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

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ABSTRACT

In this study, zeolitic imidazole framework (ZIF-8) was prepared and the 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 aqueous room temperature approach with relatively low molar ratio of ligands to metal salts. Increasing concentration of TEA/total mole ratio from 0.004 to 0.007 prompted the formation of pure phase ZIF-8, whereas TEA/total mole ration below 0.004 did not result in the yield of ZIF-8. The particle size of ZIF-8 produced was decreased from ~288 to ~133 nm with the increasing TEA/total mole ratio, with exception of TEA/total mole ratio = 0.007. However, excess TEA/total mole ratio alters the 2-MeIM chemistry and partially forms hydroxylated 2-MeIM. Thus, this study shows that the TEA concentration plays an important role in assisting the crystal formation and controlling the particle size of ZIF-8 in relative low molar ratio of ligands to metal salts, with maximum TEA/total mole ratio at 0.006. Through this finding, the proposed procedure provides limited amount of chemicals usage with high product yield to obtain pure phase nanoscale ZIF-8.

1.   Introduction

Metal-organic frameworks (MOFs) are crystalline compounds consisting of metal ions and secondary building unit or organic ligands. Interesting characteristic of MOF such as high micro-pore volume, large pore sizes, high crystallinity and a high metal contents are to achieve active sites, are some of the key features possessed by this new and emerging class of porous material [1]. Large surface area of MOF gives advantages over other porous materials like activated carbon and zeolite. Previous researchers have synthesized MOF with high Brunauer–Emmett–Teller (BET) surface areas like MOF-5 (3000 m^2/g) [2], Co-MOF-74 (1314 m^2/g) [3], Mg-MOF-74 (1332 m^2/g) [4], which is much higher than that of commercial Zeolite Y (900 m^2/g), Zeolite Beta (710 m^2/g), ZSM-5 (425 m^2/g) and Modernite (500 m^2/g). Zeolite imidazole framework (ZIF), a novel class of MOF, has recently attracted vast attentions from the material scientists. Particularly, the exceptionally chemical and thermal stability of ZIF makes it capable of diverse applications. ZIF is a porous crystalline structure with metal atoms linked through N atoms by ditopic imidazolate ($C_3N_2H_3^-$ = Im). Metal-Im-Metal angle link together at 145°, coincide with Si-O-Si angle commonly found in zeolite [5-7]. The metal ions that are commonly used for the synthesis of ZIF are Zn^{2+} and Co^{2+}, meanwhile there are many types of imidazole-type linkers such as imidazole (IM), 1-methylimidazole (mIM), 1-ethylimidazole (eIM) and 2-nitroimidazole (nIM), can be suitably used for the 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 Zn^{2+} and 2-methylimidazole (2-MeIM), is one of the most investigated MOFs. The properties of ZIF-8 have been widely studied and showed very good chemical stability against polar and nonpolar solvents [8], reorientation of its structure at high pressure [9] and high mechanical strength [10].

ZIFs can be synthesized using different routes such as solvothermal process, microwave-assisted solvothermal and aqueous room temperature. Solvothermal process is commonly used to synthesize ZIFs [6-8, 10-13]. In general, highly diluted metal salt and organic ligands in organic solvent are mixed and heated in an autoclave at temperature up to 200°C. Despite its prevalence, this approach is time consuming and requires high energy consumption [1, 14]. On the other hand, microwave-assisted solvothermal method is less time consuming compared to solvothermal process [15]. Both solvothermal and microwave-assisted synthesis process 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 tackle the issue, room temperature synthesis method has been explored. Previous works by Cravillon *et al.* [17, 18] and Pan *et al.* [19] have demonstrated that the synthesis of ZIF-8 using highly diluted zinc salt and 2-MeIM in solvent can be successfully done at room temperature, thus minimizing the energy consumption compared to solvothermal and microwave-assisted solvothermal method. Additionally, room temperature method allows high product yield, smaller crystal size, low energy requirement and short reaction time.

Controlling particle size of produced MOF is one of the most interesting features of the materials. By increase the ligands to metal ratio, highly excess ligands would cover on the crystal seed and limit the linkage with metal ions. Hence, crystal growths were hindered by the excess ligands lead to smaller particle of produced MOF [19, 20]. Another approach to control particle size of produced MOF is by incorporating modulating agent into the synthesis system. Modulating agent act as buffering ligands and ease the metal-ligands interaction. Consequently, rapid interaction between ligands and metal would promote smaller crystal [18, 21-25]. Among modulating agent, triethylamine (TEA) has been widely studied and

shows good compatibility with various MOFs [2, 26]. However, limitations on TEA concentration exist since its basicity nature would induce formation of unknown crystal [23].

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

2.   Experimental

2.1.   Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) (99% purity) was purchased from the Alfa Aesar Chemicals. 2-MeIM (99% purity) and TEA (99.5% purity) was purchased from the Sigma-Aldrich Chemicals Inc. All chemicals were used without further purification.

2.2.   Synthesis of ZIF-8

The synthesis of ZIF-8 was described in literature [28] while some changes has been done to improve the yield and reduce the chemical usage. Briefly, molar ratio of 1:6:500 of

$Zn(NO_3)_2$:2-MeIM:H_2O was used for this study. $Zn(NO_3)_2.6H_2O$ (2g, 6.72 mmol) was dissolved in 20wt% of total deionized water (12.11g). At the same time, 2-MeIM (3.312g, 40.43 mmol) was dissolved in the remaining deionized water (48.45g). Ratios of TEA added to 2-MeIM solution were relative to total mole of synthesis solution (sample A0) (**Table 1**). Both solutions were mixed under vigorous stirring at room temperature. After 30 minutes, the product was collected through centrifugation (3000 rpm for 30 minutes) and then washed with deionized water for several times before drying (60°C for at least 12 hours). The mass yield of the product was calculated using equation (1).

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

Sample	TEA/Total mole 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

$$Yield(\%) = \frac{m_{actual}}{m_{theoritical}} \times 100\% \tag{1}$$

Where m_{actual} represent the mass of ZIF-8 produced (g) and $m_{theoritical}$ represent the theoretical mass of ZIF-8 based on stoichiometry (g).

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2.3.   Characterizations

X-ray diffraction (XRD) analysis was performed using the difractometer (Siemens D5000) with CuKα radiation and wavelength (λ) of 1.54Å. to identify the crystallinity of ZIF-8 [28]. Attenuated total reflectance infrared (ATR-IR) spectroscopy analysis using the Universal ATR (UATR, Single Reflection Diamond for the Spectrum Two) (Perkin Elmer, L1600107) was used to observe the functional group of synthesized ZIF-8s. Transmission electron microscope (TEM) (JEOL, JSM-6701FJEOL 1230) was applied 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 on carbon-coated copper grids operating at 300 kV. Single point N_2 adsorption was taken at 130°C for 1 h. The apparent surface area was calculated using the BET equation. Thermo-gravimetry analyzer (TGA) (Mettler Toledo, TSO800GC1) was used to characterize the thermal stability of the prepared samples. TGA records the weight changes of sample when heated continuously. The samples were heated from 30 to 800°C at the heating rate of 10°C min^{-1}under N_2 atmosphere with a nitrogen flow rate of 20 ml min^{-1}. ^{1}H NMR spectroscopy with Bruker Avance 400 spectrometer using dimethyl sulfoxide (DMSO) as a solvent to ascertain chemical bonding and structure of the impurities.

3.   Results and Discussion

The mass yield of the product synthesized with various TEA:2-MeIM ratio was tabulated in **Table 2** and showing high production yield. Previously reported ZIF-8 synthesis via room temperature aqueous system has resultant up to 80% [19] while 100% for room temperature organic solvent method [29]. It should be noted that both research group using

highly excess $Zn(NO_3)_2$:2-MeIM ratio (1:23 to 1:70). Interestingly, high yield of ZIF-8 were obtained throughout this work with low $Zn(NO_3)_2$:2-MeIM ratio. The inclusion of TEA into aqueous system would ease the interaction between Zn^{2+} and deprotonated 2-MeIM has resulted high yield of ZIF-8.

Table 2 Properties of prepared ZIF-8s.

Sample	Yield (%)	Particle Size (nm)	BET surface area(m^2/g)
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

3.1. *X-ray diffraction analysis*

Fig. 1 shows the XRD pattern of ZIF-8 synthesized using different TEA ratio. The XRD patterns of the samples that are well established with the previously reported work [19]. At first attempt to synthesize ZIF-8 was done without any TEA additive (sample A0). The solution turned cloudy instantly upon the mixing of reactants. This observation indicated 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 low TEA/total mole ratio (0 to 0.002) was not favorable for the synthesis of ZIF-8 due to 1) the intergrowth hindrance at low ligands to metal salts ratio [30, 31], 2) insufficient amount of 2-MeIM in the solution led to low reaction rate and hindered crystal growth has hampered 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 mole ratio was increased to 0.003 (sample A3) at 2θ = 7.30,

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10.35, 12.70, and 18.00, respectively, suggested that the formation of ZIF-8 was successful. However, additional peaks were also observed, indicating that the ratio of 0.003 were still insufficient to form pure-phase ZIF-8. The phenomenon can be probably ascribed to 1) deprotonation of 2-MeIM began to take place and only intermediate ZIF-8 phase was formed, or 2) only small amount of ZIF-8 formed and XRD reflection clouded with large amount of intermediate ZIF-8 formation.
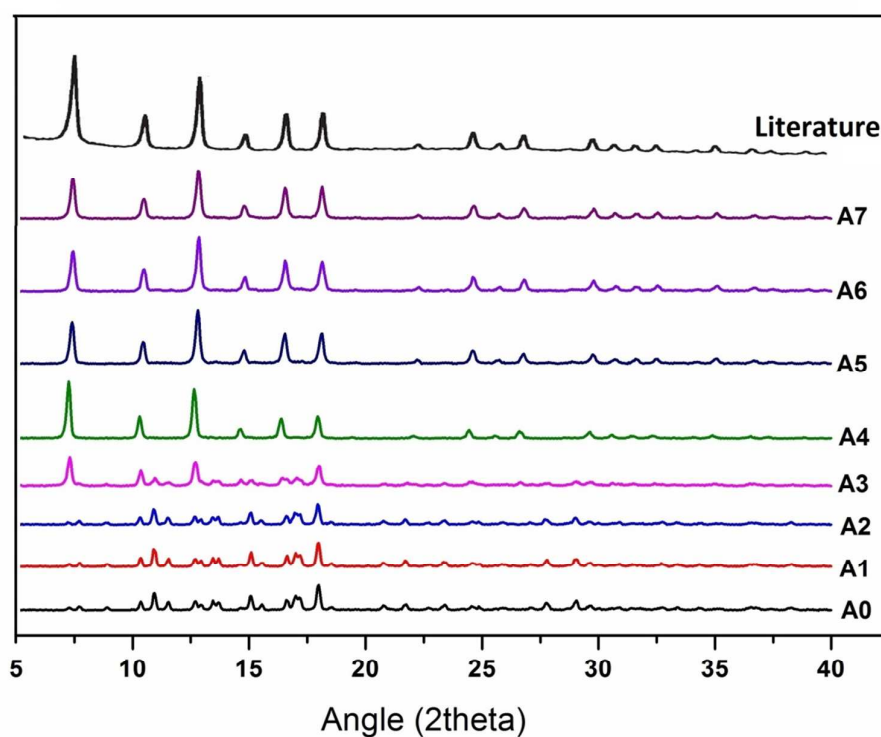
Fig. 1 XRD pattern of ZIF-8 with different TEA concentration.

As the TEA/total mole ratio increased to 0.004 (Sample A4), peak for planes {110}, {200}, {211}, {220}, {310}, and {222} can be clearly seen. No additional peaks was observed hence suggested that pure phase ZIF-8 has been successfully formed, thus implying that minimum TEA/total mole ratio at 0.004 is necessary to form ZIF-8. For higher TEA/total mole ratio, 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 minimum TEA/total mole 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, nucleates formation were initiated and rapid crystal growth commenced, which eventually led to framework formation. Therefore, pure phase ZIF-8 was successfully synthesized in less than 30 minutes reaction time at relative low molar ratio of ligands to metal salts while high product yield comparable to previous work [19]. However, further increase of the TEA/total mole ratio of 0.007 has partially led to the formation of impure component (**Fig. 2a**). The formation of this impure component has lowered the mass yield to ~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 in which the later reaction with metal salts will lead to the formation of different compounds. ATR-IR analysis of the impure component (**Fig. 2b**) showed the broad –OH stretch presence at 3550-3200 cm^{-1} in the compound, hence implied the possibility for the formation of impure component as observed in this study. The XRD pattern of the impure component is presented in **Fig. 2c** and behaves distinctly from pure phase ZIF-8 pattern. The disoriented peaks order by the impure component revealed that excess TEA would leads to formation of amorphous species. Further investigation was carried out by dissolving into dimethyl sulfoxide (DMSO) and evaluated via ^{1}H NMR to identify possible structure of the impure component (**Fig. 2d**). The peak corresponding to –CH$_3$ present at δ=2.51 ppm, –OH at δ=3.97 ppm (broad single peak, merged with DMSO water). The aromatic –H appeared at δ=7.05 ppm and –NH group was not detected may be due to moisture presence. Hence, excess TEA to the synthesis solution would hydroxylated 2-MeIM and would not assist the ZIF-8 formation.
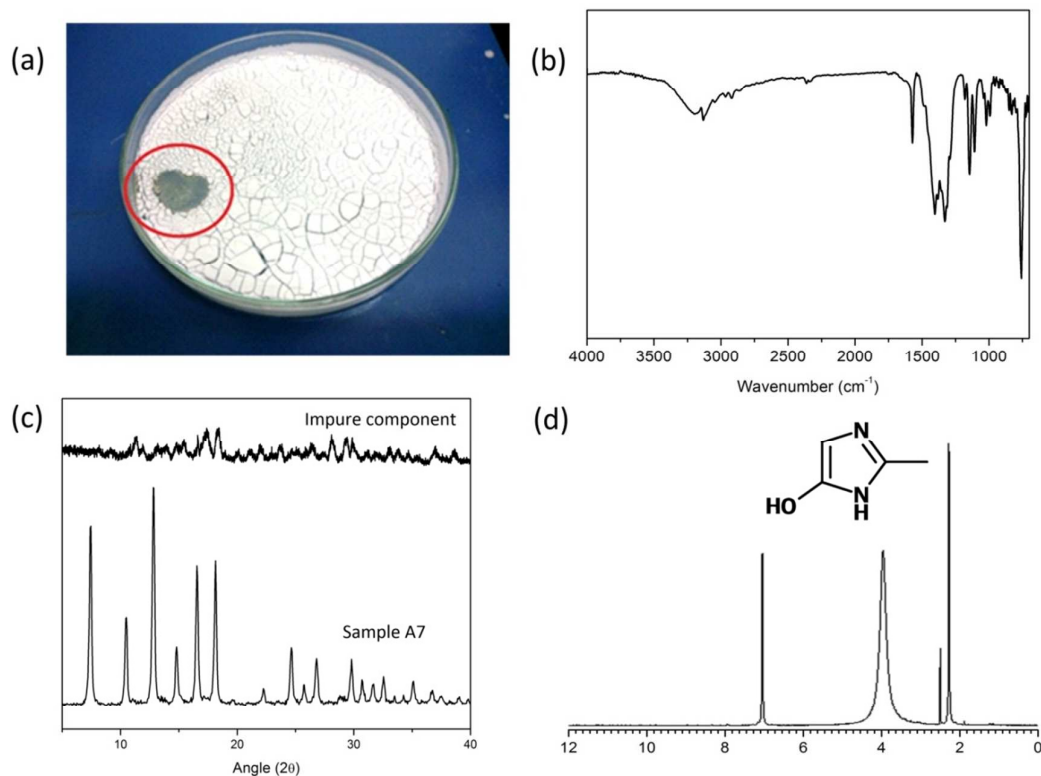
Fig. 2 Unknown component partially forms for sample A7: (a) visible through naked,

and characterized via (b) ATR-IR, (c) XRD and (d) ^{1}H NMR.

Although the crystallinity of prepared samples remains unchanged as the TEA/total

mole ratio increased above minimum value of 0.004, the ZIF-8s planes began to shift towards

higher diffraction angle. **Fig. 3** shows the low angle XRD patterns of the prepared samples in

which the characteristic planes {110} at $2\theta = 7.35°$ was compared [8]. It can be observed that

the plane {110} peak of ZIF-8 prepared at TEA/total mole = 0.004 exist at lower angle

compared to the simulated data, further increase in the ratio has led to slight shifting of planes

{110} towards higher angle. It is expected that the irregularities on the crystal were induced

through the fast reaction between Zn^{2+} and 2-MeIM where high uniform strain and stacking

faults were experienced by the particles thus resulted in shifting of XRD peak to higher angle

[32, 33]. Further understanding on the influence of TEA/total mole ratio on the crystal

irregularities of the prepared ZIF-8s was obtained through TEM analysis and will be discussed in the following section.
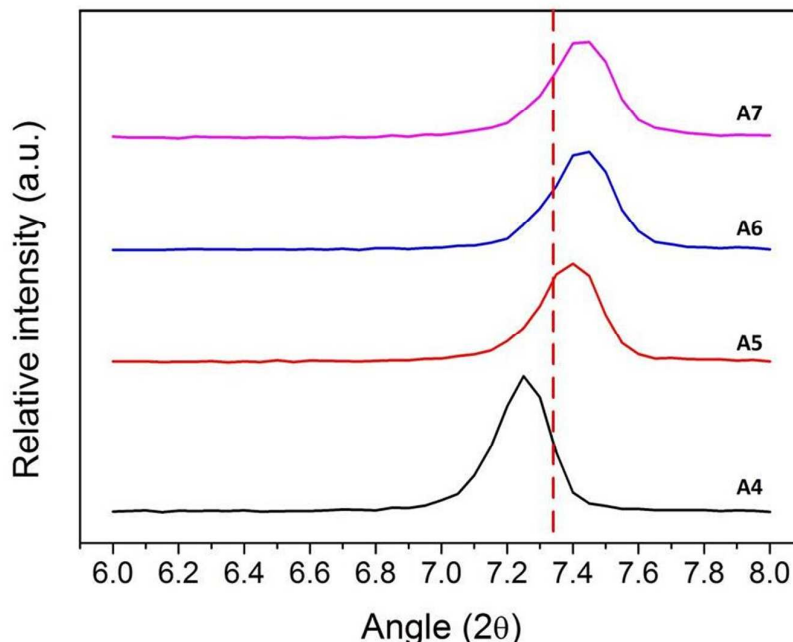

Fig. 3 Low angle XRD of prepared samples. Dotted line represent $2\theta = 7.35°$ for

planes {110} of simulated ZIF-8 [8]

Gross *et al.* [28] reported that the inclusion of TEA into aqueous synthesis system for ZIF-8 would reduce the 2-MeIM usage. Metal:ligands ratio of 1:4 to 1:16 is sufficient to obtain pure phase ZIF-8 with TEA embodied into the system, whereas metal:ligands ratio 1:70 to 1:200 is required without modulating agent [19], implying the impact of TEA on ZIF-8 formation. The author also suggest that the molar ratio of ligands/TEA>0.5 in 2255 molar ratio of water is necessary to provoke ZIF-8 formation in order to minimize the 2-MeIM requirement. However, this work presented that ligands/TEA>0.3 in only 500 molar ratio of deionized water is sufficient to formed pure phase ZIF-8 in aqueous room temperature

system. Thus, pure phase of ZIF-8 was obtained in limited amount of solvent while maintaining high product yield.

3.2.   Transmission electron microscopy analysis

The effects of TEA/total mole ratio on particle size and morphology of ZIF-8 were further evaluated using TEM (**Fig. 4**). Overall, all ZIF-8 samples showed rhombic dodecahedron shape within nano-scale range. This observation implied that nano-sized ZIF-8 can be produced with low 2-MeIM ratio (2-MeIM/Zn^{2+} < 4) with the addition of TEA at room temperature [19, 28, 34]. No nanorod-like morphology were observed as previously reported work [29] suggested stable phase of ZIF-8 formation. At the minimum TEA/total mole ratio of 0.004, particle size of ZIF-8 was about ~288 nm (**Fig. 4a**). Upon increasing TEA/total mole ratio above minimum value from 0.005 to 0.006, the particle size of ZIF-8 gradually decreasing from ~162 nm (**Fig. 4b**) to ~134 nm (**Fig. 4c**). This phenomenon is expected since high TEA/total mole ratio could induce more nuclei formation through deprotonation of 2-MeIM. The fast reaction between Zn^{2+} and deprotonated 2-MeIM prompted the formation of small particle size [21, 26, 28]. As the TEA loading increased, smaller particle size was observed. However, further increasing of TEA/total mole ratio up to 0.007 led to the formation of larger particle (**Fig. 4d**). The high reaction rate rendered by the deprotonated 2-MeIM might lead to the undesirable competition between MeIM$^-$ for Zn^{2+} sites hence resulted in the formation of larger crystal [18, 29].
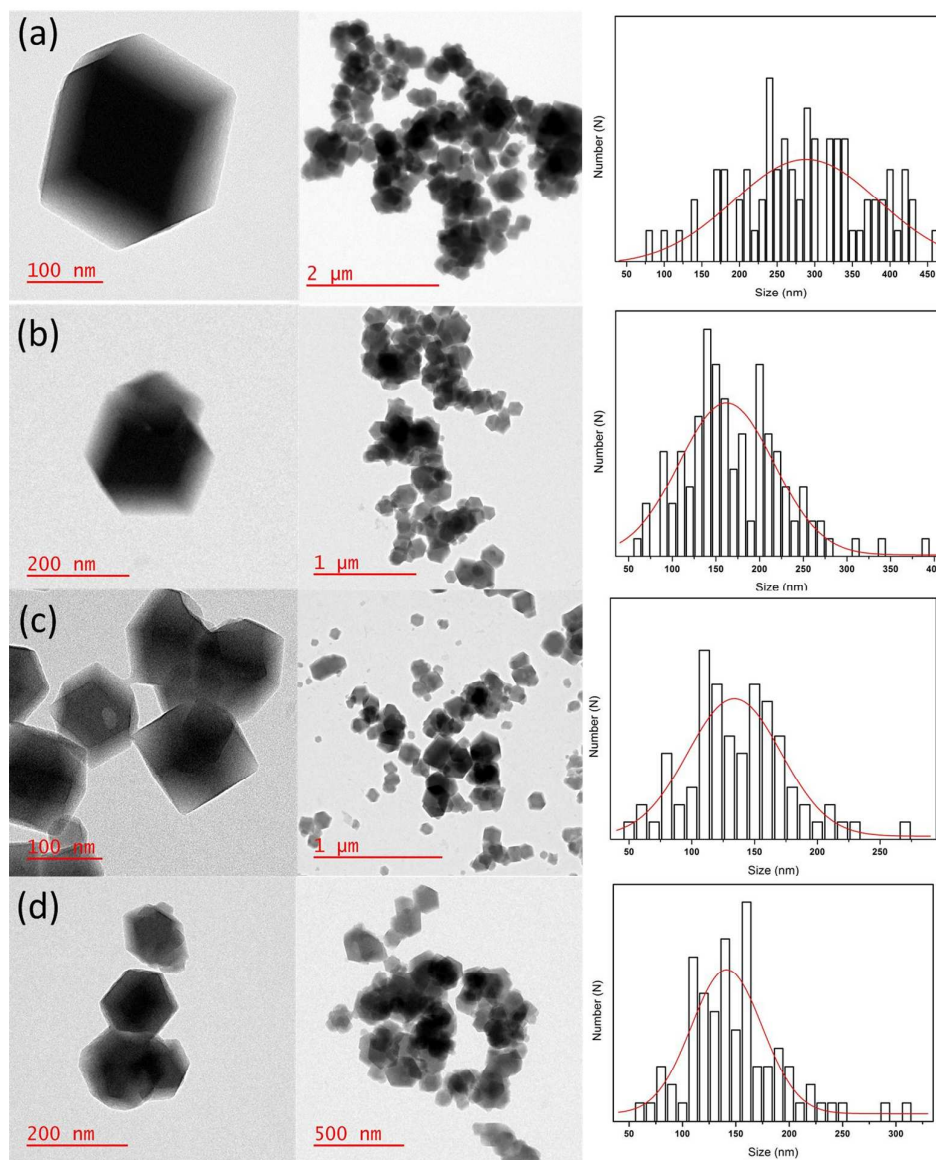
Fig. 4. TEM images for sample: (a) A4, (b) A5, (c) A6, and (d) A7 with its size distribution

(red line represent Gaussian fit).

Structural defects on the particle surface of prepared ZIF-8s were shown in **Fig. 5**. Structural defects were observed for all samples, disregards the influence of TEA/total mole ratio [18]. These structural defects can be related to the fast crystal formation since other synthesis parameters were kept constant. The crystal irregularities could be induced by crystal shearing as the solution concentration increased [23, 30]. Therefore, it is reasonable to

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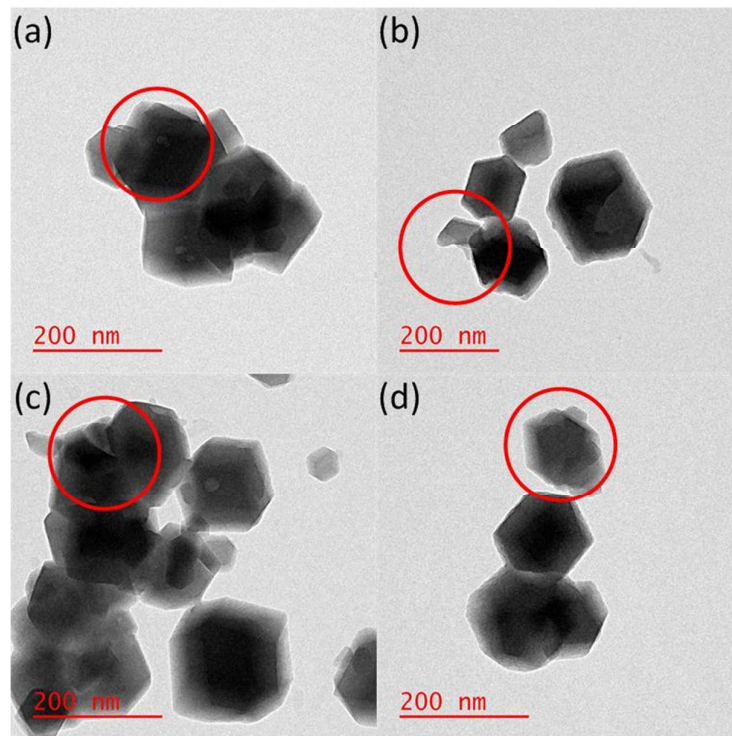
Fig. 5 Crystal irregularities (red circle) on ZIF-8 prepared at TEA/total mole ratio: (a) 0.004,

(b) 0.005, (c) 0.006, and (d) 0.007.

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

with the vibrations of the imidazole units and thus can be described based on the origin of the

bonds. It was observed that the spectra of samples A4-A7 are in well 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 characteristic peak at 1584 cm^{-1} was due to the C=N stretching mode, whereas bands

between 1350–1500 cm^{-1} can be assigned to the entire ring stretching [35]. The peak at 450

cm^{-1} shows the distinct stretching vibration of Zn-N. The absence of amine and hydroxyl functional group in the prepared ZIF-8s (with exceptional of the unknown crystal) indicated the presence of amine additive at TEA/total mole ratio from 0.004 to 0.007 does not react with the 2-MeIM [11] and only served as deprotonation agent.
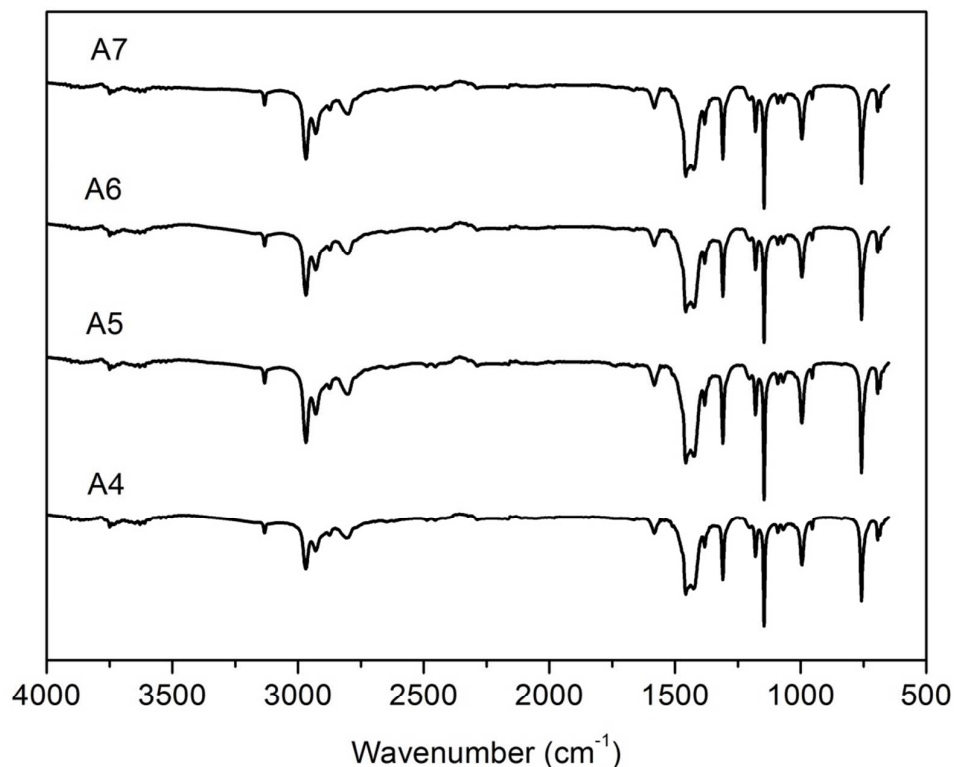
Fig. 6 ATR-IR spectrum of synthesized ZIF-8s.

The resultant impure crystal partially formed as the TEA/total mole ratio increased up to 0.007, while no products were formed at lower ratio. This observation showed the important roles of TEA concentration in influencing the ZIF-8 synthesis approach. The formation route 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 has occurred at TEA/total mole ratio below 0.004, insufficient TEA was available to deprotonate

2-MeIM, hence no product was formed. As TEA/total mole ratio increased to the range of 0.004 -0.007, formation of pure phase ZIF-8s as illustrated in Fig. 7b suggested the deprotonation 2-MeIM (**Fig. 7d**) to induce faster crystal growth which has resulted in the impure crystal formation. When excessive TEA was added, the deprotonation of ligands also occurred simultaneously. However, partially formed impure crystal associated with the presence of –OH group implied that excessive dissociated water also reacted with the ligands according to route **Fig. 7c**.
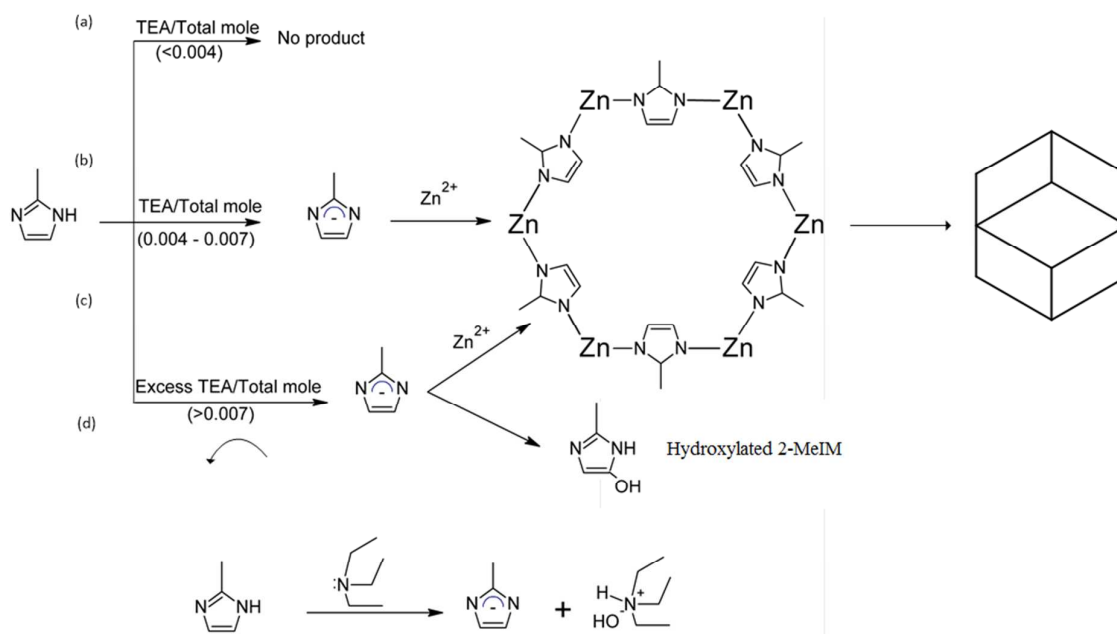

Fig. 7 The schematic illustration shows the influence of TEA concentration on ZIF-8 formation.

3. 4. *Thermo-gravimetric analysis*

The thermal stability of the prepared ZIF-8 samples was characterized with TGA analysis under N_2 atmosphere as shown in **Fig. 8a**. The first weight losses for all samples started at 100°C were attributed to evaporation of trapped solvent (deionized water) [2, 17, 36]. Second weight losses were observed around 250°C associate with carbonization of guest

molecule (2-MeIM) in ZIF-8 pores [8]. The third weight losses occurred at approximately 600°C for all prepared ZIF-8s can be corresponded to the decomposition of the organic linkers and ZIF-8 crystal. Further investigation was focused on Sample A6 since it provides minimal particle size compared to other samples. XRD pattern of Sample A6 heated in open air at 300°C, 400°C, 500°C and 600°C are presented in **Fig. 8b**. Peak intensification was observed as Sample A6 heated at 300°C indicates the absence of guest molecules to cause destructive interference in the diffracted beams. At 400°C, peaks disappearance suggest that ZIF-8 structure was collapsed and leads to amorphous solids [37] while oxidation of Zn^{2+} at 500°C and 600°C has led to formation of zinc oxide (ZnO). Contradictory between TGA and XRD data implies that the prepared ZIF-8s were able to retain its structure up to 600°C in inert atmosphere, while only at 300°C in open air due to framework sensitivity towards moisture and/or oxygen [19]. It was found that the incorporation of various TEA/total mole ratios during the synthesis gave insignificant impact on the thermal stability of ZIF-8.
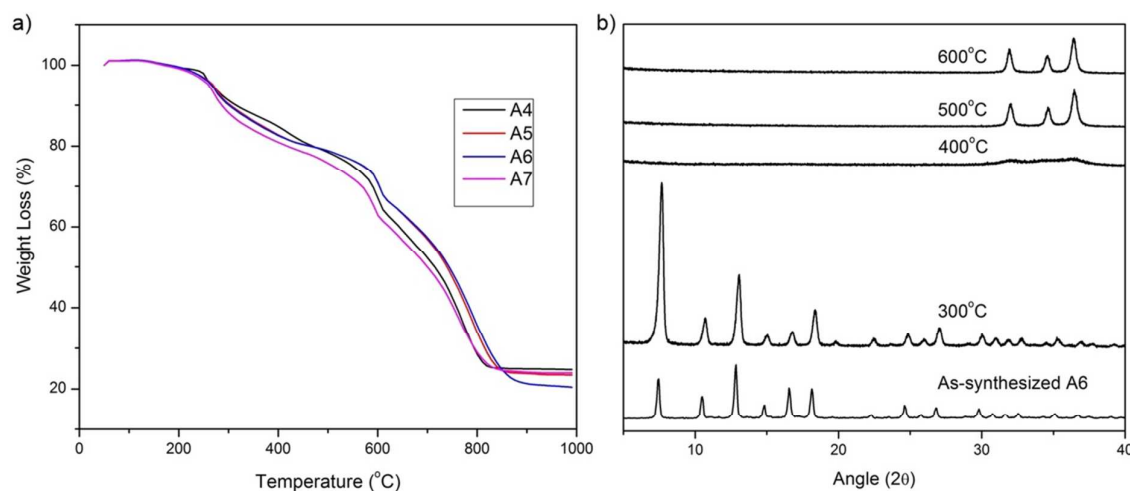
Fig. 8 Thermal stability of prepared ZIF-8s: (a) weight loss profile of ZIF-8 and (b) XRD pattern of Sample A6 heated in open air at elevated temperature.

3.5.   BET analysis

Surface area of all ZIF-8s samples was presented in **Table 2** somehow far smaller than previously reported. For example, Park *et al.* [8] reported the surface area of 1947 m^{2}g^{-1} while Cravillon *et al.* [18] reported surface area of 1617 m^{2}g^{-1}. Lowered surface area shown in this report were resulted from the guess molecule entrapment in the ZIF-8 pores have reduce the BET surface area [28]. Sample A6 then heated for 300°C in open air in attempt to evacuate the guest molecule. BET surface area increases to 1182.87 m^2/g for heated sample suggest more accessible pore availability as carbonization of guest molecule occurred.

4.   Conclusions

ZIF-8 was successfully synthesized at room temperature by using low Zn^{2+}:2-MeIM:H$_2$O ratio with TEA as an additive and limited chemicals usage were enough to synthesized while maintaining high product yield. Therefore, the proposed procedure for ZIF-8 synthesis is offerable. The presence of TEA during the ZIF-8 synthesis is crucial to promote crystallization at low metal:ligands:solvent molar ratio. From this study, the minimum TEA/total mole ratio required for the formation of ZIF-8 is determined as 0.004. The particle size decreased from ~288 to ~133 nm as the TEA/total mole increased from 0.004 to 0.006. The increase in TEA/total mole ratio did not affect the crystallinity, but has resulted in the crystal irregularities. The TEA/total mole ratio of 0.006 is suitable to produce high yield of ZIF-8, with particle size ~133 nm. It can be concluded that TEA played important role in assisting the crystal formation and controlling the particle size of ZIF-8 when relatively low of ligands/metal salts molar ratio was used in the synthesis. The lowered BET surface area of synthesized ZIF-8s were observed throughout the study were resulted from guest molecules occupying its pore. Thus, removal of guest molecule heat treatment is necessary to activate ZIF-8.

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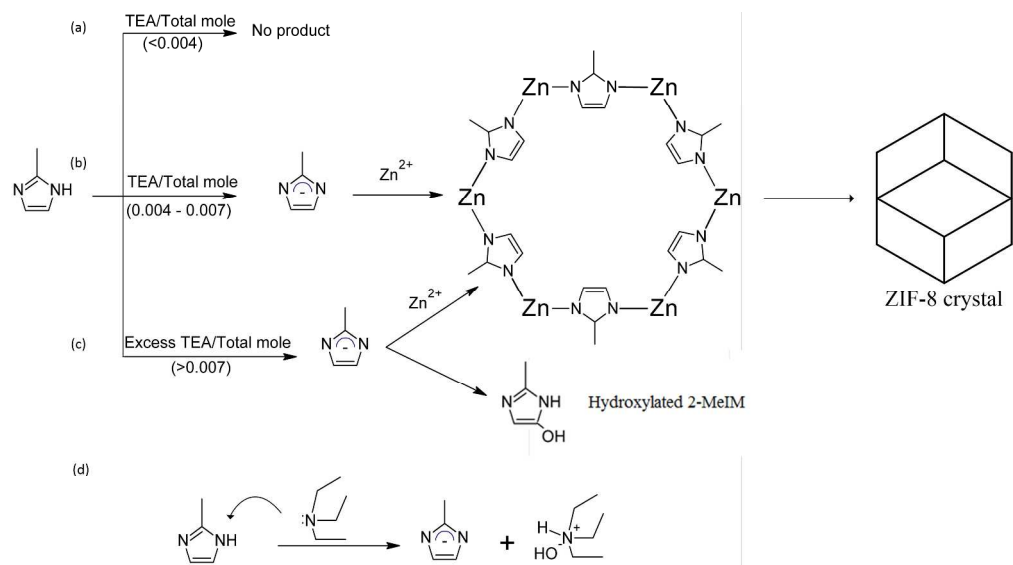
The schematic illustration shows the influence of TEA concentration on ZIF-8 formation.
282x157mm (300 x 300 DPI)