure of MOFs would provide a unique opportunity for us to explore the possibility of pressure-induced amorphization at ambient temperature. Furthermore, pressure-induced changes in crystalline structures of MOFs should strongly affect their properties, such as sorption sites. Several groups revealed the deformation of the hybrid network in response to the inclusion of guest molecules in the network cavities.[23–27] Furthermore, Chapman *et al.*[28] observed an irreversible structural transition and amorphization of $Zn(2\text{-methylimidazole})_2$ (ZIF-8) at pressurization beyond 0.34 GPa.

MOF-5, which was invented by Yaghi and co-workers[17] in 1999, has become one of most promising MOFs with numerous unique properties, such as high capacity for hydrogen storage.[21] In this paper, we report that a very low compression pressure of 3.5 MPa can induce an irreversible amorphization of MOF-5 at ambient temperature. This pressure is 100 times lower than that employed for the amorphization of other solid materials at ambient temperature.

II. EXPERIMENTAL

A. Samples preparation

MOF-5 was synthesized via the approach developed by Yaghi and co-workers,[29] and briefly described as follows: $Zn(NO_3)_2 \cdot 6H_2O$ (0.45 g, 1.5 mmol) and 1,4-benzenedicarboxylic acid (0.083 g, 0.5 mmol) were dissolved in a solution (consisting of 49 ml of dimethylformamide (DMF) and 1 ml H_2O) in a 100 ml Pyrex media bottle with a Teflon lined lid. The obtained mixture was heated in an oven at 100 °C for 7 h to yield large cube-shaped crystals. The reaction vessel was then removed from the oven and allowed to cool to room temperature and transferred to a nitrogen-filled glove bag. All subsequent manipulations were preformed in the glove bag under a nitrogen atmosphere using oven-dried glassware and anhydrous solvents. The solvent was decanted and the remained solid was washed six times with 50 ml of anhydrous DMF (each time letting the solid soak in DMF for 8 h). Then, the DMF was decanted and the remained solid was washed six times with 50 ml of anhydrous CH_2Cl_2 (again each time letting the solid soak in CH_2Cl_2 for 8 h). Finally, after the solvent was decanted, the included CH_2Cl_2 was removed at 115 °C under vacuum for 24 h to yield $Zn_4O(BDC)_3$ as colorless cube-shaped crystals.

B. Characterization

Compressing treatments. The synthesized MOF-5 sample was subjected to compressing treatments for 30 min with various pressures at room temperature by using DAKE pressure machine equipped with a round anvil press, namely, the sample was located in a cylinder-shape hole (diameter of 1 inch) and the pressurization was carried out by pushing a punch rod (the same diameter as the hole) into the hole.

Powder x-ray diffraction (XRD). X-ray diffraction data was taken at 1 atm and room temperature by using Scintag

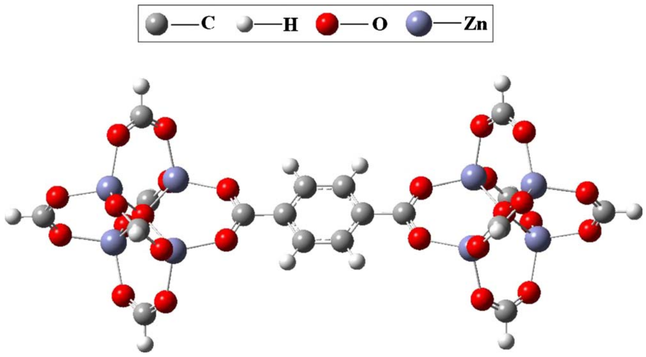

FIG. 1. (Color online) Calculation model for MOF-5.

XDS2000 powder diffractometer at 45 kV and 35 mA for Cu $K\alpha$ ($\lambda = 1.5406$ Å) radiation, with a scan speed of $1°/\text{min}$ and a step size of 0.03° in 2θ.

Surface area measurement. Surface areas were measured with a Micromeritics ASAP 2000 sorptometer using nitrogen adsorption at liquid-nitrogen temperature (77 K). Before nitrogen adsorption measurement, the sample was degassed *in situ* at 110 °C for 12 h to remove any guest molecule from the sample.

Raman spectra. Raman spectra were obtained using an Olympus BX41 spectrometer and helium-neon laser (632.8 nm) was used to excite the samples.

Thermal gravimetric analysis (TGA). TGA was carried out for MOF-5 samples in nitrogen atmosphere (100 mL/min) at a constant rate of 10 °C/min by using SDT Q600 equipment.

III. CALCULATION DETAIL

The B3LYP, which is a combination of Hartree-Fock (HF) with a density-functional theory (DFT) based on Becke's three-parameter exchange coupled with the Lee-Yang-Parr (LYP) correlation potential,[30] is one of the most popular hybrid density-functional theory methods.[31–33] In this work, the B3LYP hybrid DFT method with orbital basis set 6-31G(d) was selected for full geometry optimization and prediction of the harmonic vibrational frequencies. The model of MOF-5 for the calculation consists of two Zn_4O clusters and one benzene-1,4-dicarboxylate (BDC) group (Fig. 1). All calculations were carried out with the GAUSSIAN 03 program.[34] Furthermore, the vibrational modes were assigned by means of visual inspection using the GAUSSVIEW program.

IV. RESULTS AND DISCUSSION

MOF-5 has a crystal structure, in which inorganic $[Zn_4O]^{6+}$ clusters are joined to an octahedral array of BDC groups to form a porous cubic $Zn_4O(BDC)_3$ framework with 12.94 Å distance between the centers of adjacent clusters [Fig. 2(a)].

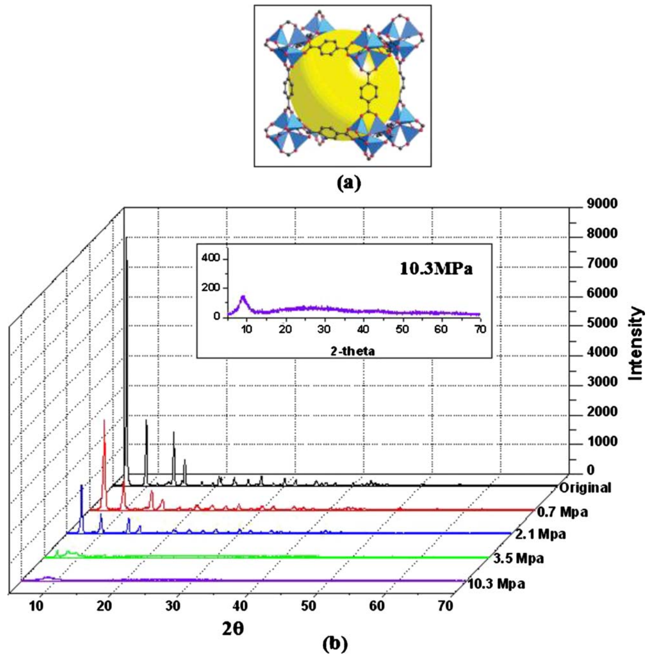

FIG. 2. (Color online) (a) Cubic crystalline MOF-5 and (b) XRD patterns of MOF-5 subjected to compressing treatments at room temperature with various pressures from 0.0 to 10.3 MPa (the original sample is MOF-5 without the treatment).

To examine the change in crystal structures due to the compressing treatments, powder XRD measurements were carried out. As shown in Fig. 2(b), one can see that the sample without compressing treatment exhibits a typical cubic crystal structure of MOF-5. However, when the sample was treated by compressing even at 0.7 MPa, the intensities of various diffraction peaks were reduced by 65%. Furthermore, the reduction in the intensity of diffraction peaks was enhanced with increasing pressure. When the pressure was increased to 3.5 MPa, the broad diffuse peaks dominate the pattern and the sample converges on an x-ray amorphous phase. Furthermore, the sample compressed at 10.3 MPa has only one broad peak in the 2θ range of $5°-70°$. This indicates that a low pressure induced the irreversible amorphization of MOF-5. It would be impressive that the pressure employed for the amorphization of MOF-5 is 100 times lower than that (several GPa) required for all other solid materials.

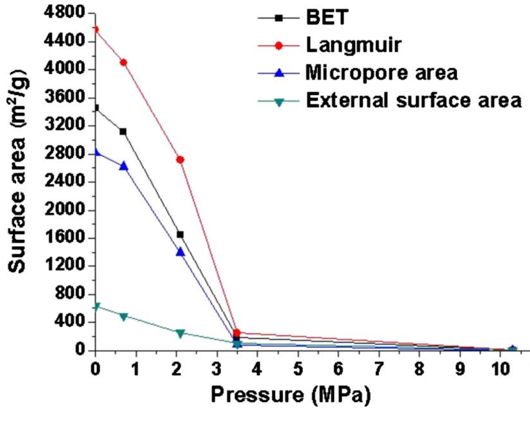

FIG. 3. (Color online) Surface areas of MOF-5 subjected to compressing treatments at room temperature with various pressures from 0.0 to 10.3 MPa (BET and Langmuir surface areas are the surface areas calculated by using BET equation and Langmuir equation, respectively).

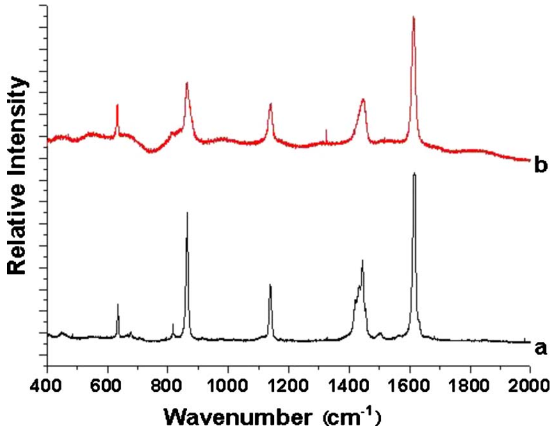

FIG. 4. (Color online) Raman spectra of (a) crystal MOF-5 and (b) amorphous MOF-5 formed via compression at 10.3 MPa at room temperature.

This demonstrates the possibility of low-pressure-induced amorphization of solid materials at ambient temperature.

It was theoretically predicted that the pressure-induced amorphizations of solid materials (such as α quartz and α berlinite) would be the result of a first-order transition associated with localized structural distortions, which become unstable upon compression.[4,35–38] In such a transition, domain nucleation would overwhelm growth and thus destroy the long-range order.[39] If the amorphization does not involve any bond breaking, the pressure-induced amorphization transition can be reversible.[39] In other words, the irreversible amorphization of MOF-5 implies that the original-crystalline topology was changed with some bond breaking.

The surface areas of the MOF-5 samples with and without compressing treatments were measured by using nitrogen adsorption at 77 K. The results are shown in Fig. 3. One can see that the total surface area and micropore surface area of MOF-5 extremely decreased with increasing pressure of compressing treatments. The crystal MOF-5 without compressing treatment has a large surface area (Langmuir: 4567 m^2/g, Brunauer-Emmett-Teller (BET): 3450 m^2/g, and micropore: 2816 m^2/g), whereas the MOF-5 sample amorphized due to the compressing treatment has a very small surface area (about 6 m^2/g). This indicates that the amorphization is associated with the collapse of pores. The changes in surface areas were consistent with the results of x-ray diffraction, which further confirms the irreversible low-pressure-induced amorphization of MOF-5.

We observed five strong Raman bands at 635, 864, 1139, 1433, and 1615 cm^{-1} for crystal MOF-5, respectively (Fig. 4). This is consistent with results reported by Bordiga *et al.*[40] Furthermore, one can see that amorphous MOF-5 has almost the same positions of the five strong Raman bands as the crystal one. However, relative intensities of those bands are different for the crystal and the amorphous MOF-5 samples, which can allow us to find some structure change due to PIA. To assign those five strong bands to their corresponding vibration modes, we performed the B3LYP/6-31G(d) DFT quantum calculations for MOF-5. Furthermore, the vibrational modes were assigned by means of visual inspection using the GAUSSVIEW program. The vibrational modes associated with the hydrogen atoms used to saturate carbons of carboxylate groups should not be taken into account. The vibrations corresponding to five strong bands with a full assignment are listed in Table I. One can see that the simulated strong bands are in very good agreement of experimental results. We are interested in two strong bands: the band at 1615 cm^{-1} associated with vibration stretching mode of organic benzene ring and the band at 1433 cm^{-1} associated with a complex stretching mode of carboxylate group. The ratio of band intensity at 1433 cm^{-1} to that at 1615 cm^{-1} decreased from 0.47 to 0.34 after the amorphization. This indicates that some carboxylate groups were destroyed by PIA, which might be the main reason why the amorphization is irreversible. It is worth noting that, although Raman spectra have widely been used to examine the change in a crystal solid into its amorphous form, it is not applicable to MOF-5 metal-organic framework. This is because MOF-5 Raman spectra can be simulated by using its basic structure (connection between two Zn_4O clusters and one benzene-1,4-dicarboxylate group), indicating that Raman of MOF-5 is only due to its basic structure. In other words, whether this basic structure is in crystal or amorphous form, it should provide the same Raman spectrum.

The thermal stability of amorphous MOF-5 was compared with crystal one by TGA. As shown in Fig. 5, one can see a

TABLE I. Raman bands of MOF-5 from both experimental measurements and B3LYP/6-31G (d) DFT calculations.

Experimental results				DFT calculations		
Crystal MOF-5		Amorphous MOF-5[a]		Modeling MOF-5		
Freq. (cm^{-1})	Intensity (relative)	Freq. (cm^{-1})	Intensity (relative)	Freq. (cm^{-1})	Intensity (relative)	Assignments
635	0.20	633	0.24	622	0.01	Organic benzene ring bending in plane
846	0.76	864	0.48	840	0.10	Organic benzene ring stretching+OCO bending of carboxylate group in plane
1139	0.34	1141	0.32	1127	0.11	Organic benzene ring breathing
1433	0.47	1445	0.34	1417	0.70	C—C stretching between organic benzene ring and carboxylate group+C═O stretching of carboxylate group
1615	1.00	1613	1.00	1603	1.00	Organic benzene ring stretching

[a] MOF-5 was amorphized by compressing treatment with a pressure of 10.3 MPa at room temperature.

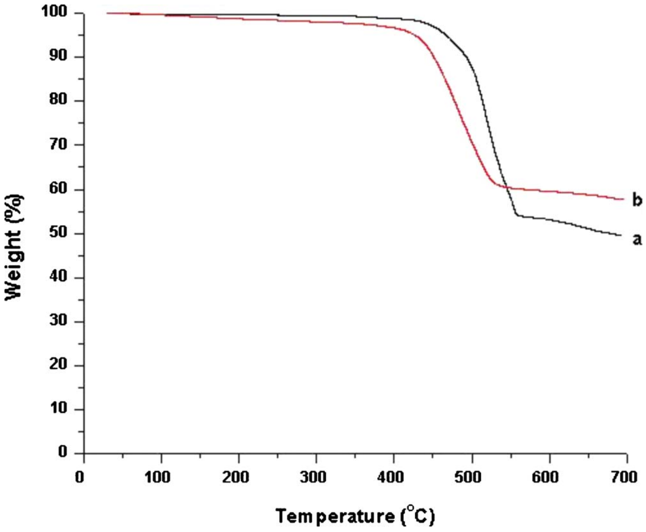

FIG. 5. (Color online) TGA curves of (a) crystal MOF-5 and (b) amorphous MOF-5 formed via compressing treatment at room temperature with a pressure of 10.3 MPa.

fast process with 45.5% weight loss in the temperature range of 400–550 °C for the crystal MOF-5, which corresponds to its structure decomposition. Furthermore, the weight loss process of amorphous MOF-5 is even faster than that of the crystal one in the temperature range of 400–530 °C. However, the weight loss (39%) from the amorphous MOF-5 is less than that (45.5%) from crystal one. Those results indicate that the amorphization changed the thermal stability of MOF-5.

It is well known that a very high pressure (GPa level) is required to induce the amorphization of an inorganic crystal solid even for porous crystal zeolites.[8–12] So far, ZIF-8 is only one metal-organic framework that was evaluated for pressure-induced amorphization. Although the pressure (0.34 GPa) required for its amorphization is lower than that for a zeolite,[28] it is 100 times higher than 3.5 MPa required for the amorphization of MOF-5. This indicates that structure of MOF-5 is much easier to be changed than ZIF-8, which is consistent with their thermal stabilities. The temperature for thermal decomposition of ZIF-8 was higher than that of MOF-5.[41] This happened because they have different structures. In ZIF-8, the five-member imidazole ring serves as the bridging unit between Zn^{2+} centers whereas BDC group is the bridge unit between $[Zn_4O]^{6+}$ clusters in MOF-5. As showed by Raman results, a carboxylate group in BDC is easier to be destroyed than a carbon ring. In other words, the existence of carboxylate group in BDC bridge unit is the reason why MOF-5 can be amorphized by a very low pressure.

V. CONCLUSIONS

In conclusion, MOF-5 can be irreversibly amorphized at ambient temperature by employing a low compressing pressure of 3.5 MPa, which is 100 times lower than that required for amorphization of other solids. The irreversible pressure-induced amorphization was due to the destroying of some carboxylate groups. Clearly, the availability of thousands of MOFs can allow ones to reveal relationships between structures and pressure-induced amorphization at a low pressure instead of a high pressure. Furthermore, the amorphous metal organic frameworks may have some physical properties different from crystal metal-organic frameworks.

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