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Aqueous room temperature synthesis of zeolitic imidazole framework 8 (ZIF-8) with various concentrations of triethylamine

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In this study, a zeolitic imidazole framework (ZIF-8) was prepared, and physico-chemical characterizations were performed to investigate the influences of triethylamine (TEA) on the crystallinity, particle size, morphology, and defects of ZIF-8 synthesized *via* an aqueous room temperature approach with a relatively low molar ratio of ligands to metal salts. Increasing the concentration of TEA by raising the TEA/total molar ratio from 0.004 to 0.007 prompted the formation of pure phase ZIF-8, whereas a TEA/total molar ratio below 0.004 did not result in a yield of ZIF-8. The particle size of ZIF-8 decreased from approximately 288 to 133 nm with increasing TEA/total molar ratio, except at a TEA/total molar ratio of 0.007. However, an excessive TEA/total molar ratio alters the 2-MeIm chemistry, and partially forms hydroxylated 2-MeIm. Thus, this study shows that at relatively low molar ratios of ligands to metal salts, up to a maximum TEA/total molar ratio of 0.006, the TEA concentration plays an important role in assisting crystal formation and in controlling the particle size of ZIF-8. The proposed procedure enables pure phase nanoscale ZIF-8 to be synthesized with a high product yield and with minimal chemical usage.

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1. Introduction

Metal-organic frameworks (MOFs) are crystalline compounds consisting of metal ions and organic ligands that function as secondary building units. MOFs are a new and emerging class of porous material that possesses interesting characteristics such as high micropore volume, large pore size, high crystallinity, and a high metal content to achieve active sites.¹ The large surface area of MOFs provides advantages over other porous materials such as activated carbon and zeolite. Previous researchers have synthesized MOF with high Brunauer-Emmett-Teller (BET) surface areas such as MOF-5 (3000 m² g⁻¹),² Co-MOF-74 (1314 m² g⁻¹),³ and Mg-MOF-74 (1332 m² g⁻¹),⁴ which are much higher than those of commercial Zeolite Y (900 m² g⁻¹), Zeolite Beta (710 m² g⁻¹), ZSM-5 (425 m² g⁻¹), and Modernite (500 m² g⁻¹).

Zeolite imidazole framework (ZIF), a novel class of MOFs, has recently attracted considerable attention from materials scientists. The exceptional chemical and thermal stability of ZIF enables numerous diverse applications for this compound. ZIF exhibits a porous crystalline structure with metal atoms linked through N atoms by ditopic imidazolate (C₃N₂H₃⁻ = Im). The Metal-Im-Metal angle links together at 145°, coinciding with the Si-O-Si angle commonly found in zeolite.⁵⁻⁷ The metal ions

that are commonly used for the synthesis of ZIF are Zn²⁺ and Co²⁺; however, there are many types of imidazole-type linkers such as imidazole (IM), 1-methylimidazole (mIM), 1-ethylimidazole (eIM), and 2-nitroimidazole (nIM) that are suitable for synthesis. Different combinations of different metal sites and imidazole organic ligands would result in ZIF with different properties, types, and structures. ZIF-8, a product formed with Zn²⁺ and 2-methylimidazole (2-MeIm), is one of the most investigated MOFs. The properties of ZIF-8 have been widely studied and exhibit excellent chemical stability against polar and nonpolar solvents,⁸ structural reorientation at high pressure,⁹ and high mechanical strength.¹⁰

ZIFs can be synthesized using different routes such as the solvothermal process, the microwave-assisted solvothermal process, and aqueous synthesis at room temperature. The solvothermal process is commonly used to synthesize ZIFs.^{6-8,10-13} A common synthesis method consists of mixing a highly diluted metal salt and organic ligands in an organic solvent and heating them in an autoclave at temperatures up to 200 °C. Despite its prevalence, this approach is time-consuming and requires high energy consumption.^{1,14} The microwave-assisted solvothermal method is less time-consuming compared to the solvothermal process,¹⁵ and both solvothermal and microwave-assisted synthesis processes have their own advantages and limitations. Although better yield and smaller particle size can be obtained through microwave-assisted synthesis, the process requires unfavorably high energy.^{3,16} To resolve the issues, a room temperature synthesis method has been explored. Previous works by Cravillon *et al.*^{17,18} and Pan *et al.*¹⁹ have

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demonstrated that the synthesis of ZIF-8 using highly diluted zinc salt and 2-MeIM in solvent can be successfully performed at room temperature, thus minimizing the energy consumption compared to the solvothermal and microwave-assisted solvothermal methods. Additional benefits of the room temperature method are a high product yield, smaller crystal size, low energy requirement, and short reaction time.

The ability to control the particle size of synthesized MOFs is one of the most interesting features of the material. By increasing the ligand-to-metal ratio, an excess of ligand would cover the crystal seed and limit the linkage with metal ions. Hence, crystal growth that was hindered by excess ligand would lead to smaller MOF particles.^{19,20} Another approach to control the particle size of produced MOF involves incorporating a modulating agent into the synthesis system that can act as a buffer for the ligands and ease the metal–ligand interaction. Consequently, rapid interaction between ligands and metal would promote smaller crystals.^{18,21–25} Among modulating agents, triethylamine (TEA) has been widely studied and shows good compatibility with various MOFs.^{2,26} However, limitations on TEA concentration exist since its basicity would induce the formation of unknown crystals.²³

Synthesis parameters such as the Zn^{2+} : 2-MeIM : solvent ratio, temperature, mixing rate, and reaction time and their control are some of the crucial and well-studied factors.^{2,17–19,27} However, previous studies on the influence of additives only focused on the particle size of the resultant ZIF-8.^{18,28} ZIF-8 studies have mainly focused on crystal formation in highly diluted zinc salt and 2-MeIM in solvent, while the effects of additives on ZIF-8 formation have not been investigated. Hence, the present work investigates the synthesis of ZIF-8 at room temperature, and the effect of reactant concentration was studied in order to minimize chemical usage. Various concentrations of TEA in the reaction mixture were used to assist ZIF-8 formation. The influence of TEA concentration on ZIF-8 particle size was investigated. The effects of TEA concentration on the morphology, crystallinity, thermal stability, and surface area of synthesized ZIF-8 were also investigated and are discussed.

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (99% purity) was purchased from Alfa Aesar Chemicals. 2-MeIM (99% purity) and TEA (99.5% purity) were purchased from Sigma-Aldrich Chemical Co., Inc. All chemicals were used without further purification.

2.2. Synthesis of ZIF-8

The synthesis of ZIF-8 has been previously described in the literature,²⁸ and a few changes were implemented in our experiments to improve the yield and reduce the chemical usage. Briefly, a molar ratio of 1 : 6 : 500 of $\text{Zn}(\text{NO}_3)_2$: 2-MeIM : H_2O was used for this study. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2 g, 6.72 mmol) was dissolved in 20 wt% total deionized water (12.11 g). At the same time, 2-MeIM (3.312 g, 40.43 mmol) was dissolved in the remaining deionized water (48.45 g). Ratios of TEA added

Table 1 Composition of TEA/total molar ratio for ZIF-8 synthesis

Sample	TEA/Total molar ratio	TEA volume (ml)
A0	0	0
A1	0.001	0.5
A2	0.002	1.0
A3	0.003	1.5
A4	0.004	2.0
A5	0.005	2.5
A6	0.006	3.0
A7	0.007	3.5

to 2-MeIM solution were relative to the total molar amount of synthesis solution (sample A0) (Table 1). Both solutions were vigorously stirred at room temperature. After 30 minutes, the product was collected by centrifugation (3000 rpm for 30 minutes) and then washed several times with deionized water before drying (60 °C for at least 12 hours). The mass yield of the product was calculated using eqn (1).

$$\text{Yield (\%)} = \frac{m_{\text{actual}}}{m_{\text{theoretical}}} \times 100\% \quad (1)$$

where m_{actual} represents the mass of ZIF-8 produced (g), and $m_{\text{theoretical}}$ represents the theoretical mass of ZIF-8 based on stoichiometry (g).

2.3. Characterizations

X-ray diffraction (XRD) analysis was performed using a diffractometer (Siemens D5000) with $\text{CuK}\alpha$ radiation and wavelength (λ) of 1.54 Å to identify the crystallinity of ZIF-8.²⁸ Attenuated total reflectance infrared (ATR-IR) spectroscopy analysis using a Universal ATR (UATR, Single Reflection Diamond for the Spectrum Two) (PerkinElmer, L1600107) was used to observe the functional group of synthesized ZIF-8s. A transmission electron microscope (TEM) (JEOL, JSM-6701FJEOL 1230) was used to observe the macrostructures of the ZIF-8. Samples were prepared by dispersing ZIF-8 powder into methanol. A drop of methanol was used for the dispersion of ZIF-8 onto carbon-coated copper grids operating at 300 kV. A single point N_2 adsorption reading was taken at 130 °C for 1 h. The apparent surface area was calculated using the BET equation. A thermogravimetric analyzer (TGA) (Mettler Toledo, TSO800GC1) was used to characterize the thermal stability of the prepared samples. The TGA records the weight changes of a sample when it is continuously heated. The samples were heated from 30 to 800 °C at a rate of 10 °C min^{-1} under a N_2 atmosphere with a nitrogen flow rate of 20 ml min^{-1} . ^1H NMR spectroscopy was performed with a Bruker Avance 400 spectrometer using dimethyl sulfoxide (DMSO) as the solvent to ascertain chemical bonding and structure of the impurities.

3. Results and discussion

The mass yields of the products synthesized with various TEA : 2-MeIM ratios are shown in Table 2 and demonstrate a high production yield. Previously reported ZIF-8 synthesis *via*

Table 2 Properties of prepared ZIF-8s

Sample	Approximate yield (%)	Particle size (nm)	BET surface area ($\text{m}^2 \text{g}^{-1}$)
A4	90	287.78 ± 86.01	491.54
A5	90	162.34 ± 57.02	420.83
A6	90	133.69 ± 41.21	418.44
A7	85	141.12 ± 46.65	428.57

the room temperature aqueous system produced resultant yields of up to 80%,¹⁹ while 100% has been reported for the room temperature organic solvent method.²⁹ It should be noted that syntheses conducted by both research groups used $\text{Zn}(\text{NO}_3)_2 : 2\text{-MeIM}$ ratios ranging from 1 : 23 to 1 : 70. Interestingly, high yields of ZIF-8 were obtained throughout this work with a low $\text{Zn}(\text{NO}_3)_2 : 2\text{-MeIM}$ ratio. The inclusion of TEA in the aqueous system eased the interaction between Zn^{2+} , and deprotonated 2-MeIM produced high yields of ZIF-8.

3.1. X-ray diffraction analysis

Fig. 1 shows the XRD pattern of ZIF-8 synthesized using different TEA ratios. The XRD patterns of the samples have been well established in the previously reported work.¹⁹ The first attempt to synthesize ZIF-8 was performed without any TEA additive (sample A0), and the solution instantly turned cloudy upon the mixing of reactants. This observation indicated that rapid nucleation occurred in the solution.³⁰ However, the absence of ZIF-8 characteristic peaks for planes {110}, {200}, {211}, {220}, {310}, and {222} suggested that a low TEA/total molar ratio (0 to 0.002) was not favorable for the synthesis of ZIF-8 due to (1) the intergrowth hindrance at a low ligand-to-metal-salt ratio,^{30,31} (2) insufficient amount of 2-MeIM in the solution, which led to a low reaction rate and hindered crystal growth, thus hampering the formation of ZIF-8, and (3) insufficient TEA concentration to deprotonate 2-MeIM to assist in the

ZIF-8 formation. Interestingly, characteristic peaks for planes {110}, {200}, {211}, and {222} appeared as the TEA/total molar ratio was increased to 0.003 (sample A3) at $2\theta = 7.30, 10.35, 12.70,$ and $18.00,$ respectively, suggesting that the formation of ZIF-8 was successful. However, additional peaks were also observed, indicating that the ratio of 0.003 was still insufficient to form pure-phase ZIF-8. The phenomenon can be probably be ascribed to (1) deprotonation of 2-MeIM that began to take place, resulting in only the formation of the intermediate ZIF-8 phase, or (2) only a small amount of ZIF-8 formed, and the XRD reflection was clouded with a large amount of intermediate ZIF-8 crystal.

As the TEA/total molar ratio increased to 0.004 (sample A4), peaks for planes {110}, {200}, {211}, {220}, {310}, and {222} can be clearly seen. No additional peaks were observed, hence suggesting that pure phase ZIF-8 had been successfully formed, and thus implying that a minimum TEA/total molar ratio of 0.004 is necessary to form ZIF-8. For higher TEA/total molar ratios, similar patterns were also observed. The results indicated that the formation of pure phase ZIF-8 can be achieved regardless of TEA loading after exceeding the minimum TEA/total molar ratio. This phenomenon was due to the deprotonation of 2-MeIM to produce more reactive sites on the ligands to facilitate the reaction with Zn^{2+} . Consequently, nucleate formation was initiated, and rapid crystal growth commenced, which eventually led to the formation of a framework. Therefore, pure phase ZIF-8 was successfully synthesized in a reaction time of less than 30 minutes at a relatively low molar ratio of ligands to metal salts with a high product yield that was comparable to that of a previous study.¹⁹ However, further increase of the TEA/total molar ratio of 0.007 led partially to the formation of an impure component (Fig. 2a). The formation of this impure component lowered the mass yield to approximately 85%.

Biemmi *et al.*²³ suggested that the introduction of excess base-type additive to the synthesis solution would introduce hydroxyl (-OH) groups on the organic ligands, which would later react with metal salts, thus leading to the formation of different compounds. ATR-IR analysis of the impure component (Fig. 2b) revealed a broad -OH stretch at $3550\text{--}3200 \text{ cm}^{-1}$ in the compound, hence implying the possibility of the formation of an impure component, as observed in this study. The XRD pattern of the impure component is presented in Fig. 2c, and it behaves distinctly from the pure phase ZIF-8 pattern. The disoriented peak order of the impure component revealed that excess TEA would lead to the formation of amorphous species. Further investigation was carried out by dissolving the impure component in dimethyl sulfoxide (DMSO) and evaluating it *via* ^1H NMR to identify a possible structure of the impure component (Fig. 2d). A peak corresponding to $-\text{CH}_3$ was present at $\delta = 2.51 \text{ ppm}$, and $-\text{OH}$ at $\delta = 3.97 \text{ ppm}$ (broad single peak, merged with DMSO water). An aromatic $-\text{H}$ appeared at $\delta = 7.05 \text{ ppm}$, and the lack of a $-\text{NH}$ group may be due to the presence of moisture. Hence, excess TEA added to the synthesis solution would hydroxylate 2-MeIM and would not assist in the formation of ZIF-8.

Although the crystallinity of prepared samples remained unchanged as the TEA/total molar ratio increased above the

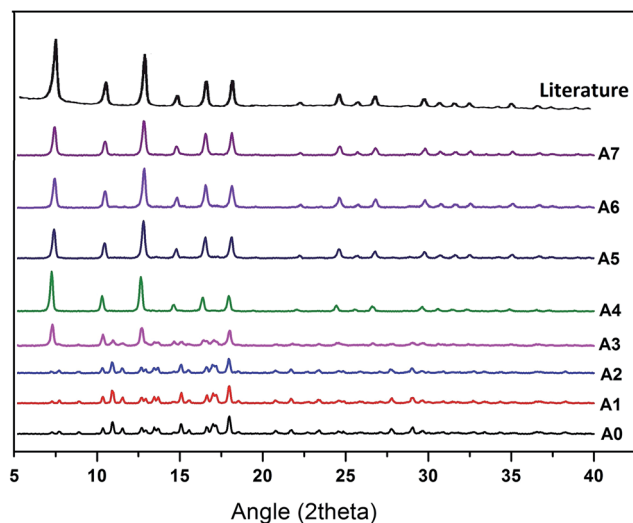


Fig. 1 XRD pattern of ZIF-8 with different TEA concentrations.

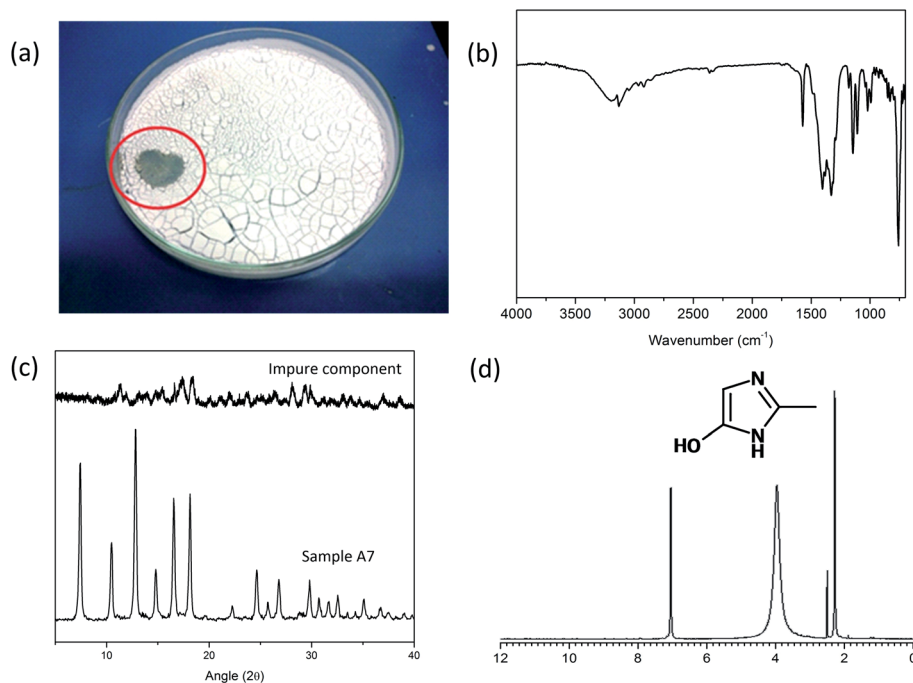


Fig. 2 Unknown component partially forms for sample A7: (a) visible to the naked eye, and characterized via (b) ATR-IR, (c) XRD, and (d) ^1H NMR.

minimum value of 0.004, the ZIF-8 planes began to shift towards a higher diffraction angle. Fig. 3 shows the low-angle XRD patterns of the prepared samples in which the characteristic planes $\{110\}$ at $2\theta = 7.35^\circ$ were compared.⁸ It can be observed that the plane $\{110\}$ peak of ZIF-8 prepared at TEA/total mole = 0.004 exists at a lower angle compared to the simulated data, and a further increase in the ratio led to the slight shifting of planes $\{110\}$ towards a higher angle. It is expected that crystal irregularities were induced through the fast reaction between Zn^{2+} and 2-MeIM, where a high uniform strain and stacking faults were experienced by the particles,

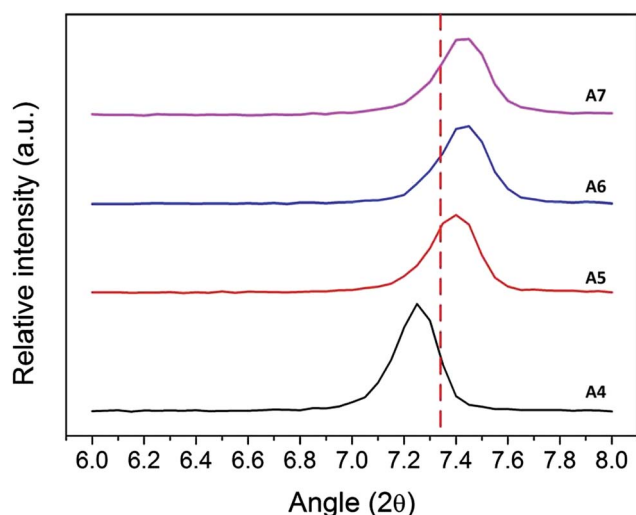


Fig. 3 Low angle XRD of prepared samples. Dotted line represents $2\theta = 7.35^\circ$ for plane $\{110\}$ of simulated ZIF-8.⁸

thus resulting in a shift of the XRD peak to a higher angle.^{32,33} Further understanding of the influence of the TEA/total molar ratio on the crystal irregularities of the prepared ZIF-8s was obtained through TEM analysis and will be discussed in the following section.

Gross *et al.*²⁸ reported that the inclusion of TEA in the aqueous synthesis system for ZIF-8 would reduce the 2-MeIM usage. A metal : ligand ratio of 1 : 4 to 1 : 16 is sufficient to obtain pure phase ZIF-8 with TEA embodied in the system, whereas a metal : ligand ratio of 1 : 70 to 1 : 200 is required without a modulating agent,¹⁹ implying the impact of TEA on ZIF-8 formation. The author also suggested that a molar ratio of ligands/TEA > 0.5 in a 2255 molar ratio of water is necessary to provoke ZIF-8 formation in order to minimize the 2-MeIM requirement. However, the current study indicated that if ligands/TEA > 0.3 in only a 500 molar ratio of deionized water, this would be sufficient to form pure phase ZIF-8 in an aqueous room temperature system. Thus, pure phase ZIF-8 was obtained in a limited quantity of solvent while maintaining high product yield.

3.2. Transmission electron microscopy analysis

The effects of TEA/total molar ratio on the particle size and morphology of ZIF-8 were further evaluated using TEM (Fig. 4). Overall, all ZIF-8 samples showed a rhombic dodecahedron shape within a nanoscale range. This observation implied that nanosized ZIF-8 can be produced with a low 2-MeIM ratio ($2\text{-MeIM}/\text{Zn}^{2+} < 4$) and the addition of TEA at room temperature.^{19,28,34} A nanorod-like morphology had been previously reported²⁹ but it was not observed in these experiments, suggesting a stable phase of ZIF-8 formation. At the minimum TEA/

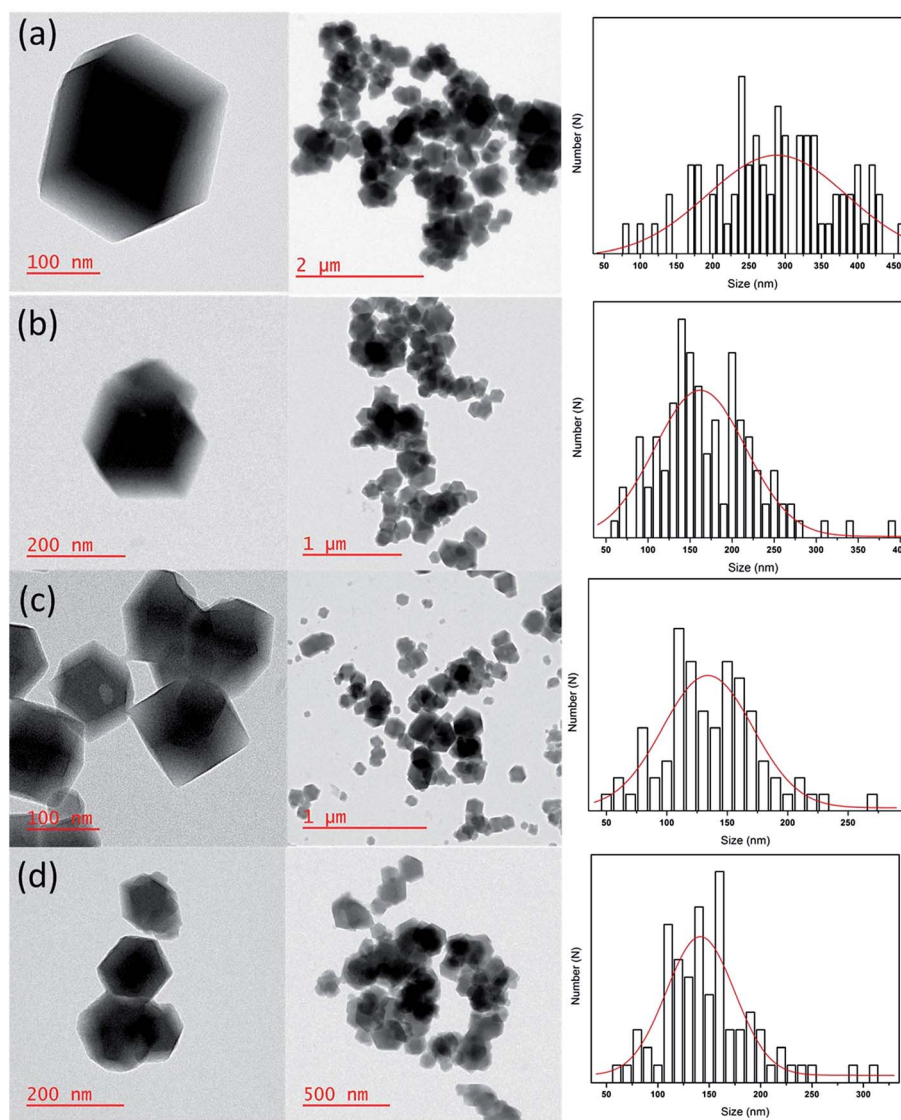


Fig. 4 TEM images for samples (a) A4, (b) A5, (c) A6, and (d) A7 with their size distribution (the red line represents a Gaussian fit).

total molar ratio of 0.004, the particle size of ZIF-8 was approximately 288 nm (Fig. 4a). Upon increasing the TEA/total molar ratio above the minimum value, from 0.005 to 0.006, the particle size of ZIF-8 gradually decreased from approximately 162 nm (Fig. 4b) to 134 nm (Fig. 4c). This phenomenon was expected due to the high TEA/total molar ratio that could induce more nuclei formation through the deprotonation of 2-MeIM. The fast reaction between Zn^{2+} and deprotonated 2-MeIM prompted the formation of small particles.^{21,26,28} As the TEA loading increased, smaller particle size was observed. However, increasing the TEA/total molar ratio up to 0.007 led to the formation of larger particles (Fig. 4d). The high reaction rate rendered by the deprotonated 2-MeIM might lead to an undesirable competition between MeIM^- for Zn^{2+} sites, resulting in the formation of larger crystals.^{18,29}

Structural defects on the particle surface of prepared ZIF-8s are shown in Fig. 5. Structural defects were observed for all samples, which indicates that the TEA/total molar ratio had no

influence.¹⁸ Because other synthesis parameters were kept constant, these structural defects can be related to the fast crystal formation. The crystal irregularities could be induced by crystal shearing as the solution concentration increased.^{23,30} Therefore, it is reasonable to deduce that the rapid crystal formation resulted from highly concentrated synthesis solution, and the crystal irregularities resulted from the addition of TEA.

3.3. Attenuated total reflected infrared spectroscopy analysis

Fig. 6 shows the ATR-IR spectra of samples A4-A7. Most of the spectra are related to the vibrations of the imidazole units and thus can be described based upon bond origin. It was observed that the spectra of samples A4-A7 are in agreement with other studies.^{8,11} Samples A4-A7 showed absorption bands between 3135 and 2929 cm^{-1} that can be attributed to the aromatic and the aliphatic C-H stretch of the imidazole, respectively. The

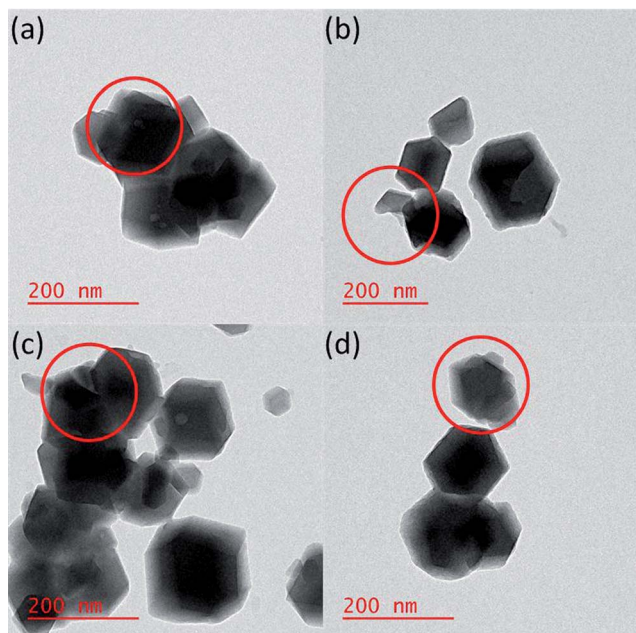


Fig. 5 Crystal irregularities (red circle) on ZIF-8 prepared with TEA/total molar ratios of (a) 0.004, (b) 0.005, (c) 0.006, and (d) 0.007.

characteristic peak at 1584 cm^{-1} was due to $\text{C}=\text{N}$ stretching, whereas bands between $1350\text{--}1500\text{ cm}^{-1}$ can be assigned to the entire ring stretching.³⁵ The peak at 450 cm^{-1} shows the distinct stretching vibration of $\text{Zn}\text{--}\text{N}$. The absence of amine and hydroxyl functional groups in the prepared ZIF-8s (with the exception of the unknown crystal) indicated the presence of an amine additive at the TEA/total molar ratio from 0.004 to 0.007 that did not react with 2-MeIM¹¹ and only served as a deprotonation agent.

The resultant impure component partially formed as the TEA/total molar ratio increased to 0.007, while no products were formed at lower ratios. This observation demonstrated the important roles of TEA concentration in influencing ZIF-8

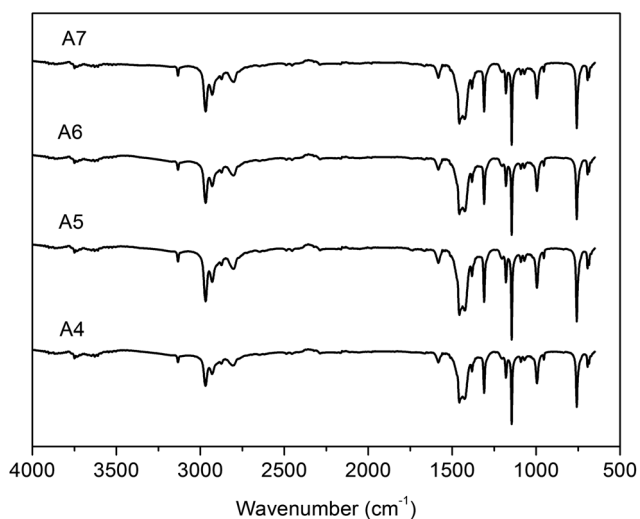


Fig. 6 ATR-IR spectrum of synthesized ZIF-8s.

synthesis. The formation of ZIF-8 through room temperature synthesis can be generally classified into three categories, as depicted in Fig. 7. As shown in Fig. 7a, although rapid nucleation occurred at a TEA/total molar ratio below 0.004, insufficient TEA was available to deprotonate 2-MeIM, and hence, no product was formed. As the TEA/total molar ratio increased to the range of 0.004–0.007, the formation of pure phase ZIF-8s as illustrated in Fig. 7b suggested that deprotonation of 2-MeIM (Fig. 7d) induced faster crystal growth, which then resulted in impure crystal formation. When excessive TEA was added, the deprotonation of ligands also simultaneously occurred. However, partially formed impure crystals associated with the presence of the --OH group implied that excessive dissociated water also reacted with the ligands, according to the route illustrated in Fig. 7c.

3.4. Thermogravimetric analysis

The thermal stability of the prepared ZIF-8 samples was characterized by TGA analysis under an N_2 atmosphere as shown in Fig. 8a. The initial weight loss for all samples occurred at $100\text{ }^\circ\text{C}$ and was attributed to the evaporation of trapped solvent (deionized water).^{2,17,36} Secondary weight losses were observed at approximately $250\text{ }^\circ\text{C}$ and were associated with the carbonization of guest molecules (2-MeIM) in ZIF-8 pores.⁸ The third weight losses occurred at approximately $600\text{ }^\circ\text{C}$ for all prepared ZIF-8s and corresponded to the decomposition of the organic linkers and ZIF-8 crystal. Further investigation was focused on sample A6 because it provided the minimal particle size compared to the other samples. The XRD patterns of sample A6 heated in open air at $300\text{ }^\circ\text{C}$, $400\text{ }^\circ\text{C}$, $500\text{ }^\circ\text{C}$ and $600\text{ }^\circ\text{C}$ are presented in Fig. 8b. Peak intensification was observed, as sample A6 heated at $300\text{ }^\circ\text{C}$ indicated the absence of guest molecules that could cause destructive interference in the diffracted beams. At $400\text{ }^\circ\text{C}$, peak disappearance suggests that the ZIF-8 structure was collapsed, resulting in the formation of amorphous solids,³⁷ while oxidation of Zn^{2+} at $500\text{ }^\circ\text{C}$ and $600\text{ }^\circ\text{C}$ led to the formation of zinc oxide (ZnO). Contradictory data between the TGA and XRD techniques implies that the prepared ZIF-8s were able to retain their structure up to $600\text{ }^\circ\text{C}$ in an inert atmosphere, whereas they could retain their structure only at $300\text{ }^\circ\text{C}$ in the open air, due to framework sensitivity towards moisture and/or oxygen.¹⁹ It was found that there was no significant impact on the thermal stability of ZIF-8 by the incorporation of various TEA/total molar ratios during the synthesis.

3.5. BET analysis

The surface area of all ZIF-8s samples is presented in Table 2, and the values are far smaller than those previously reported. For example, Park *et al.*⁸ reported a surface area of $1947\text{ m}^2\text{g}^{-1}$ while Cravillon *et al.*¹⁸ reported a surface area of $1617\text{ m}^2\text{g}^{-1}$. The decreased surface areas measured in this report resulted from guest molecule entrapment in the ZIF-8 pores that reduced the BET surface area.²⁸ Sample A6 was heated at $300\text{ }^\circ\text{C}$ in open air in an attempt to evacuate the guest molecules. The BET surface area increased to $1182.87\text{ m}^2\text{g}^{-1}$ in the heated sample, suggesting that there was more accessible pore

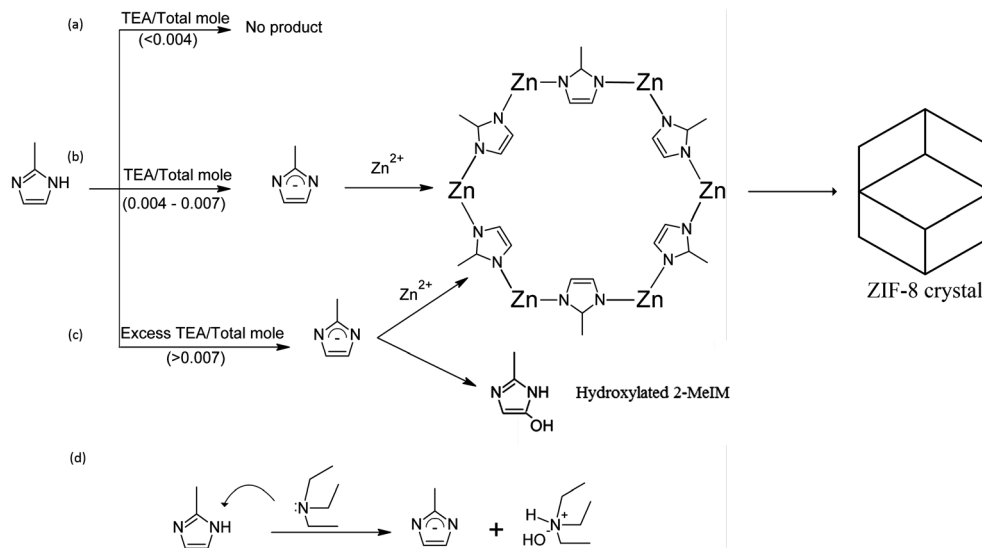


Fig. 7 A schematic illustration showing the influence of TEA concentration on ZIF-8 formation.

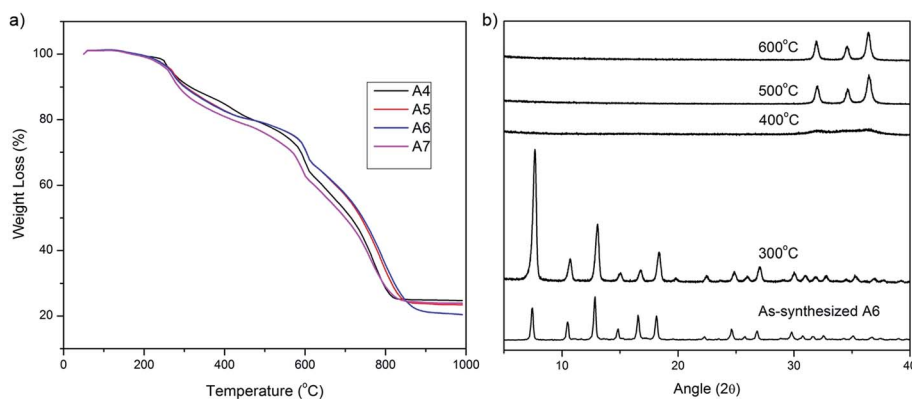


Fig. 8 Thermal stability of prepared ZIF-8s: (a) weight loss profile of ZIF-8 and (b) XRD pattern of sample A6 heated in open air at elevated temperature.

availability due to the carbonization of the guest molecules that had occurred.

4. Conclusions

ZIF-8 was successfully synthesized at room temperature using a low $\text{Zn}^{2+} : 2\text{-MeIM} : \text{H}_2\text{O}$ ratio with TEA as an additive, and limited chemical usage was sufficient for synthesis while maintaining high product yield. The presence of TEA during ZIF-8 synthesis is crucial for promoting crystallization at a low molar ratio of metal : ligand : solvent. From this study, the minimum TEA/total molar ratio required for the formation of ZIF-8 was determined to be 0.004. The ZIF-8 particle size decreased from approximately 288 to 133 nm as the TEA/total molar ratio increased from 0.004 to 0.006. The increase in the TEA/total molar ratio did not affect the crystallinity, but did result in crystal irregularities. The TEA/total molar ratio of 0.006 is suitable to produce a high yield of ZIF-8, with a particle size of approximately 133 nm. It can be concluded that TEA plays an

important role in assisting crystal formation and controlling the particle size of ZIF-8 when a relatively low molar ratio of ligand/metal salt is used in the synthesis. The lowered BET surface area of synthesized ZIF-8s that was observed throughout the study resulted from guest molecules occupying its pores. Thus, removal of guest molecules by heat treatment is necessary to activate ZIF-8.

Acknowledgements

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