



Phase Transitions in Zeolitic Imidazolate Framework 7: The Importance of Framework Flexibility and Guest-Induced Instability

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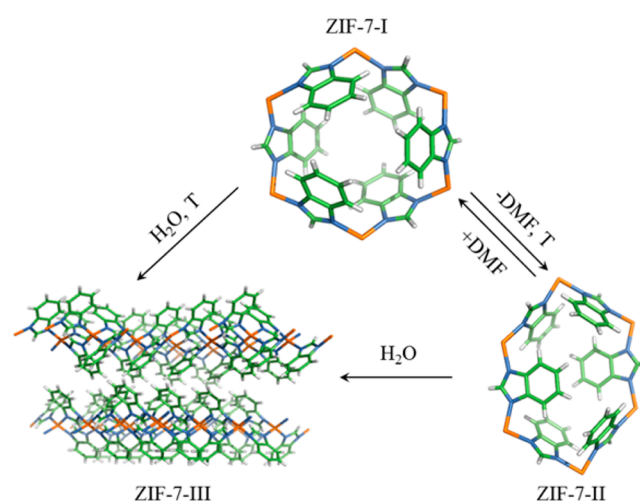
Supporting Information

Zeolite-related materials exhibit a range of novel properties and are of considerable interest for their potential engineering applications. Zeolitic imidazolate frameworks (ZIFs) display zeolite-type structures and are constructed by transitional metals and imidazole molecules.¹ With a wide variety of potential organic ligands, ZIFs present a new family of possible zeolite-related structures with tunable and functionalizable properties. Because of the coordinative metal–imidazolate bonding forming their frameworks, ZIFs are commonly more flexible than their aluminosilicate analogues. They also show unusual gas sorption capacity and related properties. Due to their framework flexibility, ZIFs can undergo structural transformations, e.g., during the sorption process² or under high temperature³ or pressure.⁴ It is of great significance to understand potential structural phase transitions since they strongly affect ZIFs' structurally-related sorption and mechanical properties, which are essential to ZIFs-based technology innovations and industrial applications.

ZIF-7 (Zn(PhIm)₂, PhIm = benzimidazolate) was one of the earliest-reported ZIFs with a prototypical structure related to that of sodalite (SOD topology).¹ In 2011, Aguado et al. compared ZIF-7's X-ray diffraction patterns and CO₂ sorption isotherms.⁵ They describe a reversible narrow-pore (np) to large-pore (lp) phase transition in guest-free ZIF-7 as a function of CO₂ pressure or temperature. Although the results provide a preliminary experimental description of the structural behavior of ZIF-7, the crystal structural details of the proposed "narrow pore" phase were not determined. In this paper, we present a study of the phase transitions in ZIF-7 as a function of guest occupancy and temperature. Our results demonstrate the importance of guest molecules in controlling structural transformations in ZIF-7 (Scheme 1).

ZIF-7 was synthesized based on the procedure given by Gücüyener et al.⁶ Raman spectra of an as-synthesized sample were collected in air between 297 and 421 K. The major contributions of the spectra come from the vibrational modes of the benzimidazolate ligand. Observed frequencies were assigned based on ref 7. Upon heating, most of the Raman bands remain similar and keep the same frequencies until 357 K, indicating that the structure of ZIF-7 seems to be stable in this temperature range. Above 357 K, strong modifications are observed in the regions corresponding to the lattice modes, the torsion modes of the imidazolate ring, and the in-plane bending

Scheme 1. Phase Transitions in ZIF-7



modes of benzimidazolate (Figure 1). These modifications are associated with a common frequency decrease and fwhm

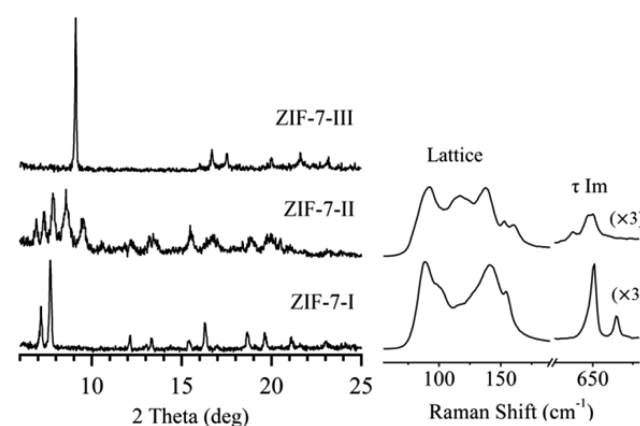


Figure 1. Phase transitions in ZIF-7 observed by X-ray powder diffraction (left) and Raman spectroscopy (right). Upper: ZIF-7-II, lower: ZIF-7-I. τ : torsion vibrational mode. Im: imidazole ring.

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increase with temperature of most of the vibrational modes. Such changes may reflect a structural rearrangement in the ZIF-7 crystal structure, probably with symmetry loss. X-ray powder diffraction studies were then carried out within 300–700 K under a dynamic vacuum of 10^{-1} Pa. Around 350 K, a phase transition was observed and found to be identical to the ZIF-7 lp to np phase transition reported by Aguado et al. (Figure 1). Here, we designate the ZIF-7 structure as the “ZIF-7-I” phase and the structure produced under heating as the “ZIF-7-II” phase. ZIF-7-II is stable up to 700 K and does not revert to ZIF-7-I during cooling. It is stable at room temperature in air for at least two weeks. The formation of ZIF-7-II is attributed to the loss of dimethylformamide (DMF) solvent molecules from the ZIF-7-I framework. This can be confirmed by the differential scanning calorimetry and thermogravimetric analysis traces of ZIF-7-I. The critical temperature of this phase transition depends on the guest-loss rate. The ZIF-7-I to ZIF-7-II phase transition can be reversed by immersing ZIF-7-II in DMF. This reversion is due to guest incorporation; in fact, it can occur very quickly and is dependent upon the guest molecule. For example, as soon as ZIF-7-II powder was soaked with ethanol, the ZIF-7-I structure could be observed by X-ray powder diffraction.

ZIF-7-II was reproduced by heating ZIF-7-I at 400 K in air for 48 h and was then investigated for its crystal structure by laboratory X-ray powder diffraction. Structure solution and refinement were performed from a starting model based on ZIF-7-I in $P1$ symmetry using rigid bodies, combined with energy minimization, to arrive at the final $P\bar{1}$ structure.⁸ X-ray powder diffraction data using synchrotron radiation were collected at beamline I11, Diamond Light Source, UK, to optimize the ZIF-7-II model.⁹ ZIF-7-II retains the same coordination motif of ZIF-7-I and can be regarded as a distorted ZIF-7-I. ZIF-7-I to ZIF-7-II phase transition is mediated by a tilting of the tetrahedral units, which is classic in natural sodalites.¹⁰ The highly-distorted and locally-strained nature of ZIF-7-II leads to its poor crystallinity, reflected by X-ray powder diffraction and scanning electron microscope. The primary guest-hosting cavity in ZIF-7-I is formed by the benzimidazole ligands in a symmetric six-membered ring of Zn atoms.¹¹ Interestingly, the angle between benzimidazole ligands and the Zn ring plane changes from 49° in ZIF-7-I to 29° , 54° , and 63° in ZIF-7-II; it explains the change of the imidazolate ring torsion vibrational modes seen in the Raman spectra. This cavity in ZIF-7-II shows no solvent accessibility.¹² The above observations provide a description of the gate-opening/closing mechanism in ZIF-7-I and ZIF-7-II during guest uptake and unloading.^{11a} Here, we should point out that while the primary guest-hosting cavity decreases in size on the transformation from ZIF-7-I to ZIF-7-II, ZIF-7-II has a larger total volume and void volume than a hypothetical model of guest-free ZIF-7-I (Table 1).¹²

The third phase of ZIF-7, “ZIF-7-III”, was produced by a slurry experiment after leaving ZIF-7-II in water at room temperature for one week. ZIF-7-I can also transform irreversibly to ZIF-7-III on heating to 400 K after DMF is exchanged with water (Figure 1). ZIF-7-III was first discovered by Yang et al. in 2008¹³ and has a (4,4) square planar grid structure formed by quadruply linked corner-shared networks of Zn(II) benzimidazolate tetrahedra. ZIF-7-III is stable in DMF with no transition observed from planar ZIF-7-III back to ZIF-7-I or ZIF-7-II frameworks. It is widely acknowledged that Zn coordinative bonds are unstable with respect to hydrolysis.¹⁴

Table 1. Crystallographic and Pore Information of ZIF-7-I, -II, and -III

	ZIF-7-I	ZIF-7-II	ZIF-7-III
formula	Zn(PhIm) ₂	Zn ₉ (PhIm) ₁₈	Zn ₄ (PhIm) ₁₆
crystal system	rhombohedral	triclinic	monoclinic
space group	$R\bar{3}$	$P\bar{1}$	$C2/c$
<i>a</i> [Å]	22.989(3)	23.948(6)	16.106(3)
<i>b</i> [Å]	22.989(3)	21.354(6)	19.511(4)
<i>c</i> [Å]	15.763(3)	16.349(4)	16.126(3)
α [deg]	90	90.28(2)	90
β [deg]	90	93.28(2)	90
γ [deg]	120.00	108.41(1)	96.37(3)
<i>V</i> [Å ³]	7214(2)	7917(3)	5036(1)
density [Mg/m ³]	1.242	1.131	1.581
<i>V</i> (void) [Å ³] ^a	1675 (23.2%)	2289 (28.9%)	0

^aVoid analysis was carried out with Mercury 3.1 using a probe radius of 1.2 Å and a grid spacing of 0.7 Å. Guests in ZIF-7-I were removed for calculation.

Thus it seems reasonable that selective hydrolysis of Zn–N bonds in the ZIF-7 3D network structure leads to the formation of a more thermodynamically stable, dense phase, ZIF-7-III. ZIF-7-III is the densest of the three ZIF-7 phases; it has an even greater density than the densest yet reported ZIF, ZIF-zni.¹⁵ The packing density of ZIFs may play an important role in the stability of these materials. ZIF-7-III can be produced from solvothermal¹³ and mechanical synthesis. By adding sodium bicarbonate into the reaction between zinc nitrate hexahydrate and benzimidazole, we provide a quantitative acid–base reaction for the mechanical synthesis of ZIF-7-III: $\text{Zn}(\text{NO}_3)_2 + 2\text{C}_7\text{H}_6\text{N}_2 + 2\text{NaHCO}_3 \Rightarrow \text{ZIF-7-III} + 2\text{NaNO}_3 + 2\text{H}_2\text{O} + 2\text{CO}_2$. Mechanical synthesis or mechanosynthesis is a clean and efficient synthesis technique and has been recently introduced to a variety of chemical synthesis.¹⁶ Using cobalt(II) as the metal source, we also obtained a new dense phase of ZIF-9 (ZIF-9-III) by the same mechanosynthesis method.

In conclusion, this is the first systematic study of guest-induced phase transitions in ZIF-7. For the first time, the structural response of ZIF-7 to guest incorporation is clearly visualized, and the previously unknown ZIF-7-II structure has been solved. This greatly advances our understanding of ZIF-7's remarkable sorption properties. Two new dense phases, ZIF-7-III and ZIF-9-III, have been identified. ZIF-7-III is the densest ZIF yet reported. Incorporating this into ZIF-7's phase transition triangle highlights the importance of guest molecule incorporation on the structural behavior of the ZIF family of materials. The stability of the ZIF-7/9-III is particularly important for applications in extreme environments. A fast and efficient mechanosynthesis route has been presented for nonporous ZIF-7-III and ZIF-9-III. Our future studies will focus on the development and application of this technique for the synthesis of porous ZIF-7 and related phases.

■ ASSOCIATED CONTENT

Supporting Information

Sample synthesis and characterization, analysis details, structure solution and refinement methods, and crystallographic 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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