



Polymorph formation for a zeolitic imidazolate framework composition - Zn (Im)₂

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ABSTRACT

We study the effect of synthesis time and temperature on the crystal formation, morphology and size of zeolitic imidazolate frameworks (ZIFs) with the Zn(Im)₂ composition by using the solution mixing method. The crystal structure, morphology and thermodynamic properties of the ZIFs were characterized by powder X-ray diffraction, scanning electron microscopy and nitrogen sorption isotherms. Our results indicate that the synthesis time significantly influences the structure and topology of crystal products. The crystal structure transforms from ZIF-coi to the progressively denser polymorphs (ZIF-zec, ZIF-nog and ZIF-zni) upon increasing synthesis time from 18 to 120 hours at 10 °C, in accordance with Ostwald's step rule. Increasing synthesis temperature does not change the formation of the ZIF-zec crystals but affects their morphologies and porosities. Both ZIF-nog and ZIF-zec exhibit relatively large surface areas (> 500 m²/g). Furthermore, heating ZIF-nog and ZIF-zec causes recrystallization to ZIF-zni and subsequent melting. Quenching the MOF-liquid results in Zn(Im)₂ glass. This work helps to understand and control the crystal formation of ZIFs, and reveals two new MOF glass formers.

1. Introduction

Zeolite imidazolate frameworks (ZIFs), a subset of metal-organic frameworks (MOFs), have attracted attention owing to their high thermal stability, chemical stability and surface area compared to many of other MOFs [1,2]. Such characteristics have led to potential applications in gas storage [3–6], separation [7–9], catalysis [10,11] and chemical sensing [12–14]. ZIFs have extended three-dimensional structures with tetrahedral topologies, which are built up by metallic nodes (M = e.g. Zn²⁺, Co²⁺, Cu²⁺, Cd²⁺) connected by imidazolate (Im, C₃H₃N₂⁻) linkers [1,15]. Polymorphism in the family has been extensively observed [16], and, like across the MOF family [17], synthetic conditions such as synthesis time, temperature, concentration and pressure are used to control the precise nature of the formed polymorphs [18–20].

For example, it has been observed that the mechanochemical synthesis of ZIF-8 causes amorphization [21], before subsequent recrystallization to dense polymorphs with the *dia* or *kat* topologies [22]. A second *in-situ* study shows that Im or 2-ethylimidazole based ZIFs also undergo polymorphic transitions, and the solvent amount influences the dynamics of the formation of the ZIFs [23]. The crystal size and

morphology of the polymorphs formed are also of great importance, with respect to their proposed applications. For instance, the gate opening pressure in a porous and flexible framework, DUT-8, is significantly influenced by the crystal size [24].

The effect of synthesis conditions on the ZIF structure, however, has not been fully understood. ZIF-4 [Zn(Im)₂], which possesses the same *cag* topology as the mineral variscite CaGa₂O₄, is of current interest due to its structural collapse [25]. In particular, it has been observed to undergo polyamorphization, recrystallization and melting before decomposition upon heating. The glass formed by quenching the ZIF-4 liquid is the first-reported hybrid glass in contrast to the conventional melt-quenched glass families (inorganic, metallic, organic systems) [26,27]. Other [Zn(Im)₂] polymorphs possess different network topologies, such as *cag*, *coi*, *crb*, *dft*, *gis*, *mer*, *nog*, *zec* and *zni* [16], and have been found to display an array of different behaviours on heating [28,29]. Calorimetric and computational studies have ordered these polymorphs in terms of density and enthalpy relative to the *zni* ground state [30–32], though a synthetic study of their formation conditions has, to the best of our knowledge, not yet been attempted.

Accordingly, here we study the influence of the synthesis conditions (time and temperature) on the crystal formation of ZIFs with the Zn

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(Im)₂ composition, by using a solution mixing method. Specifically, we found that at the synthesis temperature of 10 °C, different synthesis times lead to products with different topologies, whereas altering the synthesis temperature from 10 to 35 °C only affects the crystal morphologies and porosities of the products but does not change the crystal identity (ZIF-zec). As part of the study, we obtained two types of ZIFs, namely, ZIF-zec and ZIF-nog, and their glass-forming ability has not been reported. Powder X-ray diffraction and calorimetric results demonstrate that both undergo amorphization and recrystallization to ZIF-zni upon heating, and vitrification upon quenching as in the case of ZIF-4.

2. Experimental procedure

2.1. Synthesis

A solution mixing method was used to synthesize ZIFs with the Zn (Im)₂ composition in the present work [33]. In all synthetic procedures, 1.097 g of zinc(II) acetate dihydrate (Zn(Ac)₂·2H₂O, 5 mmol) was dissolved in 25 mL of n-propylamine, and 681 mg of imidazole (10 mmol) was dissolved in 25 mL of N,N-diethylformamide. The zinc acetate and imidazole solutions were then mixed together with magnetic stirrer (~600 rpm). Details of the synthesis time and temperature of each sample are given in Table 1. Colourless products were washed three times with dichloromethane and then the samples were filtered in vacuum with ceramic filters. The obtained products were dried in fume hood at room temperature (~23 °C) overnight. The yields of product from each synthesis process were calculated according to the molar ratio of zinc, as given in Table 1.

2.2. Characterization

Powder X-ray diffraction (PXRD) measurements of the samples were performed on a PANalytical empyrean X-ray diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation. The PXRD patterns were collected in the 2 θ range of 5–50° with a step size of 0.013°. Thermodynamic properties were determined by differential scanning calorimetry (DSC) and thermogravimetry (TGA) using Netzsch STA 404 C upon heating in argon atmosphere. The upscan rate for all DSC and TGA measurements was 10 K/min. Scanning electron microscopy (SEM) measurements were conducted using Zeiss EVO 60 SEM. For observations, samples were coated with a ~15 nm thick gold layer. Surface area and nitrogen absorption-desorption isotherm measurements were performed using a Micromeritics gas-volumetric apparatus (ASAP 2020) at liquid nitrogen temperature (77 K). Samples were degassed for 4 h at 30 °C and then under vacuum for 12 h at 100 °C before starting the absorption measurements up to a maximum pressure of 1 bar. Densities were determined by using a Micromeritics AccuPyc 1340 helium pycnometer. Liquid-state ¹H nuclear magnetic resonance (NMR) spectra of digested ZIF-nog and ZIF-zec crystals and glasses (DCl/D₂O/DMSO-*d*₆) were recorded on a Bruker DPX600 Advance spectrometer operating at a frequency of 600 MHz. Fourier transform-infrared (FTIR) spectra of the

Table 1
Synthesis conditions, topology, space group, and yield of the product of each process.

Sample No.	Time/hour	Temp/°C	Topology	Space group	Yield/%
S1	0.083	23	amorphous	–	41
S2	18	10	coi + cag	<i>I</i> 4 ₁ + <i>P</i> bca	44
S3	24	10	zec	<i>C</i> 2/ <i>c</i>	50
S4	48	10	nog	<i>P</i> 2 ₁ / <i>n</i>	48
S5	120	10	zni	<i>I</i> 4 ₁ <i>cd</i>	66
S6	24	15	zec	<i>C</i> 2/ <i>c</i>	47
S7	24	23	zec	<i>C</i> 2/ <i>c</i>	50
S8	24	30	zec	<i>C</i> 2/ <i>c</i>	90
S9	24	35	zec	<i>C</i> 2/ <i>c</i>	58

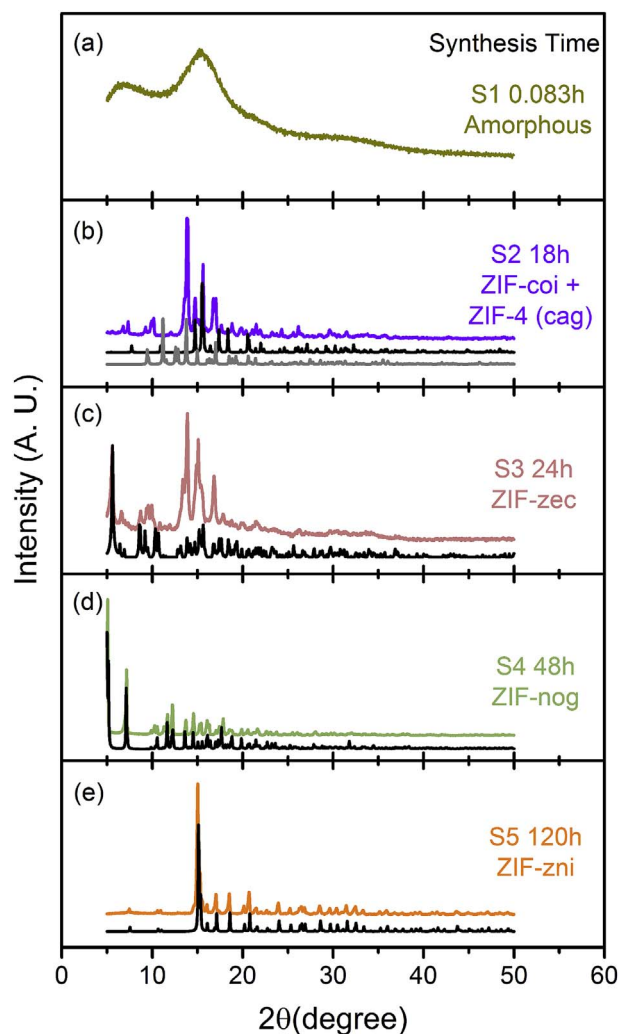


Fig. 1. Experimental and simulated (black) PXRD patterns of the samples S1–S5 obtained after different synthesis time and simulated spectra. Synthesis durations: (a) 0.083 h; (b) 18 h; (c) 24 h; (d) 48 h; and (e) 120 h.

ZIF-nog and ZIF-zec samples were performed on a Varian 640 IR spectrophotometer in transmittance mode with the KBr technique (KBr:sample = 100:1).

3. Results and discussion

3.1. Influence of the synthesis time on the crystal formation

The synthesis of ZIFs [Zn(Im)₂] was conducted by employing synthesis durations from 0.083 to 120 h at 10 °C. The powder X-ray diffraction patterns are presented in Fig. 1, from which the different identities of the products were elucidated. Fig. 1(a) shows a broad hump at ca. 15° on the PXRD pattern, indicating the amorphous feature of S1. This suggests that a synthesis time of 0.083 h is not enough for the nucleation of a crystalline region. In Fig. 1(b)–(e) clear Bragg peaks are observed, demonstrating that the S2–S5 samples have crystalline structures. The crystal identity of each sample is assigned by comparing the experimental spectra with the simulated ones. S2 synthesized for 18 h is therefore assigned as mixed phases of ZIF-4 (cag topology) and ZIF-[Zn(Im)₂]-coi (CCDC code: EQOCOC) [1,33]. With an increase of the synthesis time, the crystal topology transforms to ZIF-[Zn(Im)₂]-zec (HICGEG) and to ZIF-[Zn(Im)₂]-nog (HIFWAV), corresponding to the synthesis durations of 24 and 48 h, respectively [33]. Additionally, liquid-state ¹H NMR spectra also confirm the presence of the imidazole

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