



Facile synthesis of zeolitic imidazolate framework-8 from a concentrated aqueous solution



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ABSTRACT

This paper reports a facile method for the synthesis of zeolitic imidazolate framework-8 (ZIF-8) at room temperature in 10 min. ZIF-8 crystals were produced from stoichiometric metal and ligand (1:2) concentrated aqueous solutions in the presence of ammonium hydroxide. The resulting ZIF-8 crystals possessed high surface area, large micropore volume, and had a truncated cubic morphology with an average particle size of ca. 0.7 μm . TGA and XRD results revealed the structural stability of the as-synthesized ZIF-8 up to 250 $^{\circ}\text{C}$. The addition of an appropriate amount of ammonium hydroxide was proved to be essential for the formation of ZIF-8 crystal through deprotonation and coordination reaction. Furthermore, ZIF-8 crystals were successfully prepared from different zinc sources, and this method is promising for large-scale synthesis of ZIFs.

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1. Introduction

Zeolitic imidazolate frameworks (ZIFs) are a subclass of crystal-line porous metal–organic frameworks (MOFs) formed via a self-assembly approach [1–3], where metal ions such as Zn^{2+} and Co^{2+} are linked through N atoms of deprotonated imidazolate to form unique frameworks. The presence of nanosized pores and organic ligands in the structure of ZIFs gives them an excellent chemical tunability that is useful for many important applications such as gas storage [4–7], separations [8–10], catalysis [11,12] and chemical sensors [13,14]. In particular, ZIFs with sodalite topology, such as ZIF-8, have recently attracted considerable attention due to its high thermal and moisture stability compared to other MOF structures. A great deal of efforts have been made to synthesize nano- or micrometer sized ZIF-8 crystals by various methods, such as solvothermal [3,15], microwave [16], ultrasound [17], thermochemical [18] and accelerated aging [19] methods. Yaghi et al. first reported the synthesis of ZIF-8 crystals in dimethylformamide (DMF) using a solvothermal synthesis method at 140 $^{\circ}\text{C}$ for 24 h [3]. However, DMF solvent was trapped inside the pores because the guest organic molecule was larger than the aperture of the SOD cage and had to be removed by solvent exchange for long time. Cravillon et al. developed a rapid room-temperature route to produce ZIF-8 in methanol employing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2-

methylimidazole (Hmim) with a Hmim/Zn molar ratio of approximately 8 [20]. As methanol has a smaller kinetic diameter than DMF, and it can be easily removed from the pore network, methanol has become the most commonly used organic solvent for ZIF-8 synthesis [21].

Since organic solvents are expensive, toxic, and flammable, and they may cause environmental pollution, the synthesis of ZIFs in aqueous solution at room temperature has emerged in recent years. However, attempts to synthesize ZIF-8 in aqueous solution may end up with dense *dia* framework without porous structure [15,22]. The first successful synthesis of ZIF-8 nanocrystals in aqueous system was reported by Pan et al., where a $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was mixed with a solution containing a large excess of 2-methylimidazole (Hmim/Zn = ~70) at room temperature [23]. By using the four times diluted aqueous precursor solution (Hmim/Zn = 70), Yao et al. prepared micro-sized ZIF-8 crystals (~5 μm), and such diluted solution was beneficial for the formation of continuous and compact ZIF-8 membrane [24]. Kida et al. reported a synthesis of ZIF-8 with high surface area and micropore volume (~0.65 cm^3/g) at Hmim/Zn molar ratios higher than 40 [25]. The preparation with a relatively low concentration of Hmim (Hmim/Zn = ~16) was reported by Gross et al. [26], whereas the micropore volume of ZIF-8 (~0.32 cm^3/g) was small and the porosity was low [26]. To develop a method for high crystalline ZIF-8 preparation from stoichiometric metal and ligand precursors (Hmim/Zn = 2) in aqueous solution still remains a challenge.

By introducing a base, such as sodium formate [10], triethylamine (TEA) [27,28], polyamine [29] and n-butylamine [30],

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organic ligands would be deprotonated and their usage is reduced in the preparation of ZIFs. Chen et al. first demonstrated that the reaction could be effectively activated by using ammonium hydroxide in methanol solution, and found that ammonium hydroxide served not only as a base for deprotonation of the bridging ligands but also as a coordination buffering agent for ready release of metal ions [31]. In the presence of non-ionic triblock copolymer surfactant, ZIF-8 could be prepared in ammonium hydroxide aqueous solution from stoichiometric metal and ligand precursor [22]. The triblock copolymer surfactant should form intermediates with metal ions that avoided the formation of dense *dia* (Zn) structure in aqueous solution [22]. In this work, we report room temperature synthesis of ZIF-8 from a stoichiometric metal and ligand molar ratio of 1:2 in aqueous solutions with only addition of ammonium hydroxide. The precursor solution was concentrated, and the effect of synthesis condition on the formation of ZIF-8 was systematically investigated.

2. Experimental section

2.1. Synthesis of ZIF-8 from concentrated aqueous solutions

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2-methylimidazole (Hmim, $\text{C}_4\text{H}_6\text{N}_2$) and ammonium hydroxide (NH_3 , 28–30% aqueous solution, Sigma–Aldrich) were purchased from Sigma–Aldrich, Australia and used without further purification. In a typical process, 0.594 g of zinc nitrate hexahydrate (2 mmol) was dissolved in 3 mL of deionized water; 0.328 g of Hmim (4 mmol) was dissolved in 3.76 g of ammonium hydroxide solution (64 mmol NH_3); after that zinc nitrate and 2-methylimidazole solutions were mixed together. The final synthesis solution had a Zn:Hmim: NH_3 : H_2O molar composition of 1:2:32:157. The solution quickly turned into milk-like suspension, and stirred for 10 min at room temperature ($\sim 25^\circ\text{C}$) to complete the crystallization. The product was collected by centrifugation and washing with deionized water three times until the final product had pH value of ~ 7 , then dried at 60°C overnight.

The amount of ammonium hydroxide was changed from 0.94 (16 mmol NH_3) to 5.28 g (90 mmol NH_3) to examine the formation of ZIF-8 at the same reaction conditions as above. Other zinc sources, including zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Sigma–Aldrich) and zinc chloride (ZnCl_2 , Sigma–Aldrich) were also investigated to the synthesis of ZIF-8.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Philips PW1140/90 diffractometer with $\text{Cu K}\alpha$ radiation (25 mA and 40 kV) at a scan rate of $2^\circ/\text{min}$ with a step size of 0.02° . Scanning electron microscopy (SEM) images were obtained by using a FEI-NOVA NanoSEM 450 scanning electron microscope operated at 15 kV. The particle size distribution of ZIF-8 crystals was determined by manual measurement of the crystals in SEM image with a Photoshop software. ZIF samples were coated with Pt by thermal evaporator before imaging to minimize charging problems. About 100 particles in the FE-SEM image were measured to determine the average particle size. Nitrogen adsorption–desorption isotherms were measured at liquid nitrogen temperature (77 K) using a volumetric adsorption analyzer (Micromeritics ASAP 2020), and the samples were degassed at 100°C for 4 h prior to analysis. Brunauer–Emmett–Teller (BET) surface area, Langmuir model surface area, and micropore volume were calculated from the nitrogen adsorption–desorption isotherms. The total pore volume and micropore volume were calculated from the amount of nitrogen adsorbed at P/P_0 of 0.99 and via the t -plot method, respectively.

The change of pH value during the coordinated reaction was measured at room temperature using a HANNA-Hi 4221 pH meter. Thermal gravimetric analysis (TGA) was carried out with a Perkin Elmer, Pyris 1 analyzer under air flow at a heating rate of $5^\circ\text{C}/\text{min}$ up to 700°C . Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Fourier-Transform infrared spectrometer by using the KBr wafer technique.

3. Results and discussion

3.1. Characterization of as-synthesized ZIF-8 crystals

XRD pattern of the product prepared with Zn:Hmim: NH_3 : H_2O molar ratio of 1:2:32:157 at room temperature is shown in Fig. 1a, which is similar to the simulated SOD-type ZIF-8 structure, confirming that the sample has pure ZIF-8 phase [3]. SEM image in Fig. 1b shows that micrometer-sized crystals have uniform cubic shapes. For the enlargement SEM image in Fig. 1c, the “cubes” with truncated edges expose 6 {100} and 12 {110} faces. The statistical particle size distribution of the crystals measured from a SEM image is shown in Fig. 1d, and the mean particle size is ca. $0.7\ \mu\text{m}$. The yield of ZIF-8 is about 73% on the basis of amount of zinc, which is comparable to those reported in the literature [20,23].

N_2 adsorption–desorption isotherm of the as-synthesized ZIF-8 is shown in Fig. 2, indicating a type I isotherm. The high nitrogen adsorption at very low relative pressures is due to the presence of micropores; while a second uptake at high relative pressure indicates the existence of textural macroporosity formed by packing of ZIF-8 crystals. Total pore volume and micropore volume of the resulting ZIF-8 are about 1.08 and $0.50\ \text{cm}^3/\text{g}$, respectively. BET and Langmuir surface areas are 1079 and $1430\ \text{m}^2/\text{g}$, respectively, which are higher than those ZIF-8 prepared in aqueous solutions [23,26].

Fig. 3a shows TGA curve of the as-synthesized ZIF-8 performed under air flow and the TGA curve is similar to ZIF-8 crystals prepared in an aqueous solution [26]. The first weight-loss step of about 20% (ambient temperature to 250°C) corresponds to the release of H_2O and other absorbed unreacted molecules. The molecular formula of the as-synthesized ZIF-8 was estimated to be $\text{Zn}(\text{C}_4\text{H}_5\text{N}_2)_2 \cdot 3.1\text{H}_2\text{O}$ based on the TGA result when the weight loss in the first step was assumed to the loss of H_2O . A sharp weight drop of 52% from 250 to 650°C is due to a structural degradation and decomposition of organic ligands. In addition, the total weight loss of about 65% occurs between 250 and 650°C , which is in good agreement with the calculated weight loss of 64%; this indicates that ZIF-8 structure ($\text{Zn}(\text{C}_4\text{H}_5\text{N}_2)_2$, molecular weight: 227) is completely converted into zinc oxide (ZnO , molecular weight: 81) [26].

Thermal stability of the as-synthesized ZIF-8 was tested in open air at elevated temperature for 2 h. XRD patterns (Fig. 3b) show that the sample could maintain ZIF-8 structure up to 250°C , indicating the release of guest molecules (e.g., H_2O) does not damage the framework structure. SEM image shows that the morphology of ZIF-8 does not change after calcination at 250°C for 2 h (Fig. 3c). When the sample was heated at 300°C for 2 h, the intensity of XRD peaks reduces significantly, and the sample transforms into amorphous structure, and the color of the sample changes from white to light yellow. SEM image shows the particles have irregular shapes formed by aggregated particles with several micrometers in size (Fig. 3d). XRD result indicates the samples become pure ZnO after being heated at 400°C for 2 h (Fig. 3b).

Fig. 4 shows FT-IR spectra of the as-synthesized ZIF-8 and the ZIF-8 thermally treated at 250°C for 2 h; almost all of the FT-IR bands are in good agreement with those of previously reported ZIF-8 [3,20,32,33]. For example, the bands at 3135 and $2929\ \text{cm}^{-1}$ are attributed to the aromatic and the aliphatic C–H

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