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Ionothermal synthesis of zeolitic imidazolate frameworks and the synthesis dissolution-crystallization mechanism

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ABSTRACT

A cooling-induced crystallization process was used to synthesize **sod** (RCSR symbol)- and **zni** (RCSR symbol)-type zeolitic imidazolate frameworks (ZIFs) ionothermally in 1-ethyl-3-methylimidazolium bromide ionic liquid and a urea-choline chloride deep eutectic solvent. The products were characterized by X-ray diffraction, scanning electron microscopy, nuclear magnetic resonance spectroscopy, infrared spectroscopy and thermal gravimetric analysis. The effect of the synthesis conditions on the crystallinity, size and morphology of the product was studied. The dissolution-crystallization mechanism of ZIFs was discussed. The cooling rate affected the product morphology. When the synthesis solution was cooled by rapid cooling, the shape of the **sod**-type product was spherical and the morphology of the **zni**-type product was rod-like or plate-like. With a programmed cooling, the **sod**-type product was polyhedron in shape and the **zni**-type product was in the form of clusters.

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1. Introduction

Zeolitic imidazolate frameworks (ZIFs) are a new class of metal-organic framework with a zeolite-type topology and structure. They are constructed from a transition metal ion such as Zn or Co bridged by imidazole or imidazole derivatives (*n*-RIm, R: substituents of the imidazole ring; *n*: the position of substituents) [1,2]. ZIFs can be used as a catalyst or catalyst carrier due to their large pore volume, thermal stability and acidity and basicity on the external surface [3–5]. They also have potential applications in gas separation and storage, and as sensors and magnetic materials due to their large specific surface area and good mechanical properties [6–13]. ZIF-8 and ZIF-67 which both feature a **sod** framework structure are archetypal open framework ZIFs consisting of Zn and Co linked

with 2-methylimidazole ($\text{Zn}(2\text{-MIm})_2$ and $\text{Co}(2\text{-MIm})_2$) [6]. Their synthesis method and synthesis mechanism have attracted wide attention since they were first synthesized [14–24]. At present, several synthesis methods for ZIF-8 are available, including liquid phase diffusion synthesis [14], solvothermal synthesis [6,15–20], microwave-assisted ionothermal synthesis [21], mechanochemical synthesis [22] and vapor-assisted conversion synthesis [23,24]. The main synthesis method for ZIF-67 is solvothermal synthesis [25]. In a study on the synthesis mechanism, Venna et al. [17] and Cravillon et al. [18] utilized X-ray diffraction (XRD), transmission electron microscopy (TEM) and *in situ* small-angle and wide-angle X-ray scattering (SAXS/WAXS) to investigate the crystallization mechanism of ZIF-8 synthesized in methanol. The authors proposed that the crystal growth involved the formation of

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amorphous clusters, nucleation, crystallization and growth. The kinetics of the transformation followed Avrami's classical model and the crystallization mechanism followed the solution- and solid-mediated mechanism, which is a classic crystallization mechanism for a zeolite.

zni-type $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ are typical densely structured ZIFs containing Zn and Co linked with imidazole [13,25]. The main synthesis method for $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ is by solvothermal synthesis [12,13,25,26]. Hikov et al. [13] used *in situ* time-resolved static (TR-SLS), *in situ* dynamic light scattering (TR-DLS) and scanning electron microscopy (SEM) characterization to study the crystallization process of $\text{Zn}(\text{Im})_2$ synthesized in methanol, and noted that the crystallization included the formation of metastable primary particles (~100 nm) and a monomer addition process where the primary particles acted as the monomers.

Ionothermal synthesis, utilizing either an ionic liquid (IL) or a deep eutectic solvent (DES) as the medium, is a novel method for the synthesis of crystalline materials [27,28]. Dybtsev et al. [29] and Bu's group [30,31] synthesized a series of MOFs by ionothermal synthesis, including $[\text{Cu}_3(\text{tpt})_4](\text{BF}_4)_3 \cdot (\text{tpt})_{2/3} \cdot 5\text{H}_2\text{O}$ (tpt: 2,4,6-tris(4-pyridyl)-1,3,5-triazine) synthesized in 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquids, $\text{M}_x(\text{bdc})_y$ (M^{3+} : In^{3+} , Y^{3+} , Nd^{3+} , Sm^{3+} and other trivalent metals, bdc:1,4-benzenedicarboxylate) and zinc boron imidazolate frameworks synthesized in a deep eutectic solvent. Recently, we reported an alternative route for the synthesis of ZIF-8 in an urea-choline chloride (urea-ChCl) deep eutectic solvent from which ZIF-8 was precipitated by a cooling-induced crystallization [32]. As an extension of our work, we synthesized ZIF-8, ZIF-67, **zni**-type $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ by ionothermal synthesis in 1-ethyl-3-methylimidazolium bromide ([emim]Br) ionic liquid and an urea-ChCl deep eutectic solvent in the present work. We investigated the synthesis process and discussed the dissolution-crystallization mechanism of ZIF formation in the ionothermal synthesis system.

2. Experimental

2.1. Synthesis of the ionic liquid and deep eutectic solvent

The [emim]Br IL was prepared according to Ref. [33]. An appropriate amount of redistilled *N*-methylimidazole was placed in a flask. Ethyl bromide was added dropwise into the *N*-methylimidazole at a molar ratio of 1.5:1. The mixture was heated to 80 °C and stirred for 8 h. Finally, excess ethyl bromide was removed by rotary evaporation, and the ionic liquid obtained was used. The urea-ChCl deep eutectic solvent was prepared according to the method described in Ref. [34]. Appropriate amounts of urea and choline chloride were mixed homogeneously in a molar ratio of 2:1. The mixture was heated to 80 °C to melt it. The melted mixture served as the deep eutectic solvent used in the present work.

2.2. Synthesis of ZIFs

The synthesis of ZIF-8 in [emim]Br ionic liquid was

performed as follows. 2-methylimidazole, zinc nitrate hexahydrate and the melted [emim]Br ionic liquid were mixed in a beaker in the following proportions: Zn^{2+} :2-MeIm:[emim]Br = 1:8:45. After several minutes of stirring, the mixture was transferred into a 30 ml teflon-lined stainless steel autoclave and heated at the dissolving temperature for several minutes. Then the autoclave was subjected to rapid cooling (ice-water bath) or programmed cooling (0.1 °C/min). ZIF-8 was crystallized from the [emim]Br ionic liquid during cooling. The product was filtered, washed with distilled water and anhydrous ethanol, and dried at 110 °C overnight.

The synthesis of ZIF-67 in [emim]Br ionic liquid as well as **zni**-type $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ in the urea-ChCl deep eutectic solvent was similar to that of ZIF-8 in the ionic liquid. The details of the synthesis conditions are listed in Table 1 and Table 2. The samples synthesized in the ionic liquid were named ILs-Rx and ILs-Px. The samples synthesized in the deep eutectic solvent were denoted as DES-Rx and DES-Px. R and P denote a sample that was obtained by rapid cooling and programmed cooling, respectively, and x indicates the sample number.

2.3. Characterization of the ZIFs

The crystalline phase of the samples was characterized by powder XRD on a PANalytical X' Pert PRO diffractometer fitted with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$) operating at 40 mA and 40 kV. The sample morphology was observed using a Hitachi S4800 field emission SEM. The ^{13}C MAS NMR spectra of the samples were characterized on a Varian Infinityplus-400 nuclear magnetic resonance spectrometer. The sample was also characterized by a Bruker Equinox55 type infrared spectrum apparatus with a KBr sheeting method. The thermal behavior of the samples (2–2.5 mg) was investigated by a Netzsch Sta449F3 TGA instrument under N_2 . The heating rate was 10 °C/min and the temperature range was 30 to 900 °C.

Table 1

Synthesis conditions for the ionothermal synthesis of ZIF-8 and ZIF-67 in [emim]Br.

Sample	M^{2+} :2-MIm:S *	$T/^\circ\text{C}$	Cooling rate ($^\circ\text{C}/\text{min}$)	Product
ILs-R1	1:8:45	140	rapid cooling	ZIF-8
ILs-P1	1:8:45	140	0.1	ZIF-8
ILs-R2	1:10:45	100	rapid cooling	ZIF-67
ILs-P2	1:10:45	100	0.1	ZIF-67

* Molar ratio; M^{2+} : Zn^{2+} or Co^{2+} ; S: solvent, [emim]Br.

Table 2

Synthesis conditions for the ionothermal synthesis of **zni**-type $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ in [emim]Br and urea-ChCl.

Sample	M^{2+} :Im:S *	$T/^\circ\text{C}$	Cooling rate ($^\circ\text{C}/\text{min}$)	Product
ILs-R3	1:8:8:45	120	rapid cooling	$\text{Zn}(\text{Im})_2$
ILs-R4	1:10:45	100	rapid cooling	$\text{Co}(\text{Im})_2$
DES-R3	1:8:88	120	rapid cooling	$\text{Zn}(\text{Im})_2$
DES-P3	1:8:88	120	0.1	$\text{Zn}(\text{Im})_2$
DES-R4	1:10:88	100	rapid cooling	$\text{Co}(\text{Im})_2$
DES-P4	1:10:88	100	0.1	$\text{Co}(\text{Im})_2$

* Molar ratio; M^{2+} : Zn^{2+} or Co^{2+} ; S: solvent, [emim]Br or urea-ChCl.

3. Results and discussion

3.1. Ionothermal synthesis of ZIF-8 and ZIF-67 in [emim]Br

ZIF-8 and ZIF-67 were ionothermally synthesized in the [emim]Br ionic liquid according to the synthesis conditions listed in Table 1. There was no detectable solid product in the synthesis solution which was clear after heating at the dissolving temperature for several minutes. After cooling to room temperature, the synthesis solution became cloudy, and the solid product was obtained. When the solution was cooled by rapid cooling, the product was mixed with the solution in the bulk phase. When programmed cooling was used, the product mainly adhered to the autoclave wall. This phenomenon was similar to that observed in the urea-ChCl deep eutectic solvent [32], indicating that ZIF-8 and ZIF-67 precipitated from the [emim]Br ionic liquid in the cooling step.

Figure 1 shows the XRD patterns of the ZIF-8 and ZIF-67 samples. The XRD patterns of the samples matched well with the patterns simulated from the **sod**-type single crystal data reported in Ref. [6]. This indicated that the samples obtained by rapid or programmed cooling were pure phase **sod**-type ZIFs. Figure 2 exhibits the SEM images of the samples. ZIF-8 and ZIF-67 samples obtained by rapid cooling were aggregate spherical in shape with sizes of 0.5 and 0.35 μm , respectively (Fig. 2(a) and Fig. 2(c)). ZIF-8 and ZIF-67 samples that were cooled by programmed cooling were truncated rhombic dodecahedra in shape with sizes of 50 and 5 μm (Fig. 2(b) and Fig. 2(d)). These results demonstrated that the size and morphology of a programmed cooling sample was larger and more regular than that of a rapid cooling sample. According to the Ref. [6,23], ZIF-67 is isostructural with ZIF-8 and their textural properties are almost the same. Two representative samples, ILs-R1 and ILs-P1, were characterized by nitrogen adsorption. This is shown in Fig. 3. The nitrogen adsorption measurement of ILs-R1 sample gave BET and Langmuir surface areas and a micropore volume of 1428 m^2/g , 1724 m^2/g and 0.617 cm^3/g . The nitrogen adsorption measurement of ILs-P1 sample gave relatively smaller BET and Langmuir surface areas

Fig. 1. XRD patterns of ZIF-8 and ZIF-67 samples ionothermally synthesized in [emim]Br. (1) Simulated pattern; (2) ILs-R1; (3) ILs-P1; (4) ILs-R2; (5) ILs-P2.

Fig. 2. SEM images of ZIF-8 and ZIF-67 samples ionothermally synthesized in [emim]Br. (a) ILs-R1; (b) ILs-P1; (c) ILs-R2; (d) ILs-P2.

and micropore volume (1211 m^2/g , 1583 m^2/g and 0.558 cm^3/g). The differences in the surface area and micropore volume may be due to the small crystallite size and inter-granular pores of the rapid cooling product.

Figure 4 shows the FTIR spectra of 2-methylimidazole and

Fig. 3. N_2 adsorption-desorption isotherms at $-196\text{ }^\circ\text{C}$ for ILs-R1 and ILs-P1.

Fig. 4. FTIR spectra of 2-methylimidazole (1) and ZIF-8 sample (ILs-R1) (2) ionothermally synthesized in [emim]Br.

Fig. 5. ^{13}C NMR spectrum of ZIF-8 sample (ILs-R1) ionothermally synthesized in [emim]Br.

the ZIF-8 sample (ILs-R1). The FTIR spectrum of the ILs-R1 sample indicated the vibrational peaks corresponding to the N-H bond of 2-MIm at 3335–2500 and 1820 cm^{-1} had disappeared. The result indicated that the 2-MIm coordinated to Zn was completely deprotonated. Furthermore, the FTIR spectrum failed to show the vibrational peaks of the [emim]Br ionic liquid. Figure 5 shows the ^{13}C NMR spectrum of ZIF-8 sample (ILs-R1). The peaks at 151.3, 124.3, and 14.0 ppm corresponded to the resonance signals of the C atom of the N-C-N, N-C-C-N, and $-\text{CH}_3$ substituents of 2-MIm, respectively. The spectrum did not display the resonance signal of the C atom of the [emim]Br ionic liquid. Figure 6 exhibits the TG curve of the ZIF-8 sample (ILs-R1). The small weight loss observed up to 270 $^{\circ}\text{C}$ may be due to water. A long plateau from 300 to 550 $^{\circ}\text{C}$ was also observed. The framework structure collapsed at 550 $^{\circ}\text{C}$. These results highlighted the exceptional thermal stability of the ZIF-8 sample synthesized in the ionic liquid. Generally, an ionic liquid act as a template or structure-directing agent (SDA) in ionothermal synthesis [27,28]. However, the TG, FTIR, and ^{13}C NMR results demonstrated that the ionic liquid was not a templates or SDA in the ionothermal synthesis of ZIF-8 but instead provided a novel synthesis environment for ZIF-8, as reported by Lai et al. [15] and Cravillon et al. [35] who synthesized ZIF-8 in water and methanol without adding a template or SDA.

Fig. 6. TG-DTG curve of ZIF-8 sample (IL-R1) ionothermally synthesized in [emim]Br.

3.2. Ionothermal synthesis of **zni**-type $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ in urea-ChCl and [emim]Br

zni-type $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ were ionothermally synthesized in the urea-ChCl deep eutectic solvent and [emim]Br ionic liquid according to the synthesis conditions listed in Table 2. During the synthesis, no solid product precipitated from the synthesis solution after heating at the dissolving temperature for several minutes. When subjected to rapid or programmed cooling, the synthesis solution became cloudy and crystals precipitated. This observation resembled the cooling-induced crystallization process of soluble salts in a solvent [36].

Figure 7 shows the XRD patterns of the $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ samples (ILs-R3, ILs-R4, DES-R3, DES-P3, DES-R4 and DES-P4). The XRD patterns of the samples were in excellent agreement with the samples simulated from the **zni** topology structure data reported in Ref. [25]. The results indicated that the samples produced by rapid or programmed cooling were the single phase **zni**-type $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$. Figure 8 shows SEM images of the $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ samples. The rapid cooling samples (DES-R3, DES-R4, ILs-R3, and ILs-R4) were irregular rod-like with hollow areas and cracks and were 600, 200, 500 and 200 μm , respectively. Moreover, there were some spherical crystallites of 3 μm (Fig. 8(a), Fig. 8(c) and Fig. 8(e)–8(f)). The programmed cooling samples (DES-P3 and DES-P4) were formed of clusters and had a size of 100 and 50 μm , respectively (Fig. 8(b) and Fig. 8(d)). The results indicated that the dimension and morphology of the programmed cooling samples were larger and more regular than the rapid cooling samples. The controlling of the cooling rate to adjust the product morphology and particle size is also widely used in the precipitation of soluble salts [37]. The **zni**-type $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ are dense structure ZIFs, and their Langmuir surface areas were only 0.8 m^2/g .

Figure 9 shows the FTIR spectra of the imidazole and $\text{Zn}(\text{Im})_2$ sample synthesized in the urea-ChCl deep eutectic solvent (DES-R3). The FTIR spectrum of the $\text{Zn}(\text{Im})_2$ sample revealed that the vibrational peaks corresponding to the N-H

Fig. 7. XRD patterns of the $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ samples ionothermally synthesized in [emim]Br and urea-ChCl. (1) Simulated pattern; (2) ILs-R3; (3) ILs-R4; (4) DES-R3; (5) DES-P3; (6) DES-R4; (7) DES-P4.

Fig. 8. SEM images of $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ ionothermally synthesized in $[\text{emim}]\text{Br}$ and urea- ChCl . (a) DES-R3; (b) DES-P3; (c) DES-R4; (d) DES-P4; (e) ILs-R3; (f) ILs-R4.

bond of imidazole at 3335–2500 and 1820 cm^{-1} had disappeared. The result indicated that the imidazole coordinated to Zn was completely deprotonated. In addition, the spectrum did not show the vibrational peaks for the components of the urea- ChCl deep eutectic solvent. Figure 10 shows the TG curve of the $\text{Zn}(\text{Im})_2$ sample synthesized in the urea- ChCl deep eutectic solvent (DES-R3). The thermal gravimetric analysis was performed under a nitrogen atmosphere. The small weight loss that was observed up to 300 °C was attributed to water loss. There was little weight loss between 300 and 600 °C. The framework structure of the sample began to decompose at 630 °C. This analysis confirmed the excellent thermal stability of **zni**-type $\text{Zn}(\text{Im})_2$ synthesized by ionothermal synthesis. The TG and FTIR results demonstrated that the deep eutectic solvent did not act as a template or SDA, but instead it supplied a different synthesis environment for $\text{Zn}(\text{Im})_2$ as compared to solvothermal synthesis.

Fig. 9. FTIR spectra of imidazole (1) and $\text{Zn}(\text{Im})_2$ samples (DES-R3) (2) ionothermally synthesized in urea- ChCl .

3.3. The dissolution-crystallization mechanism of ZIFs in the ionothermal synthesis system

ZIF-8 precipitated from the urea- ChCl deep eutectic solvent by cooling-induced crystallization at the cooling step instead of crystallizing at the dissolving temperature due to its enhanced solubility in DES. Furthermore, the controlling of the cooling rate can change its size and morphology [32]. As mentioned above, the experimental observation of ZIF-8, ZIF-67, $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ precipitating from the ionic liquid and deep eutectic solvent was similar to that of ZIF-8 in the DES. In this section, we specifically investigated the precipitation process of $\text{Zn}(\text{Im})_2$ in the DES.

The crystallinity of the $\text{Zn}(\text{Im})_2$ product was calculated using the intensity of the diffraction peak at 15.07° in the XRD pattern (Fig. 7). Figure 11 shows the curve of crystallinity versus dissolving time. It indicated that time has little effect on the crystallinity. However, the crystallizing curve of ZIF-8 synthe-

Fig. 10. TG-DTG curve of a $\text{Zn}(\text{Im})_2$ sample (DES-R3) ionothermally synthesized in urea- ChCl .

Fig. 11. Effect of dissolving time on the crystallinity of $\text{Zn}(\text{Im})_2$ ionothermally synthesized in urea- ChCl using rapid cooling from 80, 100, 120, and 140 °C.

sized in methanol was sigmoidal [17]. This indicated that the crystallizing process included three stages: (1) nucleation: there was an induction time required to nucleate corresponding to the initial region of the crystallizing curve; (2) growth: the crystallizing rate quickened and the crystallinity increased with time, corresponding to the rising region of the crystallizing curve; (3) stationary phase: the crystallizing rate was constant and the crystallizing curve appeared flat again [17,38]. As seen in Fig. 11, it was observed that the synthesis process of $\text{Zn}(\text{Im})_2$ in DES failed to show these three stages, demonstrating that the synthesis process of $\text{Zn}(\text{Im})_2$ in DES was not a crystallizing process.

As described above, the precipitation process of $\text{Zn}(\text{Im})_2$ most likely resembled the cooling crystallization process of a soluble salt. A soluble salt has an enhanced solubility in a solvent where it dissolves and precipitates. In the present work, the solubility of $\text{Zn}(\text{Im})_2$ in the urea- ChCl deep eutectic solvent was measured by the “last crystal disappearance” method [32,39]. As listed in Table 3, the solubility increased with increasing temperature. When the temperature ranged from 60 to 90 °C, the solubility rose slightly from 0.0114 to 0.0473 g/g DES. From 90 to 150 °C, a sharp rise to 0.5334 g/g DES was

apparent. Thus, it can be seen that $\text{Zn}(\text{Im})_2$ did not precipitate until the DES system was cooled. In addition, $\text{Zn}(\text{Im})_2$ can re-precipitate from the urea- ChCl deep eutectic solvent by rapid or programmed cooling after some $\text{Zn}(\text{Im})_2$ sample redissolved, which was similar to the recrystallization process of a soluble salt. Thus, the precipitation process of $\text{Zn}(\text{Im})_2$ in DES was a cooling-induced crystallization process that followed a dissolution-crystallization mechanism.

Cooling crystallization is a broadly applied method in the precipitation of a soluble salt. Supersaturation, which is essential for the crystallization of soluble salts from a solvent, drives crystal nucleation and growth. When the synthesis solution was cooled by rapid cooling, supersaturation is reached quickly and an excess of nuclei was formed. Consequently, the particle size is unevenly distributed. When the solution is subject to programmed cooling, supersaturation occurred gradually. As a result, the nucleation rate is slow, with the forming of an appropriate amount of nuclei, and the particle size is uniformly distributed. Moreover, the shapes of the products varied depending on the two cooling methods employed [40,41]. The crystals adhered to the vessel wall as the solution was cooled by programmed cooling, revealing that a temperature gradient has formed in the autoclave. The temperature of the region near the autoclave wall was lower than that of the bulk phase, initially generating a high degree of local supersaturation. Therefore, nuclei were preferentially generated in this area by a heterogeneous nucleation mechanism [42]. $\text{Zn}(\text{Im})_2$ with the **zni** topology structure belongs to the tetragonal crystal system, and it grew along with the *c* axis when the solution was cooled by rapid cooling [10,25,40]. The crystal shape was rod-like with some defects such as hollow areas and cracks (Fig. 8(a)). During programmed cooling, the crystals uniformly grew along the *c* axis. The shape which was cluster-like was more regular, and the particle size was distributed homogeneously (Fig. 8(b)).

ZIF-8 exhibited dissolvability in the urea- ChCl deep eutectic solvent [32]. We also found that ZIF-8 had dissolvability in the [emim]Br ionic liquid, as listed in Table 3. Moreover, all of the ZIF-8, ZIF-67, **zni**-type $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ samples dissolved in the deep eutectic solvent and ionic liquid. Therefore, achieving supersaturation is essential for precipitation from the solution. Evaporation and cooling are the two frequently applied methods for achieving supersaturation [40]. However, this is too hard to accomplish when ZIFs are ionothermally synthesized by evaporation. Since an ionic liquid or a deep eutectic solvent has a low vapor pressure, much energy is needed and the operation is difficult. Consequently, cooling crystallization is a convenient and efficient method for the ionothermal synthesis of ZIFs. In summary, the precipitation of ZIFs from an ionic liquid or a deep eutectic solvent is similar to that of soluble inorganic salts. Initially, zinc salt or cobalt salt, 2-methylimidazole or imidazole are present in the solvent in the form of Zn^{2+} or Co^{2+} , 2-MIm[−] or Im[−] at the dissolving temperature. Subsequently, in the cooling step, the synthesis system reach supersaturation, and nucleate, and grow large crystals by the monomer addition of Zn^{2+} or Co^{2+} , 2-MIm[−] or Im[−]. ZIFs precipitated from an ionic liquid or a deep eutectic solvent by a cooling-induced crystallization and the precipitation fol-

Table 3
Solubility of $\text{Zn}(\text{Im})_2$ and ZIF-8.

$\text{Zn}(\text{Im})_2$		ZIF-8	
<i>T</i> /°C	<i>S</i> (g/g urea- ChCl DES)	<i>T</i> /°C	<i>S</i> (g/g [emim]Br ILs)
60	0.0114	—	—
70	0.0178	—	—
80	0.0269	80	0.0349
90	0.0473	90	0.0590
100	0.0906	100	0.0671
110	0.1150	110	0.0893
120	0.1552	120	0.1147
130	0.2160	130	0.1408
140	0.3503	140	0.1798
150	0.5334	150	0.2305

lows a dissolution-crystallization mechanism. For the discussion of the precipitation kinetics, further studies are still needed.

4. Conclusions

ZIF-8, ZIF-67, **zni**-type $\text{Zn}(\text{Im})_2$ and $\text{Co}(\text{Im})_2$ were ionothermally synthesized in an [emim]Br ionic liquid and an urea-ChCl deep eutectic solvent. The ZIFs dissolved in the ionic liquid or the deep eutectic solvent, and they precipitated from the solvent by cooling-induced crystallization in the cooling step. This precipitation followed the dissolution-crystallization mechanism instead of the solution- and solid-mediated mechanism, which is a classical crystallization mechanism for zeolites. Controlling of the cooling rate can change the crystal morphology and size in the ionothermal synthesis. The present work provides a safe, convenient and efficient strategy for the synthesis of ZIFs and a novel understanding for their synthesis mechanism.

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Graphical Abstract

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Ionothermal synthesis of zeolitic imidazolate frameworks and the synthesis dissolution-crystallization mechanism

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Zeolitic imidazolate frameworks are ionothermally synthesized in an ionic liquid and a deep eutectic solvent. They precipitate from the synthesis solution by a cooling-induced crystallization process following the dissolution-crystallization mechanism.

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离子热法合成沸石咪唑骨架材料及其溶解-结晶机理研究

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摘要: 基于沸石咪唑骨架材料在离子液体和低共熔溶剂中冷却结晶的析出方式, 开发了一种离子热法合成沸石咪唑骨架材料的新途径, 采用X射线衍射、扫描电镜、核磁共振光谱、红外光谱以及热重分析等方法对制备的产物进行了表征, 研究了合成条件对产物结晶度、尺寸和形貌的影响, 探讨了沸石咪唑骨架材料在离子热合成体系中的溶解-结晶析出机理. 研究发现, 冷却速率能够影响产物形貌, 急速冷却时, **sod** (RCSR代码)型产物的形貌为球形, **zni** (RCSR代码)型产物为棒状或平板状; 程序控制冷却时, **sod**型产物的形貌为多面体, **zni**型产物呈团簇状.

关键词: 离子热合成; 沸石咪唑骨架材料; 溶解-结晶机理; 溶解度; 冷却析出

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1. 前言

沸石咪唑骨架材料(ZIFs)是一类具有沸石拓扑结构的新型金属有机骨架材料(MOFs), 由Zn(或Co)等过渡金属离子与咪唑(Im)或咪唑衍生物(*n*-RIm, R为咪唑环上的取代基, *n*为取代基的位置)配位而成^[1,2]. 沸石咪唑骨架材料具有较大的孔体积、热稳定性以及B酸和L酸性位, 可以用作催化剂或者催化剂的载体^[3-5]; 此外, 该材料还具有较高的比表面积和良好的机械性能, 在气体分离和储存、传感器以及磁性材料等方面有广阔的应用前景^[6-13]. ZIF-8和ZIF-67是典型的开放骨架结构的ZIFs材料, 具有**sod**型拓扑结构, 分别由Zn和Co与2-甲基咪唑(2-MIm)配位而成(Zn(2-MIm)₂和Co(2-MIm)₂)^[6]. 自问世以来, 其合成方法和生成机理一直是人们研究的热点^[14-24], 目前, ZIF-8的合成方法有液相扩散法^[14]、溶剂热法^[6,15-20]、微波辅助离子热法^[21]、机械化学法^[22]以及蒸汽辅助法^[23,24]等; ZIF-67的合成方法主要有溶剂热法^[25]. 在机理研究方面, Venna等^[17]和Cravillon等^[18]采用X射线衍射(XRD)、透射电镜(TEM)、原位小角/广角X

射线散射(SAXS/WAXS)等表征手段, 研究了ZIF-8在甲醇中的晶化机理. 作者认为, ZIF-8在甲醇中的生长过程包括Zn²⁺和2-MIm生成无定形的簇状物、簇状物转变为晶核和晶核晶化生长为ZIF-8晶体三个阶段, 其晶化动力学方程符合阿夫拉米方程模型, 晶化机理遵循液固双相转变机理.

具有**zni**型拓扑结构的Zn(Im)₂和Co(Im)₂是典型的致密型ZIFs材料, 分别由锌和钴与咪唑(Im)配位而成^[13,25]. Zn(Im)₂和Co(Im)₂材料的合成方法主要有溶剂热法^[12,13,25,26], 此外, Hikov等^[13]采用原位静态/动态光散射(TR-SLS/DLS)和扫描电镜(SEM)等表征方法, 研究了Zn(Im)₂在甲醇中的晶化过程. 结果发现, Zn(Im)₂在甲醇中的晶化分为两个阶段: 第一阶段生成亚稳态初级粒子(~100 nm); 第二阶段亚稳态初级粒子作为单体, 通过单体添加的方式生长成为Zn(Im)₂晶体.

离子热合成法是一种以离子液体(ILs)或低共熔溶剂(DES)为介质的材料合成新方法^[27,28]. Dybtsev等^[29]和Bu课题组^[30,31]采用离子热法合成了一系列的MOFs材料, 例如, 在1-甲基-3-丁基咪唑四氟硼酸([bmim]BF₄)离

子液体中合成 $[\text{Cu}_3(\text{tpt})_4](\text{BF}_4)_3 \cdot (\text{tpt})_{2/3} \cdot 5\text{H}_2\text{O}$ (tpt: 1,3,5-三吡啶基-2,4,6-三唑)、在低共熔溶剂中合成 $\text{M}_x(\text{bdc})_y$ (M^{3+} 代表 In^{3+} , Y^{3+} , Nd^{3+} , Sm^{3+} 等金属离子, bdc为1,2-二苯甲酸)和锌硼咪唑骨架材料等. 最近, 我们报道了一种以尿素和氯化胆碱(urea-ChCl)组成的低共熔溶剂为介质合成ZIF-8的新途径, 在该合成过程中, ZIF-8以冷却结晶的方式析出^[32].

作为前述工作的扩展, 本文采用离子热法在1-甲基-3-乙基溴化咪唑([emim]Br)离子液体中合成了ZIF-8和ZIF-67、在urea-ChCl低共熔溶剂中合成了zni型的 $\text{Zn}(\text{Im})_2$ 和 $\text{Co}(\text{Im})_2$, 详细研究了合成过程, 探讨了沸石咪唑骨架材料在离子热合成体系中的溶解-结晶析出机理.

2. 实验部分

2.1 离子液体和低共熔溶剂的合成

参照文献^[33]的方法制备[emim]Br离子液体. 取适量经二次蒸馏提纯的*N*-甲基咪唑加入到三口烧瓶中, 通 N_2 保护, 按照溴乙烷/*N*-甲基咪唑的摩尔比为1.5:1, 滴加溴乙烷; 滴加完毕后, 升温至80 °C, 搅拌混合物回流反应8 h, 用旋转蒸发仪除去混合物中未反应的溴乙烷, 即得[emim]Br离子液体.

参照文献^[34]的方法制备urea-ChCl低共熔溶剂. 按照尿素/氯化胆碱的摩尔比为2:1, 将适量的尿素和氯化胆碱混合均匀, 加热至80 °C, 使该固体混合物熔化, 即得低共熔溶剂.

2.2. ZIFs材料的合成

以[emim]Br离子液体中合成ZIF-8为例: 将2-甲基咪唑、六水合硝酸锌与熔化的离子液体按照一定的比例混合于烧杯中, 在100 °C搅拌, 使之混合均匀. 将此混合物转移到30 ml不锈钢反应釜中, 然后将反应釜置于烘箱中, 升温至溶解温度下保持一段时间. 结束后, 采用急速冷却(冰水浴中冷却)或程序控制冷却(程序温度控制器调节, 冷却速率为0.1 °C/min)对反应釜降温, ZIF-8产物在冷却过程中结晶析出, 混合物经抽滤、去离子水和无水乙醇反复洗涤, 于110 °C烘干, 即得ZIF-8产物.

在[emim]Br离子液体中合成ZIF-67 (见表1)以及在urea-ChCl低共熔溶剂中合成 $\text{Zn}(\text{Im})_2$ 和 $\text{Co}(\text{Im})_2$ (见表2)的过程与前述合成过程类似. 离子液体中合成的样品命名为ILs-Rx和ILs-Px, 低共熔溶剂中合成的样品命名为DES-Rx和DES-Px, R表示样品经急速冷却所得, P表示样品经程序控制冷却所得, x为样品序号.

2.3. ZIFs材料的表征

采用荷兰Philips公司X'PertPro型X射线衍射仪测定样品的晶相结构, Cu, K_α 射线($\lambda = 0.15418 \text{ nm}$), Ni滤薄片, 电压40 kV, 电流40 mA, 扫描范围 $2\theta = 5^\circ\text{--}55^\circ$, 扫描速率 $5^\circ/\text{min}$. 采用Hitachi S4800型场发射SEM观察样品的形貌. 采用Varian Infinityplus-400型核磁共振波谱仪测定样品的核磁共振(NMR)波谱. 采用Bruker公司Equinox55型光谱仪测定样品的红外光谱(FTIR), 仪器分辨率 4 cm^{-1} , 扫描次数80, KBr压片法. 采用Netzsch公司STA449F3型热分析仪进行热重(TG)分析, 样品装量2–2.5 mg, 升温速率 $10^\circ\text{C}/\text{min}$.

3. 结果与讨论

3.1. ZIF-8和ZIF-67的离子热合成与表征

按照表1的合成条件, 在[emim]Br离子液体中合成了ZIF-8和ZIF-67. 在该合成过程中, 合成溶液在溶解温度下澄清, 没有固体产物析出, 冷却至室温, 溶液变浑浊, 经抽滤, 可得固体产物. 急速冷却时, 产物在体相与合成溶液混合; 程序控制冷却时, 产物主要附着在反应釜壁, 此现象与ZIF-8在低共熔溶剂中合成的实验现象相似^[32], 表明ZIF-8和ZIF-67在[emim]Br离子液体合成体系的冷却阶段析出.

图1为ZIF-8和ZIF-67样品的XRD谱. 由图可见, 各样品的XRD谱与文献^[6]中报道的sod结构单晶数据模拟的XRD完全匹配, 可见, 急速冷却或程序控制冷却得到的产物结构均为纯相的sod结构. 图2为产物的SEM照片. 急速冷却时, ZIF-8和ZIF-67产物分别为 $0.5 \mu\text{m}$ 和 $0.35 \mu\text{m}$ 左右的团聚球形(图2(a)和图2(c)); 程序控制冷却(降温速率 $0.1^\circ\text{C}/\text{min}$)时, ZIF-8和ZIF-67产物分别为 50 和 $5 \mu\text{m}$ 左右的截角十二面体(图2(b)和图2(d)). 结果表明, 程序控制冷却所得产物的尺寸较大、形貌较为规整. 研究发现^[23], ZIF-8和ZIF-67同属sod结构, 相同条件下合成的ZIF-8和ZIF-67, 织构性质几乎相同. 本文主要对ZIF-8产物ILs-R1和ILs-P1进行了 N_2 吸附-脱附测量, 结果如图3所示. 急速冷却所得样品ILs-R1的BET和Langmuir比表面积分别为 1428 和 $1724 \text{ m}^2/\text{g}$, 微孔体积达 $0.617 \text{ cm}^3/\text{g}$. 程序控制冷却所得样品ILs-P1的BET和Langmuir比表面积分别为 1211 和 $1583 \text{ m}^2/\text{g}$, 微孔体积达 $0.558 \text{ cm}^3/\text{g}$. ILs-R1样品的晶粒尺寸较小, 且样品间存在较多的晶间孔, 造成两种降温方式所得样品的织构参数不同.

图4为ZIF-8产物ILs-R1和2-甲基咪唑的FTIR谱. 可以看出, 对于ILs-R1样品, 位于 $3335\text{--}2500$ 和 1820 cm^{-1} 处

的2-甲基咪唑环上N-H的振动峰消失,表明与锌配位的2-甲基咪唑完全去质子化,且未出现[emim]Br离子液体的振动峰。图5为ZIF-8产物ILs-R1的 ^{13}C NMR谱。分别将151.3, 124.3和14.0处的谱峰归属为2-甲基咪唑环上N-C-N、N-C-C-N和取代甲基的碳原子共振信号,由图可见,未出现[emim]Br离子液体的碳原子共振信号。图6为ZIF-8产物ILs-R1在 N_2 气氛下的TG曲线。50–270 $^{\circ}\text{C}$ 范围内的失重归属为吸附水,300–550 $^{\circ}\text{C}$ 间并没有明显的失重,550 $^{\circ}\text{C}$ 时产物骨架开始坍塌。在离子热合成过程中,离子液体通常作为模板剂或结构导向剂填充在产物的孔道中^[27,29],而在合成ZIF-8时,产物的TG、FTIR和 ^{13}C NMR结果表明,离子液体并未起到模板或结构导向的作用,而是为ZIF-8提供了一种新的合成环境。Lai等^[15]和Cravillon等^[35]曾报道在甲醇和水中合成ZIF-8时,也不需要添加模板剂或结构导向剂。

3.2. zni型 $\text{Zn}(\text{Im})_2$ 和 $\text{Co}(\text{Im})_2$ 的离子热合成与表征

按照表2的合成条件,在urea-ChCl低共熔溶剂和[emim]Br离子液体中合成了zni型的 $\text{Zn}(\text{Im})_2$ 和 $\text{Co}(\text{Im})_2$ 。在该合成过程中,合成溶液在溶解温度下保持一段时间,未经冷却时澄清,没有固体产物析出,经急速冷却或程序控制冷却至室温,溶液变浑浊,有尺寸较大的晶粒析出,这一现象类似于可溶性盐结晶析出的过程^[36]。

图7为 $\text{Zn}(\text{Im})_2$ 和 $\text{Co}(\text{Im})_2$ 产物的XRD谱。由图可见,产物的XRD与文献^[25]中报道的zni结构单晶数据模拟的XRD相匹配,表明急速冷却或程序控制冷却所得产物 $\text{Zn}(\text{Im})_2$ 和 $\text{Co}(\text{Im})_2$ 的结构均为纯相的zni结构。图8为 $\text{Zn}(\text{Im})_2$ 和 $\text{Co}(\text{Im})_2$ 产物的SEM照片。急速冷却时,DES-R3, DES-R4, ILs-R3和ILs-R4样品晶粒尺寸约为600, 200, 500和200 μm ,其形貌均为不规整的棒状,呈现中空和裂纹。此外,产物中还存在一些尺寸约为3 μm 的球形晶粒(图8(a), 图8(c), 图8(e), 图8(f));程序控制冷却(降温速率为0.1 $^{\circ}\text{C}/\text{min}$)时,DES-P3和DES-P4样品晶粒尺寸约为100和55 μm ,其形貌均为团簇状(图8(b)和图8(d))。可见,程序控制冷却所得产物形貌比急速冷却所得产物的形貌规整、尺寸均匀,在可溶性盐的析出过程中,也经常通过控制冷却速率来调节产物形貌和平均粒径^[17,37]。zni型 $\text{Zn}(\text{Im})_2$ 和 $\text{Co}(\text{Im})_2$ 材料为四元环致密结构,其Langmuir比表面积仅为0.8 m^2/g 。

图9为 $\text{Zn}(\text{Im})_2$ 产物和咪唑的FTIR谱。由图可见,在 $\text{Zn}(\text{Im})_2$ 咪唑环上N-H键的振动峰(335–2500, 1820 cm^{-1})消失,表明与锌配位的咪唑完全去质子化,且未出现低共熔溶剂中任一组分的振动峰。图10为 $\text{Zn}(\text{Im})_2$ 产物在

N_2 中的TG曲线。100–300 $^{\circ}\text{C}$ 内的失重归属为吸附水,300–600 $^{\circ}\text{C}$ 内几乎没有失重,630 $^{\circ}\text{C}$ 时产物的骨架开始坍塌,表明 $\text{Zn}(\text{Im})_2$ 产物具有优异的热稳定性。TG和FTIR结果表明,低共熔溶剂并未起模板或结构导向的作用,而是为 $\text{Zn}(\text{Im})_2$ 的合成提供了一种新型的合成环境。

3.3. ZIFs材料在离子热合成体系中的溶解-结晶析出机理

ZIF-8在urea-ChCl低共熔溶剂中有较大的溶解度,未能在溶解温度下晶化析出,而是在体系的冷却阶段以结晶的方式析出,通过控制冷却速率可以调节产物的尺寸和形貌^[32]。如前文所述,ZIF-8和ZIF-67在[emim]Br离子液体中以及zni型的 $\text{Zn}(\text{Im})_2$ 和 $\text{Co}(\text{Im})_2$ 在[emim]Br离子液体与urea-ChCl低共熔溶剂中析出现象均与ZIF-8在低共熔溶剂中合成时相似,在此具体考察了 $\text{Zn}(\text{Im})_2$ 在urea-ChCl低共熔溶剂中的析出过程。

以XRD谱(图7)中15.07 $^{\circ}$ 处衍射峰的强度计算 $\text{Zn}(\text{Im})_2$ 产物(DES-R3)的相对结晶度。图11给出了相对结晶度随溶解时间的变化曲线。可见,相对结晶度并未随着时间的增加发生明显的改变。ZIFs材料在甲醇中的生成过程是一个晶化过程,其晶化曲线呈S型,晶化过程包括以下三个阶段:(1)成核。在晶化初期相当长的一段时间,晶化曲线呈平缓趋势;(2)晶化生长阶段。晶化开始后晶化速率逐渐加快,晶化曲线呈快速上升的趋势;(3)稳定阶段。晶化后期晶化速率逐渐减慢,晶化曲线再次呈现平缓^[17,38]。然而,由图11可见, $\text{Zn}(\text{Im})_2$ 在低共熔溶剂中合成时,并未经历此晶化的三个阶段,其合成过程并不是一个晶化过程。

如前文所述, $\text{Zn}(\text{Im})_2$ 在urea-ChCl低共熔溶剂中的析出过程,类似于可溶性盐的结晶析出过程。可溶性盐在溶剂中有较大的溶解度,既可以溶解于溶剂中,又可以通过控制某些条件从溶剂中结晶析出。采用“last crystal disappearance”的方法^[32,39]测量了 $\text{Zn}(\text{Im})_2$ 在urea-ChCl低共熔溶剂中的溶解度(表3)。 $\text{Zn}(\text{Im})_2$ 的溶解度随着温度的升高而增加,当温度由60升至90 $^{\circ}\text{C}$ 时,溶解度由0.0114缓慢增至0.0473 g/g DES,当温度由90升至150 $^{\circ}\text{C}$,溶解度由0.0473迅速增至0.5334 g/g DES。由此可见,urea-ChCl低共熔溶剂合成体系未经冷却时 $\text{Zn}(\text{Im})_2$ 产物不能析出,冷却后结晶析出。此外,将一定量的 $\text{Zn}(\text{Im})_2$ 产物溶解在urea-ChCl低共熔溶剂中,采用急速冷却或程序控制冷却对其降温, $\text{Zn}(\text{Im})_2$ 能够重新结晶析出,这与可溶性盐的重结晶过程相似。综上分析, $\text{Zn}(\text{Im})_2$ 在urea-ChCl低共熔溶剂中的析出过程为冷却结

晶的过程, 遵循溶解-结晶的析出机理。

冷却结晶是可溶性盐析出常用的一种方法, 过饱和度是析出时成核和晶体生长的驱动力。急速冷却时, 溶液能够迅速达到过饱和状态, 爆速成核, 生成的晶粒尺寸分布不均; 程序控制冷却时, 溶液均匀缓慢达到过饱和, 成核较慢、生成的晶核数目适中, 形成的晶粒尺寸分布较为均匀; 两种冷却条件下, 生成的产物形貌也不尽相同^[40,41]。在低共熔溶剂合成体系的冷却过程中, 由于热传递效应, 反应釜内的溶液存在温度梯度, 在靠近反应釜壁区域的溶液率先达到过饱和, 优先在此区域处成核, 遵循非均相成核机理^[42]。**zni**型的 $\text{Zn}(\text{Im})_2$ 属四方晶系, 急速冷却时, 晶体沿着 *c* 轴快速生长^[10,25,40], 得到的晶体呈棒状, 晶粒存在很大的缺陷, 例如, 中空、劈裂等, 晶粒尺寸分布不均匀(图8(a)); 程序控制冷却时, 体系降温速率缓慢, 晶粒沿 *c* 轴均匀的生长, 得到的晶体产物形貌较为规整(由棒状团簇而成的球形), 晶粒几乎不存在劈裂等缺陷, 颗粒尺寸分布较为均匀(图8(b))。

ZIF-8能够溶解于urea-ChCl低共熔溶剂中^[32], 经测量ZIF-8在 $[\text{emim}]\text{Br}$ 离子液体中也具有一定的溶解性(表3)。ZIF-8, ZIF-67, $\text{Zn}(\text{Im})_2$ 和 $\text{Co}(\text{Im})_2$ 等均能溶解于Urea-ChCl低共熔溶剂和 $[\text{emim}]\text{Br}$ 离子液体中, 因而溶液达到过饱和是它们结晶析出的重要条件。蒸发结晶和冷却结

晶是可溶性盐结晶析出常用的两种方法^[40], 但是离子液体和低共熔溶剂蒸汽压很低, 采用蒸发结晶制备ZIFs材料, 能耗大、操作困难、不易于实现, 冷却结晶成为ZIFs材料由此种溶剂析出的方便快捷的方法。综上可见, 沸石咪唑骨架材料在离子液体和低共熔溶剂中的析出过程与可溶性无机盐的析出方式一致。首先, 在溶解温度下原料硝酸锌或硝酸钴以及2-甲基咪唑或者咪唑在溶剂中以 Zn^{2+} 或 Co^{2+} , MIm^- 或 Im^- 离子的形式存在, 然后, 在冷却过程中, 体系达到过饱和, 成核, Zn^{2+} 与 MIm^- 或 Im^- 通过单体添加的方式生长成为ZIFs晶体, 该材料的析出遵循溶解-结晶机理, 而对于其动力学的讨论, 则还需更进一步的研究。

4. 结论

采用离子热法在离子液体和低共熔溶剂中合成了ZIF-8, ZIF-67以及**zni**型的 $\text{Zn}(\text{Im})_2$ 和 $\text{Co}(\text{Im})_2$ 材料。沸石咪唑骨架材料在离子液体和低共熔溶剂中有较大的溶解度, 它以冷却结晶的方式析出, 其析出遵循溶解-结晶机理。离子热法合成ZIFs材料时, 通过调节降温速率, 可以控制晶体的形貌和尺寸。本文为ZIFs材料的合成提供了一种安全、简单、快速的新途径, 对其合成机理提供了一种新的认识。