Crystals as Molecules: Postsynthesis Covalent Functionalization of Zeolitic Imidazolate Frameworks

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The ability to covalently functionalize molecules is a long standing practice in organic chemistry that has led to advances in the synthesis of natural products, pharmaceuticals, and polymers. However, the analogous chemistry of crystalline extended solids remains undeveloped because they generally lose their structural integrity under the reaction conditions required to carry out meaningful organic transformations. Recent reports showed the viability of functionalizing the organic links of porous metal−organic frameworks using mild organic reactions.[1] Here, we extend this strategy to zeolitic imidazolate frameworks (ZIFs), which have unusual thermal and chemical stability, and thus are ideal platforms for performing useful organic transformations under strong reaction conditions.[2] Specifically, the imidazolate-2-carboxyaldehyde (ICA) links, which join tetrahedral zinc(II) centers in a new porous ZIF (vide infra), have been reduced by $NaBH_4$ to the corresponding alcohol derivative, and converted to an imine functionality in refluxing methanol (Scheme 1). Despite these strong reaction conditions, the integrity of the ZIF structure and its crystallinity are maintained throughout the synthesis. The isolated ZIF derivatives indicate that those organic reactions proceeded in high conversions. In essence the success in achieving typical organic reactions in crystals of extended structures like ZIFs makes the idea of using the "crystal as a molecule"[3] a reality and opens many opportunities for employing the arsenal of organic reactions in the covalent functionalization of extended structures.

A new crystalline ZIF structure (termed ZIF-90, Figure 1) was synthesized by heating a solution mixture of H-ICA and $Zn(NO_3)_2 \cdot 4H_2O$ (3:2 mol ratio) in *N,N*-dimethylformamide (DMF) at 100 °C for 18 h. The same material can also be obtained by diffusion of a triethylamine and hexane solution into a DMF mixture of H-ICA and $Zn(NO_3)_2 \cdot 4H_2O$ at 25 °C for 24 h. Elemental analysis performed on guest free ZIF-90 gave the expected formula, $Zn(C_4H_3N_2O)_2$.[4,5]

Crystals of as-synthesized ZIF-90 where examined by single crystal X-ray diffraction (XRD) techniques and the structure was found to be related to the sodalite topology (SiO_2, **sod**, Figure 1A−C) by replacing the Si and O with Zn(II) and ICA links, respectively.[6,7] This leads to an expanded ZIF structure with large voids (Figure 1B) and an extended 3-D ZIF structure with an aperture of 3.5 Å in diameter and a pore size of 11.2 Å (Figure 1C).[8]

To perform the postsynthesis functionalization on crystals of ZIF-90, we first examined its porosity and structural integrity. Solvent guests in the as-synthesized form of ZIF-90 were removed by first immersing the crystals in methanol then evacuating (0.01 Torr) at 25 °C for 24 h. The N_2 adsorption isotherm for the resulting sample measured at 77 K (Figure 2) showed a steep rise in the low-pressure region indicating the permanent porosity of the ZIF-90 framework.
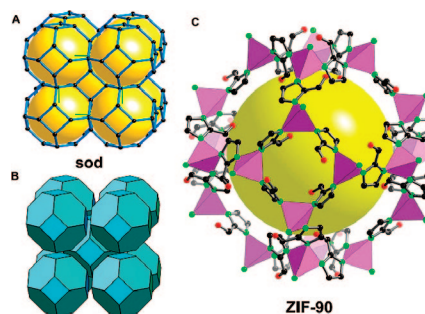

Figure 1. Crystal structure of ZIF-90 presented as (A) a net (blue line and black dot drawing), (B) a tiling to show the subdivision of space (turquoise polyhedra) in the sodalite topology, and (C) a cut away view of one of the ZIF cages with ZnN_4 tetrahedra in pink polyhedra and the ICA links in ball-and-stick representation (C, black; N, green; O, red). The yellow ball represents the largest sphere to fit in the porous cage without contacting the van der Waals spheres of the framework. H atoms have been omitted for clarity.

Scheme 1. Transformation of ZIF-90 (A) by Reduction with $NaBH_4$, and Reaction with Ethanolamine To Give ZIF-91 (B) and ZIF-92 (C)
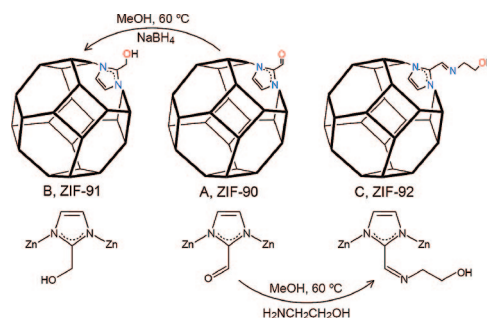

The small step at higher pressure with a hysteresis loop is attributed to a slight constriction of the pores due to the presence of the aldehyde functionality on the ICA links.[5] Nevertheless, this does not prevent access to the pores by N_2 molecules, and thus the calculated Langmuir and BET surface areas from the adsorption data for ZIF-90 were 1320 and 1270 m^2 g^{-1}, respectively.

Thermogravimetric analysis on the evacuated framework of ZIF-90 showed a plateau region of no significant weight loss in the temperature range 300−500 °C. Furthermore, the high chemical stability of ZIF-90 was evidenced by the unaltered powder X-ray diffraction (PXRD) patterns upon boiling the solid in water, toluene, and methanol for 24 h.[5] To ensure that the bulk crystals of ZIF-90 possess aldehyde functionality, the solid state, ^{13}C cross polarization magic angle spinning (CP/MAS) NMR and FTIR spectra were measured. The ^{13}C CP/MAS NMR spectrum showed the expected resonances at 129, 150, and 178 ppm for the symmetrically equivalent 4- and 5-carbon atoms of the imidazolate, the 2-carbon
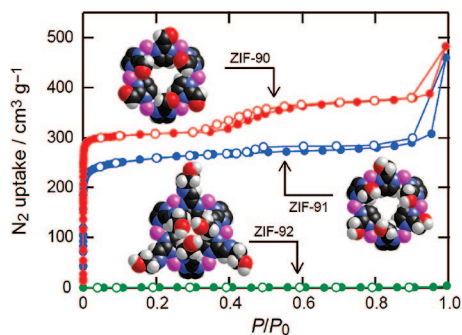
Figure 2. N$_2$ isotherms of ZIF-90 (red), ZIF-91 (blue), and ZIF-92 (green) measured at 77 K. ZIF-90, 91, and 92 pore apertures are shown as space filled representations.
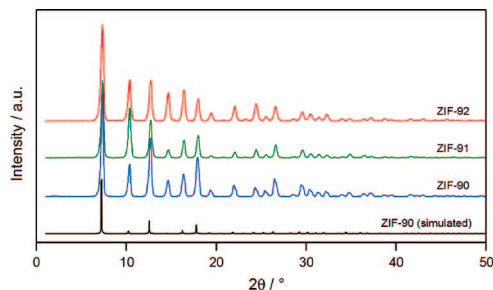
Figure 3. PXRD patterns of simulated ZIF-90 (black), ZIF-90 (blue), ZIF-91 (green), and ZIF-92 (red).

atom of the imidazolate and the aldehyde carbon atom, respectively.[5] A strong band at 1678 cm^{-1} ($\nu_{C=O}$) observed in the FTIR spectrum provided further evidence for the presence of aldehyde in bulk ZIF-90 samples.[5]

Given the permanent porosity of ZIF-90 and its exceptional chemical stability, we sought to carry out useful organic transformations on its evacuated crystalline samples. Specifically, reduction of aldehyde to alcohol functionality was successfully achieved by reacting ZIF-90 with NaBH$_4$ in methanol at 60 °C for 24 h to give ZIF-91 (Scheme 1B). Remarkably, ZIF-91 maintained the high crystallinity of the parent framework (ZIF-90) as confirmed by their coincident PXRD patterns (Figure 3). The presence of the alcohol group in ZIF-91 bulk samples was revealed by ^{13}C CP/MAS NMR spectroscopy. This showed the appearance of four imidazolate carbon atom resonances suggesting that two chemically distinct imidazolate links were present within the framework. Furthermore, the observation of peaks attributable to both aldehyde and alcohol functional groups indicated that reduction was incomplete. To quantify the extent of reduction, a sample of ZIF-91 was digested in 20% DCl/D$_2$O and analyzed by solution ^{1}H NMR. Comparison between the integrated peak intensities of the reduced and unreduced imidazolate species indicated that approximately 80% conversion had been achieved.[5] In addition, confirmation of covalent modification was demonstrated by electrospray ionization mass spectrometry performed on samples of digested ZIF-91. The observation of peaks at 95.2 and 97.3 m/z were consistent with the negative parent ions of the aldehyde and alcohol functionalized imidazole links, respectively.[5] It is worthy to note that porosity of ZIF crystals was maintained throughout the conversion reaction of ZIF-90 to ZIF-91 (surface area of ZIF-91: 1070 and 1010 m^2 g^{-1} for Langmuir and BET surface areas, respectively). The observed slight decrease in surface area may be due to the smaller pore aperture of ZIF-91 relative to that of ZIF-90 (Figure 2).

The chemical versatility of the aldehyde group was highlighted by performing another organic transformation on the ICA link of ZIF-90. Reaction of ZIF-90 with ethanolamine in methanol at 60 °C gave ZIF-92 (Scheme 1C). Quantitative conversion to the imine was completed within three hours as verified by ^{13}C CP/MAS NMR and FTIR. The ^{13}C solid state NMR spectrum of ZIF-92 showed resonances at 154 and 60 ppm for the imine and methylene carbons and resonances at 149 and 128 ppm for the imidazolate carbon atoms. A complete absence of any resonances due to ZIF-90 confirmed the quantitative imine formation of ZIF-92. Additionally, the FTIR spectrum of ZIF-92 was devoid of the $\nu_{C=O}$ stretching frequency at 1678 cm^{-1} and showed the appearance of a peak at 1637 cm^{-1} due to the $\nu_{C=N}$ bond of the imine. As was the case for the conversion of ZIF-90 to ZIF-91, the high crystallinity of the ZIF structure was maintained as evidenced by the PXRD pattern of ZIF-92 (Figure 3). The presence of the imine functionality in ZIF-92 severely constricts the pore aperture and prevents N$_2$ molecules from accessing the interior of the pores, as confirmed by its gas adsorption isotherm behavior (Figure 2).

This report shows that useful organic transformations can be performed on crystalline ZIFs without altering the original structural integrity. The fact that these reactions proceed to high conversions under the same reaction conditions required in solution realizes the idea of "crystals as molecules". Indeed the high porosity and openness of the ZIF structures provide the medium for these reactions and allow for chemical transformations to take place in precise and well-defined spatial arrangements.

Supporting Information Available: Detailed experimental description. This material is available free of charge via the Internet at http://pubs.acs.org.

References

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(3) Expressed by J. Fraser Stoddart in reference to reticular chemistry of MOFs, Reading, U.K. (June 26, 2008).

(4) Elemental analysis. Calcd for C$_8$H$_6$N$_4$O$_2$Zn: C, 37.60; H, 2.37; N, 21.92%. Found: C, 37.63; H, 2.76; N, 20.48%.

(5) See Supporting Information for full experimental details.

(6) Single-crystal XRD for ZIF-90: Zn(C$_4$H$_3$N$_2$O)$_2$, Cubic, $I\bar{4}3m$, $a = 17.2715(4)$ Å, $V = 5152.2(2)$ Å^3, $Z = 12$, F(000) = 1728, $T = 100(2)$ K, crystal size 0.18 × 0.16 × 0.16 mm^3; Cu Kα radiation ($\lambda = 1.5418$ Å). Refinement of 26 parameters and 2 restrains on 317 independent reflections out of 6748 measured reflections ($R_{int} = 0.0297$) led to R1 = 0.1447 [$I > 2\sigma(I)$], wR2 = 0.3474 (all data) and GOF = 1.836; CCDC 693596.

(7) Three letter designations are assigned to net topologies as in the Reticular Chemistry Structure Resource: http://rcsr.anu.edu.au.

(8) The atoms nearest to the center of the cavity are O. A van der Waals radius of 1.52 Å was used for O in determining the appropriate sphere size. All calculations were done using *Cerius^2* software (version 4.2; MatSci; Accelrys, Inc., San Diego) and on the single crystal X-ray structure of ZIF-90 with guests removed and disorder effects averaged.

JA805222X