Room Temperature Synthesis and Characterizations of ZIF-8 Formation at Water-Fatty Alcohols Interface

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Abstract. In this study, Zn based ZIF-8 metal-organic framework were successfully synthesized in a green synthesis approach eliminating hazardous solvents and the need to use surfactant. In this method, the syntheses were done at room temperature followed by a simple hydrothermal method using palm oil derived fatty alcohols (POFDA) with 12 carbon chain in various solvents. The effect of several co-solvents on the formation of ZIF-8 materials and on morphology were investigated. The peak positions agreed well with the simulated ZIF-8. However, as the co-solvents became more polar the (011) peak shifted to a higher 2θ value suggesting that the interplanar d-spacing were reduced. The addition of fatty alcohols promoted the formation of MOF-5 and ZIF-8 at the water-fatty alcohols interfaces by viscosity lowering effect similar to those when using commercial surfactants. The mechanism of the formation was suggested to be similar to those at water-alcohol insoluble monolayer interfaces at the liquid-gas interaction. As the polarity of solvents increased, the miscibility of Zn²⁺ ions and deprotonated methylimidazole linkers were enhanced causing higher interaction with metal ions which resulted in a smaller unit cell. ZIF-8 exhibited elongated rhombic dodecahedron and truncated dodecahedron morphology at less than 100 nm.

1. Introduction

Metal-organic frameworks (MOFs) materials are a class of porous polymeric hybrid organic-inorganic materials that are rapidly expanding. MOFs consist of metal oxide interconnected by organic ligands to link them together resulting in a geometrically well-defined crystalline structure [1]. MOF materials have great potential as adsorbents and catalysts due to their extremely large surface area, well-ordered nanoporous structures and diverse surface functionalities from the organic-inorganic framework that were available for easy functionalization [2-4].

Furthermore, the metal-organic pore framework resulted in flexible and permanent porosity. Based on these excellent structure-related properties, MOF materials are prominent advanced porous materials for adsorptive removals by hydrogen bonding [5]. Adsorptive removal or separation field is the most important applications of MOF materials due to their ease of surface modifications to increase the hydrogen bonding sites desired for adsorption separation. Compared to other advanced
porous materials such as zeolites, activated carbons and mesoporous silica, MOF materials pore framework was versatile and flexible to accommodate several size and chemical reactivity of the adsorptive molecules. The surface structure of MOF materials can be easily modified by changing metal and organic precursors, impregnation or loading with enzymes and drugs, grafting of short functional ligands at metal or organic linkers as well as making composites with other nanostructured materials [6]. Abundance of hydrogen bonding sites in either pristine or modified MOF was necessary requirements for surface structure-related properties for adsorptive molecules to interact with the surface [5-8].

The adsorption of water by porous solids is important for many applications requiring capture and release of water especially in energy applications [9]. Microporous oxides such as zeolites are commercially used to capture water in applications as dehumidifiers. Temperature-triggered capture and release of atmospheric water is expected to be useful in climates where there is a large temperature difference between day and night. In most water capture applications, three criteria are important in the design of a viable porous material [10]. First, the pore filling or condensation of water into the pores of the solid must occur at low relative pressure (relative humidity) and exhibit a steep uptake behavior. The former is important because water is being captured from media where it is present at low concentrations, and the latter is related to the working capacity of the material [10, 11].

On the other hand, zeolitic imidazolate frameworks (ZIF-8) synthesized using Zn or Co metal ions are the extension of metal organic framework MOF-5 exhibited higher hydrostability and chemical stability [12]. ZIF-8 structure was cubic I-43m space group analogous to zeolites due to metal-imidazolate-metal (M-I-M) framework that was similar to Si-O-Si chemical bond in zeolite built upon 4 connected nets of tetrahedral units wherein lies the metal ions that are linked through N atoms in ditopic imidazolate anions [7]. Current synthesis method of both MOF-5 and ZIF-8 widely employed solvothermal method with the use of surfactants and corrosive solvents such as chloroform and dimethylformamide (DMF) [5-8].

Thus, in this paper we report for the first time a simple approach combining both room temperature mixing followed by low temperature hydrothermal treatment of MOF-5 and ZIF-8 using palm oil derived fatty alcohols (PODFA) as replacement to surfactants with water as the green solvent. In order to study the effect of co-solvents with different polarity on formation of MOF materials at water-fatty alcohol interfaces, the co-solvent were changed accordingly.

2. Experimental Procedure

ZIF-8 were synthesized using green approach employing PODFA, water, short-chain alcohols while eliminating the use of trimethylamine (TEA). The co-solvents were needed to promote stability in the “pre-Ouzo” region for a surfactantless microemulsion [13].

2.1 Materials and Methods

Zinc (II) nitrate hexahydrate (>99%, Zn(NO$_3$)$_2$.6H$_2$O) were purchased from Sigma Aldrich, ethanol (99.8%, C$_2$H$_5$OH), 2-Methylimidazole (>99%, 2-MIM) were purchased from Merck. Palm oil derived fatty alcohol (PODFA), dodecyl alcohol (dodecanol, C12) were purchased from Emery Oleochemical (M) Sdn Bhd. Methanol, ethanol, n-butanol and acetone (analysis grade) were purchased Sigma Aldrich. All materials were used in as-received condition without further purification. The synthesis approach using PODFA followed the procedure as reported [14]. Generally, the metal organic framework materials were made up of two precursors mixtures. The first solution comprised of 2-MIM in a co-solvent of either methanol (MetOH), ethanol (EtOH), n-butanol (ButOH) and acetone (Ace). The second solution consisted of zinc salt in water. Both metal and organic precursor solutions were mixed and stirred thoroughly at room temperature. Then, an amount of PODFA as a modulating agent was added into the solution to promote the formation of “pre-Ouzo” effect in the surfactantless mixture. The ZIF-8 control sample was synthesized without using any PODFA with methanol as the
polar co-solvent. Then, the resulting viscous solution was aged overnight at room temperature to promote the growth of ZIF crystals. The stirring power, temperature and time were kept constant during the synthesis. The co-solvents were changed accordingly for subsequent ZIF-8 synthesis. The obtained solids were filtered and washed for several times using distilled water and dried overnight at 358 K to obtain the as-synthesized, dried ZIF-8 materials.

2.2 Characterizations

As-synthesized ZIF-8 samples were subjected to X-ray diffraction (XRD) analyses using Shimadzu XRD-6000 with CuKα radiation at λ=1.54 nm at 30 kV and 20 mA, scan speed of 2°/min and scan step of 0.02°. The range were at 2θ = 5° - 50°. The scanning electron microscopy (SEM) images were done Zeiss Supra VP 35 at acceleration voltage of 5 kV for ZIF-8 samples. The TGA analyses were done using TGAQ500 at temperature range of 100 °C to 850 °C. UV-Vis analyses were done using UV-vis Perkin-Elmer Lambda 35 using 1 cm quartz cell at ca. 200 nm to 600 nm.

3. Results and discussion

The X-ray diffraction patterns of as-synthesized ZIF-8 samples prepared using various polarity solvents with or without PODFA additions are shown in Figure 1. All XRD patterns exhibited good agreements with the simulated patterns as reported suggesting successful formation of ZIF-8 [12,13]. The first 6 peaks at ca 2θ 7.3°, 10.2°, 12.7° were attributed to the reflections from (011), (002), (112) planes of a rhombic dodecahedron with truncated corners. The subsequent three peaks could be assigned to (022), (013) and (222) planes of a truncated rhombic dodecahedron. Adding the PODFA resulted in the increment of (112) reflection peaks originated from truncated rhombic plane compared to (011) plane reflection peaks of actual rhombic crystal structure.

![Figure 1. X-ray diffraction patterns of ZIF-8 synthesized with/without PODFA with various co-solvents.](image-url)
SEM images of ZIF-8 prepared with or without PODFA in various solvents are shown in Figure 2. ZIF-8 prepared in methanol without PODFA addition exhibited smaller crystal structures at ca. 100 nm. As the polarity of solvents increased the miscibility of organic linker and metals salts with PODFA were increased at the water-fatty alcohols interface. Hence, ZIF-8 crystal evolution rates were changed resulted in various morphology [8]. In high polarity solvent such as methanol, ZIF-8 exhibited highly faceted rhombic dodecahedron. The resulting morphology observed when using ethanol as solvent was faceted rhombic dodecahedron and thinner dodecahedron flakes. However, in less polar solvent such as in n-butanol, the morphology changed to thinner dodecahedron to almost pill

Figure 2. SEM images of as-synthesized ZIF-8 with/without PODFA in various solvents.
-like morphology without distinct facets. In acetone the resulting ZIF-8 exhibited globular aggregates at ca. less than 100 nm. The various morphology observed in this study was due to the hydrogen bond donation ability of solvent molecules that governed the crystallization rates. Higher crystallization rate resulted in less faceted structure. Furthermore, the various solvents used gave different capabilities to dissolve and to solvate Zn$^{2+}$ and NO$_3^-$ ions as well as the organic ligand because of their different dielectric constants, dipole moment and van der Waals volume [8]. The TGA spectrum of a representative ZIF-8 synthesized using PODFA of C12 in ethanol as solvent is shown in Figure 3. The spectrum showed ca. 2 % weight loss in the temperature range of 25–150 °C corresponding to the removal of solvent molecules which were methanol molecules in this case. Then, there existed a gradual weight loss of ca. 25 % till 350 °C were observed corresponding to the removal of guest molecules from the cavities and some unreacted species from the surface of the materials. Therefore, a guest-free phase Zn (MIM)$_2$ was formed until 350 °C.

![Figure 3. TGA curve of ZIF-8 synthesized using C12 PODFA in methanol.](image)

After 350 °C, the TGA curve exhibited a sharp weight loss of ca. 45 % up to the temperature of 700 °C. It was due to the thermal decomposition of ZIF-8 as 2-MIM decomposed at high temperature leading to the formation of zinc oxide (ZnO) as the final calcination product of ZIF-8 nanocrystals. These results suggested that ZIF-8 prepared in this study exhibited higher thermal stability as reported [7]. The representative UV-visible absorption spectra of ZIF-8 prepared using methanol as solvent with and without the presence of PODFA are shown in Figure 4. Both ZIF-8 samples exhibited a characteristic absorption peak at ca 215 nm [8]. A broad hump centered started at ca. 320 nm to ca. 380 nm suggesting the interactions of solvent molecules with the ZIF-8 framework.

4. Conclusion

ZIF-8 materials were successfully synthesized at room temperature in various solvents with different polarity in the presence of palm oil derived fatty alcohol (PODFA) having C12 carbon chain other than those already reported for the synthesis of this MOF. Monodispersed ZIF-8 with truncated rhombic dodecahedron was obtained in highly polar solvent of methanol without TEA with the aid of
PODFA that increase the immiscibility of precursor mixtures. Thus, the method used in this study was successful in eliminating TEA and surfactant to produce ZIF-8 at room temperature.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** UV-visible spectra of ZIF-8 prepared with various solvents.

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