Synthesis of ZIF-8 in a deep eutectic solvent using cooling-induced crystallisation

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A B S T R A C T

We report an alternative route for the synthesis of ZIF-8 in a choline chloride--urea deep eutectic solvent (DES). Zinc nitrate hexahydrate and 2-methylimidazole were dissolved in the hot DES. The ZIF-8 sample could precipitate from the DES when the solution was cooled using rapid cooling or programmed cooling. The effect of the synthetic conditions, including the cooling rate of synthesis system and the reaction temperature, on the particle size and morphology of the ZIF-8 sample were investigated. The product was characterised using PXRD, SEM, TG, the particle size analysis and gas-sorption. When the system was chilled via rapid cooling, the product was 0.35 \( \mu \)m in size, agglomerating to form irregular spheres. After programmed cooling, the product was 5–50 \( \mu \)m with a rhombic dodecahedron or truncated rhombic dodecahedron morphology, depending on the cooling rate and reaction temperature. In addition, the precipitation of ZIF-8 in DES is also discussed. ZIF-8 synthesised in DES also displayed excellent thermal and chemical stability, as well as good gas adsorption and separation performances.

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1. Introduction

Zeolitic imidazolate frameworks (ZIFs) have neutral zeolite-type framework structures and are constructed from Zn or Co atoms coordinated with imidazole or imidazole derivatives. These materials have become a specialised and rapidly developing subclass of MOF materials, due to their regular porous channels, permanent porosity and large pore diameters\cite{1,2}. Among ZIFs, ZIF-8 with a SOD topology framework contains zinc linked with 2-methylimidazole (2-Melm), leading to the formula Zn(2-Melm)\textsubscript{2}: this prototypical and popular ZIF material has potential applications in catalysis, gas separation and storage\cite{3–7}. Initially, ZIF-8 was synthesised using the liquid-phase diffusion method reported by Huang et al. and a solvothermal method disclosed by Park et al.\cite{3,4}. Afterward, the synthesis of ZIF-8 has been extensively explored. Synthesising ZIF-8 in a methanolic system at room temperature, as reported by Huber and co-workers, is a popular method for studying the synthesis of ZIF-8\cite{8,9}. Undoubtedly, several other prominent methods have also been developed, including the room temperature mecanochemical synthesis adopted by Friscic and co-workers\cite{10}, the steam-assisted conversion synthesis reported by Dong and co-workers\cite{11}, the sonochemical route applied by Coronas and co-workers\cite{12} and Ahn and co-workers\cite{13} and the aqueous room temperature synthesis carried out by Lai and co-workers and Gross et al.\cite{14,15}. In addition, the size and shape of the ZIF-8 prepared in the methanolic system could be tuned by adding modulating agents or stabilisers, such as bridging bidentate ligands, simple monodentate ligands or surfactants (e.g., 1-methylimidazole, n-butylamine or poly(diaryl-dimethylammonium chloride)), etc.\cite{9,16}. Moreover, the crystallisation mechanism for ZIF-8 nanocrystals synthesised in methanol has also been investigated using various characterisation techniques\cite{17–19}. Carreon and co-workers\cite{17} utilised PXRD, TEM and SAED to observe the phase transformation of ZIF-8. The crystallisation of ZIF-8 occurs through a solution- and solid-mediated transformation mechanism. Wiebcke and co-workers\cite{18} monitored the crystallisation process for ZIF-8 nanocrystals using in-situ SAXS/WAXS, demonstrating that the crystal growth process involves cluster formation, nucleation, growth and nanocrystal formation. Attfield and co-workers\cite{19} used in-situ AFM to track the surface growth of \{100\} facet of ZIF-8, revealing that the crystal growth of ZIF-8 follows “birth and spread” and spiral growth mechanisms on different regions of the face simultaneously. These studies show that the crystal growth mechanism of ZIF-8 in methanolic systems is similar to the crystallisation process for zeolites.
Deep eutectic solvents (DES), a type of ionic solvent, are liquid at near-ambient temperatures below 150 °C [20]. In general, these substances are obtained by mixing a quaternary ammonium salt (e.g., choline chloride) with a hydrogen-bond donor (e.g., amine, citric acids) [21,22]. The components of a DES can associate with each other through hydrogen bond interactions; these interactions can substantially depress the melting point of the DES. The melting point of a DES is much lower than that of its individual components [20,21]. DES also exhibit excellent solubility, low volatility, low toxicity, good economy, convenient preparation and other advantages [20–22].

Currently, DES has become an attractive medium for MOF syntheses. Bu and co-workers synthesised [Nd(bdc)2(choline)][m-urea], [Yb2(btc)2(urea)] filled with cationic choline guests, a porous anionic C4N4-type ([In3(btc)4]6-n) (btc = 1,3,5-benzenetricarboxylate) framework and a zinc(II)–boron(III)–imidazole framework ([Zn2(im)Cl2Bi(im)4]) with unusual pentagonal channels and other MOF materials in urea-derived DES liquids [23–25]. Morris and co-workers synthesised lanthanide/organic-derived MOFs, such as Ln(DMA)(DMU) (Ln: La–Nd–Eu; DMA: CH3(NDMA)); in a ChCl/dimethylurea DES [26]. During synthetic processes, DES can act as a structure directing agent and a ligand. Furthermore, DES can also stabilise water-sensitive metal-halogen bonds because the reactivity of water is significantly decreased due to the strong binding interactions between the water molecule and the DES through hydrogen bond networks. It offers an approach toward MOFs that cannot be obtained using common methods [20,22–26].

2. Experimental section

2.1. Synthesis of ZIF-8

A 50 ml beaker was charged with 6 g of urea and 7 g of choline chloride, in a molar ratio of 2:1 [21]. After the choline chloride–urea mixture melted at 80 °C, 1.23 g of 2-methylimidazole (2-Melm) and 0.51 g of zinc nitrate hexahydrate (or 0.38 g zinc acetate dihydrate) were added to the hot DES with the following composition: Zn2+·2-Melm·DES = 1:8.88. After several minutes of electromagnetically stirring, the solution was transferred into a 30 ml Teflon-lined stainless autoclave and heated to the reaction temperatures (80–140 °C) for several minutes (0–1440 min), generating a homogeneous solution. Afterward, the autoclave was subjected to rapid or programmed cooling. The rapid cooling was performed in the ice-water bath; the hot autoclave was chilled over approximately 30 min to reach room temperature. During the programmed cooling process, the hot autoclave was cooled at 0.1–1.6 °C/min to room temperature using the programmed temperature controller on the oven. Finally, the solid product was filtered, thoroughly washed with distilled water and anhydrous ethanol and dried at 110 °C overnight.

The detailed synthesis conditions, the yield and the relative crystallinity of the final solid products are given in Table 1. The samples synthesised under different conditions were denoted Rx-y and Py-x-y, where Rx-y represents the ZIF-8 products synthesised using rapid cooling from the reaction temperatures x °C (80–140 °C) at which the solution reacted over y min (0–1440 min) in DES. Py-x-y denotes the ZIF-8 products that were prepared using programmed cooling at z °C/min (0.1–1.6 °C/min) cooled from the reaction temperatures x °C (80–140 °C) at which the synthesis solution reacted over y min (0–1440 min) in DES. The relative crystallinity of the rapid cooling sample and the programmed cooling sample was calculated using the powder X-ray diffraction data, respectively. These data were normalised to 100%, and the intensity was contributed from the total Bragg reflections at 110, 200, 211, 310 and 222 for ZIF-8.

ZIF-67 was also synthesised in DES using the same synthesis process as ZIF-8 except that the zinc salt was replaced with a cobalt salt (0.46 g, cobalt nitrate hexahydrate or cobalt acetate tetrahydrate).

2.2. Solubility and recrystallisation of ZIF-8 sample in DES

The solubility of the ZIF-8 sample in DES was determined via the “last crystal disappearance” method [28]. The initial weight of DES was approximately 2.2 g. The deep eutectic solvent was melted at 60 °C, before a known amount of ZIF-8 was gradually added to the stirred solution maintained at 60 °C. When the added portion was completely dissolved, the next portion was introduced. The added amount gradually decreased as the solution approached saturation; the approach of saturation was assessed using the time required for each portion to completely dissolve. The solution was considered saturated when the last portion remained undissolved. The weight of the last portion was approximately 0.001 g in this experiment. Afterward, the temperature was increased to the next necessary measurement temperature. The solubility of ZIF-8 in DES was calculated using the total mass introduced.

The recrystallisation and solubility experiments are reversible. The recrystallisation experiment was tested at 100 °C as follows: 0.3 g of ZIF-8 was dissolved in 13 g of DES at 100 °C. The hot solution was enclosed in a 30 ml preheated autoclave, and the autoclave was placed in an oven kept at 100 °C for 30 min. Subsequently, the autoclave was cooled via rapid cooling in the ice-water bath over approximately 30 min or by programmed cooling at 0.1 °C/min. The final product was obtained after filtering, washing and drying at 110 °C overnight.

2.3. Characterisation

The powder X-ray diffraction (PXRD) analyses of the as-synthesised samples were performed on a PANalytical X’Pert PRO diffractometer using Cu Kα radiation (λ = 1.5418 Å) and operating at 40 mA and 40 kV. The Bragg-Brentano theta–theta geometry was used. The samples were front-pressed into the holder. The scanning electron microscopy (SEM) experiments were carried on Hitachi S4800 field-emission scanning electron microscopes, and the samples were pre-treated with sputtered gold. The FT-IR was performed on a Bruker Equinox 55 type infrared spectrum apparatus with KBr sheeting method. The mean particle size was measured on a PANalytical X’Pert PRO diffractometer using Cu Kα radiation (λ = 1.5418 Å) and operating at 40 mA and 40 kV. The Bragg–Brentano theta–theta geometry was used. The samples were front-pressed into the holder. The scanning electron microscopy (SEM) experiments were carried on Hitachi S4800 field-emission scanning electron microscopes, and the samples were pre-treated with sputtered gold. The FT-IR was performed on a Bruker Equinox 55 type infrared spectrum apparatus with KBr sheeting method. The mean particle size was measured on a PANalytical X’Pert PRO diffractometer using Cu Kα radiation (λ = 1.5418 Å) and operating at 40 mA and 40 kV. The Bragg–Brentano theta–theta geometry was used. The samples were front-pressed into the holder.
obtained on a PCT apparatus (Advanced Material Corporation, USA) at 77 and 298 K. The CO₂ and CH₄ adsorption isotherms were measured on a Micromeritics ASAP 2020 instrument at 273 K.

3. Results and discussion

3.1. Synthesis of ZIF-8 in DES

Zinc nitrate hexahydrate and 2-methylimidazole were added to hot DES. After heating at the appropriate temperature, the synthesis solution became transparent; no crystals were observed. After the autoclave was cooled to room temperature using either rapid or programmed cooling, the clear solution turned cloudy. Subsequently, the solid product could be collected by filtration (Table 1). The PXRD patterns indicate that the product is single-phase ZIF-8, as shown in Fig. 1. The X-ray diffraction peaks of the sample 140–0 produced using rapid cooling broadened significantly due to its small crystallite size (Fig. 2). For the large crystal dimension (~50 µm) of polyhedron product 140–0–0.1 obtained using programmed cooling (Fig. 3), the X-ray diffraction peaks sharpened significantly and the PXRD pattern showed the preferential orientation of the (211) plane (2θ at 12.7°). The FT-IR spectrum of polycrystalline ZIF-8 sample indicated that the 2-Melm linked in ZIF-8 sample was fully deprotonated and there was no DES molecules filled in the pores of ZIF-8 sample (Fig. 4).

In addition, the size and shape of the ZIF-8 sample differ between the two methods. When the autoclave was cooled by rapid cooling, the crystallites mixed with the solvent in the bulk phase. The size and shape of the polycrystalline sample R₁₄₀–₀ are approximately 0.35 µm with irregular spherical agglomerates (Fig. 2A). The size and morphology of polycrystalline product keep consistent regardless of the reaction temperature or time (Figs. 2 and 5). The yield of the polycrystalline product remains 76–79% (Table 1). After the programmed cooling process, numerous single-crystalline grains adhered to the autoclave wall. The size and shape of the single-crystalline sample P₁₄₀–₀–₀.₁ are truncated rhombic dodecahedra of approximately 50 µm (Fig. 3A). When the reaction time is extended from 0 to 1440 min, the single-crystalline ZIF-8 product remains nearly 50 µm in size and retains its truncated rhombic dodecahedral shape; the yield of the single-crystal sample remains 85–89% (Table 1 and Fig. 3). Moreover, the two representative samples R₁₄₀–₀ and P₁₄₀–₀–₀.₁ were used for the nitrogen adsorption measurement. The nitrogen adsorption measurement for polycrystalline ZIF-8 sample R₁₄₀–₀ reveals a high Brunauer–Emmett–Teller (BET) surface area, a high Langmuir surface area and a large micropore volume (1841 m²/g, 2201 m²/g and 0.791 cm³/g). The single-crystalline ZIF-8 sample P₁₄₀–₀–₀.₁ exhibits BET and Langmuir surface areas of 903 and 1087 m²/g, while the micropore volume is 0.396 cm³/g. The differences of the surface area and the micropore volume between the polycrystalline and single-crystal sample might be induced by the small crystallite dimension and intergranular pores of polycrystalline ZIF-8 products.

Consequently, ZIF-8 crystals might crystallise in DES during the cooling step. Therefore, the precipitation process for the ZIF-8 synthesised in DES is most likely similar to the cooling-induced crystallisation of soluble salts or organic compounds in solvent. The soluble salts and organic compounds can precipitate and dissolve in solvent. In the present work, the solubility of ZIF-8 in DES was measured, which rises with the temperature increasing (Fig. 6). From 60 to 100 °C, the solubility rose slightly from 0.0111 g/g DES to 0.0789 g/g DES. When the temperature ranged from 100 to 160 °C, a sharp rise to 1.1053 g/g DES was apparent. Therefore, the supersaturation that is essential for the crystallisation of soluble salts or organic compounds from solvent [28] drove the crystal nucleation and growth as ZIF-8 precipitated from DES. No solid product was observed at the reaction temperature due to the high solubility of ZIF-8 in DES. As the synthetic system was cooled by rapid cooling, the supersaturation could be achieved swiftly, forming excessive nuclei and accelerating the formation of small crystals [29]. Therefore, ZIF-8 crystallites rapidly precipitate from DES as agglomerated polycrystalline material (Figs. 2 and 5). When the solution was subjected to programmed cooling, the supersaturation was approached gradually. Consequently, the nucleation rate was slow, forming an appropriate amount of nuclei. ZIF-8

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rapid cooling</th>
<th>Programmed cooling</th>
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<tr>
<td>t (min)</td>
<td>Yield (%)</td>
<td>RC (%)</td>
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<tr>
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<tr>
<td>R₁₄₀–₁₄₄₀</td>
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Table 1: The detailed synthetic conditions, yields and relative crystallinity of the ZIF-8 samples synthesised in DES.

*RC = relative crystallinity.
crystal can grow homogenously and precipitate gradually. As a result, high quality single-crystalline grains with sizes on the micron scale and regular polyhedral shapes were produced (Fig. 3).

As shown in Table 1 the relative crystallinity of the ZIF-8 sample synthesised in DES remains almost unchanged after lengthening the reaction time for both rapid and programmed cooling scenarios at 140 °C. During the crystallisation process for ZIF-8 in methanol, the relative crystallinity is related to the crystallisation time; and the crystallisation curve appears sigmoid [17,30], similar to zeolites [31,32]. An induction time is needed to nucleate the ZIF-8 or zeolite phase during the formation of the intermediate metastable amorphous phases [17,18,33]. In contrast, the precipitation of ZIF-8 in DES fails to involve the formation of intermediate amorphous phases, and the ZIF-8 crystals do not form at the reaction temperature (Table 1 and Figs. 2 and 3). Therefore, the precipitation of ZIF-8 from DES does diverge from the crystallisation process of ZIF-8 in methanol and that of the zeolite.

3.2. Effect of the cooling rate on the particle size and morphology of ZIF-8

The cooling rate affects the particle sizes of soluble salts and organic compounds during crystallisation in solvent [34,35]. As mentioned above, ZIF-8 precipitates from DES during cooling. Therefore, we systematically studied the effect of the cooling rate on the particle size and morphology of ZIF-8 sample using an
increase from 0.1 to 1.6 °C/min (Figs. 7 and 8) when the reaction temperature was changed from 80 to 140 °C.

Fig. 7 shows that the mean particle size of the ZIF-8 sample decreases sharply when increasing the cooling rate. Specifically, the mean particle size increases significantly as the period of crystal growth lengthens (the cooling rate decreasing from 1.6 to 0.1 °C/min). Therefore, the crystallisation of ZIF-8 in DES might obey the Ostwald ripening mechanism [36]. The small particles have a high surface free energy and tend to dissolve in the solvent where they mature to form large particles, lowering the total surface free energy. In addition, the edges and corners of single-crystalline grains cooled at 0.1 °C/min are distinct (Fig. 3). However, when the cooling rate was increased from 0.2 to 1.6 °C/min, the edges and the corners of crystal particles gradually faded (Fig. 8). In particular, the angularity of the crystals synthesised at 80 °C with cooling rates beginning at 0.2 °C/min disappears. When increasing the cooling rate, supersaturation is achieved relatively quickly, forming more nuclei while shortening the cooling time; this scenario leaves insufficient time for the complete growth of every crystallographic face. Therefore, the mean particle size of ZIF-8 is attenuated, and the edges of crystallographic faces of ZIF-8 become less defined (Figs. 7 and 8).

3.3. Effect of the reaction temperature on the size and shape of ZIF-8 product

To investigate the effect of the reaction temperature, it was increased from 80 to 140 °C. When the system was cooled at 0.1 °C/min, the product size increases from 20 to 50 µm (Fig. 6). The morphology of sample could include rhombic dodecahedra or truncated rhombic dodecahedra (Figs. 3 and 9).

When the solution was cooled by rapid cooling, the temperature decreased quickly, possibly achieving supersaturation quickly and thickening. The solid product suddenly and uniformly precipitates from the DES mixture. During programmed cooling, the temperature gradually decreased, slowly approaching a supersaturated and viscous state. The crystalline grains slowly precipitate and stick to the vessel wall, revealing the temperature gradient in the autoclave [29] (Fig. 7). The temperature of the region near the autoclave wall is lower than that of bulk phase, initially generating a high degree of local supersaturation. The nucleus is preferentially generated in this area through a heterogeneous nucleation mechanism [36]. However, the bulk phase fails to establish a supersaturated state concurrently. The degree of supersaturation in the total reaction system decreases as the reaction temperature increases. Consequently, the rate of nucleation is slowed, and the
Fig. 8. SEM images of the ZIF-8 samples synthesised using programmed cooling at 0.2 °C/min (A, E, I and M), 0.4 °C/min (B, F, J and N), 0.8 °C/min (C, G, K and O) and 1.6 °C/min (D, H, L and P) from 140 °C, 120 °C, 100 °C and 80 °C, respectively.
The reprecipitated product retains the single SOD phase structure (Fig. 10). The X-ray diffraction peaks for the reprecipitated sample obtained after rapid cooling crystallisation are severely broadened. The reprecipitated product is approximately 0.35 μm in size, forming irregular spherical agglomerates (Fig. 11A). The size and morphology of the reprecipitated sample obtained using programmed cooling at 0.1 °C/min forms rhombic dodecahedra of approximately 25 μm (ZIF-8 was dissolved in DES at 100 °C) (Fig. 11B). Therefore, the reprecipitation process for ZIF-8 in DES resembles the recrystallisation process of a soluble salt from solvent. In summary, ZIF-8 can dissolve and deposit in DES reversibly. Therefore, the precipitation of the ZIF-8 synthesised in DES follows a fast cooling crystallisation process instead of the classical crystallisation mechanism utilised by zeolites, as illustrated in Scheme 1.

Moreover, we have also synthesised ZIF-67 (Co(MeIm)2 SOD framework) in DES. The PXRD data show that the product has a pure SOD phase (Fig. 12). When the system was cooled by rapid cooling, the diffraction peaks broaden slightly. The product forms approximately 0.5 μm particles with an irregular spherical shape (Fig. 13A). After programmed cooling, the diffraction peaks sharpen. ZIF-67 forms particles approximately 2 μm in size with a truncated rhombic dodecahedral morphology (Fig. 13B). Additionally, ZIF-67 is also soluble in DES. The precipitation and reprecipitation of ZIF-67 from DES are similar to those of ZIF-8 from DES. Therefore, the precipitation process for ZIF-67 in DES is also a fast cooling crystallisation process.

3.4. Precipitation process of ZIF-8 in DES

Cravillon et al. [9] and Venna et al. [17] synthesised ZIF-8 in methanol at room temperature. The crystal sizes increased from 0.05 to 0.5 μm when the crystallisation time was elongated from 10 min to 24 h. The crystals formed truncated rhombic dodecahedra. ZIF-8 has an excellent stability in methanol [3]. The crystallisation occurs through a transformation from a metastable amorphous phase to a crystalline phase, similar to the solution- and solid-mediated transformation mechanism for zeolites [17,18]. Zhu and co-workers [27] added water and ethanol into the urea–choline chloride eutectic mixture for the synthesis of hexagonal facet ZIF-8 nanocrystals with 0.05–0.3 μm. The water was supposed as the precipitant to deprotonate the Hmim, favouring the formation of ZIF-8. However, in the present work, ZIF-8 products precipitate from DES by cooling-induced crystallisation. The crystal size could approach 0.35 μm within 30 min, reaching 50 μm when modulating the cooling rate. The crystals can form spherical agglomerates, truncated rhombic dodecahedra or rhombic dodecahedra. ZIF-8 has a high solubility in DES (Fig. 6), rendering it unable to precipitate from DES until the mixture is cooled. No metastable amorphous phase is observed during the precipitation process (Table 1 and Fig. 2). Moreover, ZIF-8 could reprecipitate from DES using rapid or programmed cooling after a certain quantity of ZIF-8 was dissolved, as described in Section 2.3. The reprecipitated product retains the single SOD phase structure (Fig. 10). The X-ray diffraction peaks for the reprecipitated sample obtained after rapid cooling crystallisation are severely broadened. The reprecipitated product is approximately 0.35 μm in size, forming irregular spherical agglomerates (Fig. 11A). The size and morphology of the reprecipitated sample obtained using programmed cooling at 0.1 °C/min forms rhombic dodecahedra of approximately 25 μm (ZIF-8 was dissolved in DES at 100 °C) (Fig. 11B). Therefore, the reprecipitation process for ZIF-8 in DES resembles the recrystallisation process of a soluble salt from solvent. In summary, ZIF-8 can dissolve and deposit in DES reversibly. Therefore, the precipitation of the ZIF-8 synthesised in DES follows a fast cooling crystallisation process instead of the classical crystallisation mechanism utilised by zeolites, as illustrated in Scheme 1.
Fig. 11. SEM images of the recrystallised ZIF-8 product obtained by (A) rapid cooling or (B) programmed cooling at 0.1 °C/min.

Scheme 1. Illustration of ZIF-8 crystals precipitating from DES.

Fig. 12. PXRD patterns of the ZIF-67 sample synthesised using (A) rapid cooling or (B) programmed cooling.

Fig. 13. SEM images of the ZIF-67 sample synthesised using (A) rapid cooling or (B) programmed cooling.

Fig. 14. TG curve of polycrystalline ZIF-8 sample.
The thermal gravimetric analysis (TGA) of the polycrystalline ZIF-8 sample was performed under nitrogen (Fig. 14). Therefore, a small weight loss (5.81%) exhibited up to 300 °C might be contributed from the removal of guest molecules, such as water, from the cavities or various species (e.g., Hmim) from the crystallite surfaces. A long plateau is apparent from 300 to 550 °C, revealing the exceptional thermal stability of the ZIF-8 sample synthesised in DES. The large-single ZIF-8 crystal synthesised in DMF by Yaghi and co-workers exhibited a weight-loss of 28.3% up to 450 °C attributed to DMF molecules in the pores. The structural frameworks decompose at 550 °C under nitrogen [3]. The nanosized ZIF-8 prepared in methanol by Wiebcke and co-workers may remain stable up to 200 °C in air [8]. These materials also exhibit a small weight-loss (1%) attributed to methanol acting as a guest molecule.

The hydrogen adsorption isotherms for polycrystalline ZIF-8 sample were collected at 77 K, as shown in Fig. 15. The hydrogen uptakes are 139.3 cm$^3$/g STP when approaching 760 torr and 365 cm$^3$/g STP under 40 bar (high-pressure). This large H$_2$ adsorption capacity is expected because the polycrystalline ZIF-8 sample synthesised in DES has a large specific surface area and a high micropore volume.

The carbon dioxide adsorption capacity under high-pressure was tested for the polycrystalline ZIF-8 sample at 298 K. The CO$_2$ uptake reaches 82.8 cm$^3$/g STP (approximately 43.7% of weight capacity) at 30 bar (Fig. 16). In addition, the adsorbed amount of CO$_2$ and CH$_4$ gases were also examined at 273 K, as shown in Fig. 17. The adsorption capacity for CO$_2$ (up to 34 cm$^3$/g) is more than six-fold higher than that of CH$_4$ (5 cm$^3$/g) due to the stronger interaction between the framework and the CO$_2$ molecule (CO$_2$ has a large quadruple moment, 13.4 × 10$^{-40}$ cm$^2$, and while CH$_4$ is non-polar) [38]. The results demonstrate that the ZIF-8 synthesised in DES also may also be utilised for H$_2$/CH$_4$, H$_2$/CO$_2$, and CO$_2$/CH$_4$, etc. and other gas separations.

4. Conclusion

In conclusion, we synthesised ZIF-8 in DES and studied its fast cooling crystallisation process. We determined that the particle size and shape of ZIF-8 could be manipulated through controlling the cooling rate and the reaction temperature without adding any extra additives. The present work may provide a simple and fast route toward the preparation of ZIFs. Similar to those synthesised using an alternative method, our ZIF-8 sample also exhibits exceptional thermal stability, as well as excellent gas adsorption and separation performances. Our findings will help elucidate the crystallisation mechanism for MOFs and other porous materials synthesised in DES, favouring the development of syntheses for novel materials.

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