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CONCENTRATIONS OF METAL IONS AND LIGANDS ON THE FORMATION OF NANO TO SUBMICRON ZINC IMIDAZOLE FRAMEWORK-8 PARTICLES

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Abstract

The purpose of this study was to evaluate the effects of concentrations of metal ions and ligands on the formation of Zinc Imidazole Framework (ZIF-8) in the liquid-phase synthesis. In the experimental procedures, zinc nitrate and imidazole (as models of metal ions and ligands, respectively) were mixed and reacted in the methanol solution at room temperature. To confirm the analysis, several characterizations were carried out Such as Electron Microscope (SEM), Fourier Transform Infrared (FTIR) and X-Ray Diffraction (XRD). Experiment results showed that concentrations of metal ions and ligands gave great impacts on the formation of ZIF-8 particles, shown by different outer diameters. No change in the XRD phase and pattern when changing the concentrations of metal ions and ligands, bringing information that metal ions and ligands are very reactive to form ZIF-8 and the unreacted components did not form other types of by-products. The changes in the amounts of metal ions and ligands gave consequences in the modification in nucleation and growth of ZIF-8 particles. Increases in the amount of metal ions and/or decreases in the amount of ligands significantly led to the faster growth process, resulting in the formation of larger particles. However, increases in the ligand concentrations permitted the faster nucleation rate, giving consequences in the formation of smaller particles. This study demonstrated the important consideration of the concentrations of metal ions and ligands for the production of the metal-organic framework with controllable sizes and morphologies.

Keywords: Growth, Liquid-phase synthesis, Metal-organic framework, Nucleation, ZIF-8.

1. Introduction

Zinc Imidazole Framework-8 (ZIF-8) is a sub-class of the organic metal framework (MOF). This material has been known due to its high porosity crystalline material, consisting of organic-inorganic compounds formed by coordination bonds between ions or metal clusters and organic ligands [1-3]. In short, ZIF-8 is formed by reacting metal ions (i.e., Zn2+ ions) and ligands (containing N atoms from imidazole-based groups) [4-6]. This material is attractive and becomes candidates for various applications such as energy storage, CO2 adsorption, catalysts, hydrocarbon adsorption/separation, sensors, magnetism, drug delivery systems and others [1, 7].

Many attempts were made to synthesize and obtain ZIF-8 material with superior physicochemical properties. So far, various ZIF-8 synthesis methods have been reported, including solvothermal, microwave, sonochemical, electrochemical, and mechanochemical method. The common method used for ZIF-8 synthesis is solvothermal method. However, the time-consuming process and high-energy consumption are inevitable, creating problems in the high costs of synthesis. Microwave-solvothermal synthesis method has been also reported, but it requires high energy consumption [1, 8]. To solve this problem, it is necessary to explore synthesis methods that are energy-efficient, consume short time and low costs. One of the reports is using a liquid-phase synthesis, reacting ligands and metal ions in the room pressure. This brings ideas for further analysis of several parameters involved in the synthesis process.

Here, we investigated the effects of concentrations of metal ions and ligands on the formation of ZIF-8 particles with controllable outer diameters. The experiment was done by reacting zinc salts and imidazole in the methanol solvent.

Although many approaches have reported the way how to manipulate the particle size and morphological shape of metal-organic framework materials, such as varying solvent, concentration and reactant molar ratio, temperature, and reaction time [8, 9-11], the analysis is still not clear.

For example, some researchers used sodium formate that acts as a basic agent in the deprotonation equilibrium of ligand reaction. Other researchers used surfactants such as poly (diallyldimethylammonium chloride), cetyltrimethylammonium bromide, or gelatine biopolymers as a growth inhibitor of crystal shape and particle size [12-14]. These additional surfactants or additives can create additional particle formation mechanism, creating difficulties in understanding what phenomena happen in the formation of ZIF-8 particles.

Different from other reports, to clarify the effect of these concentrations, all processes were conducted in the absence of additional components (i.e., surfactant). Thus, we can get a clear relationship between the concentration of reactant and physicochemical properties of the ZIF-8 product. An explanation of the proposal for the particle formation was also added to support this study.

2. Method

ZIF-8 particles were synthesized using the reaction of zinc nitrate ($Zn(NO_3)_2.6H_2O$; as a model of metal ion) and methyl imidazole (as a model of ligand). In short, metal ions and ligands were dissolved in the methanol solution in different glass reactors (Each chemical dissolved into 20 mL of methanol). Then, the dissolved solutions were put into the 100-mL borosilicate reactor and vigorous mixed (1500 rpm) for 24 hours at room temperature. After the reaction is complete, a milky white suspension was formed. Then, the suspension was put into the centrifugation (11,000 rpm for 5 minutes; washed with methanol). The centrifuged sample was then dried an electrical oven at 50°C for 30 minutes. To understand the effect of concentrations of metal ions and ligands, metal ions were varied from 0.00 to 75.00 g/L, whereas ligands were from 0.00 to 82.5 g/L. All chemicals were purchased from Sigma-Aldrich, US and used without further purification.

Several characterizations to confirm the successful synthesis of ZIF-8 particles were the analysis of the morphological structure using an electron microscope (SEM; JSM-6360LA; JEOL Ltd., Japan), analysis of the functional groups using Fourier Transform Infrared (FTIR; FTIR-4600, Jasco Corp., Japan), and analysis of the crystal structure using an X-Ray Diffraction (XRD; PANalytical X'Pert PRO; Philips Corp., The Netherland).

3. Result

Figure 1 shows the SEM images of particles prepared with various concentrations of metal ions and ligands. Experimental results showed that the change in the concentrations gave impacts on the change of particle outer diameters. Feret sizes of the particles prepared using metal ions/ligands of 0.15/0.165; 0.30/0.33; 1.50/3.30; and 3.00/3.30 are 69.10; 97.90; 255.30; and 511.50 nm, respectively.

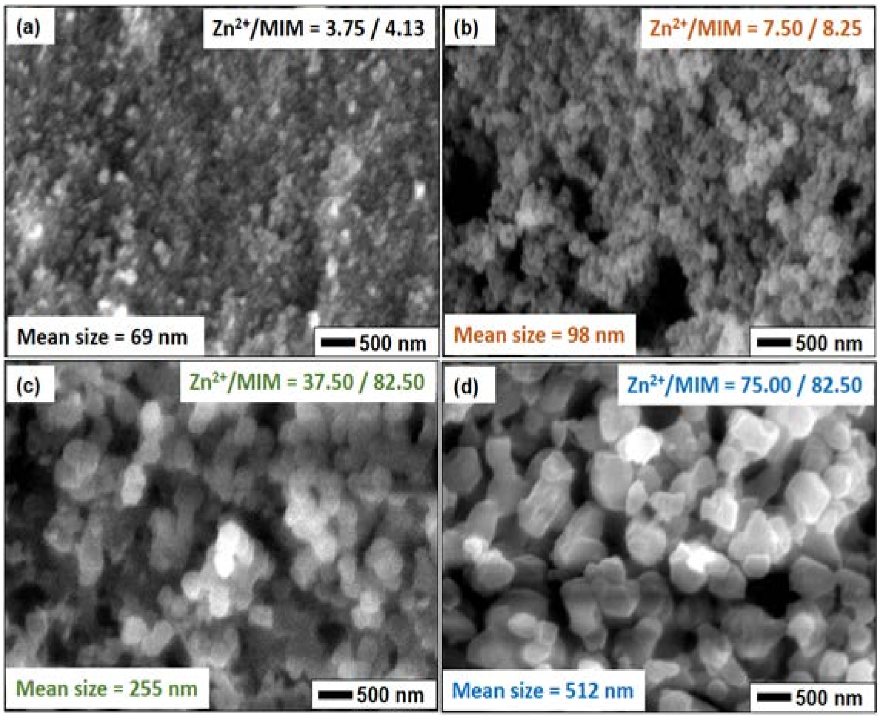

Fig. 1. SEM images of particles prepared using various concentrations of metal ions and ligands.

Figure 2 shows the correlation of particle sizes as a function of concentrations of reactants. Figures 2(a) and (b) are the effects of concentrations of metal ions and ligands, respectively, on the formation of particles.

Figure 3 shows the FTIR spectra of particles prepared using various concentrations of reactants. The results showed that identical peaks were detected, in which the major peaks were in regions of 1590 cm^{-1}, between 1494 and 1382 cm^{-1}, from 1350 to 900 cm^{-1}, 760 cm^{-1}, and 690 cm^{-1}. Typical bonding peaks for CH and CN were also identified [15]. These peaks were identical to the ZIF-8 FTIR patterns of ZIF-8 [16, 17]. Detailed explanations of the peaks are shown in Table 1.

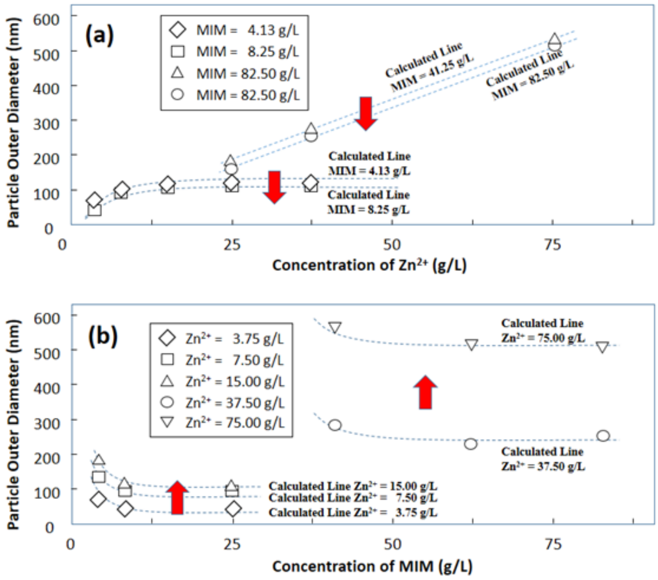

Fig. 2. Correlation between final particle outer diameter and concentrations of reactants: (a) and (b) Samples based on different initial concentrations of metal ions and ligands, respectively.

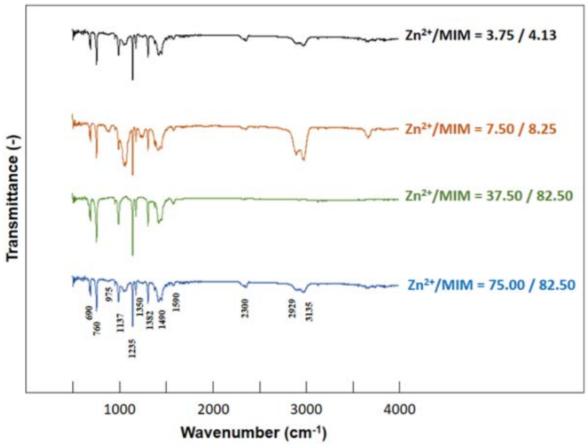

Fig. 3. FTIR analysis results of samples prepared with various concentrations of metal ions and ligands.

Table 1. Possible chemical bonding based on FTIR analysis.

Absorption wavenumber (cm^{-1})	Possible type of chemical bonding
690	Zn-N
760	Zn-O
975	sp^2 C-H bend of aromatic
1137	
1235	
1350	Mode stretching of mode
1382	
1490	Mode stretching of mode $C = N$

The XRD patterns of the particles prepared with various amounts of metal ions and ligands are presented in Fig. 4. Identical XRD phases and patterns for all samples were identified, which is in a good agreement with literature for ZIF-8 material [2, 3, 5, 18]. Different peak intensities were obtained, in which, this is due to the different crystal structure. Indeed, these results are in a good agreement with SEM images in Fig. 1. The smaller particles tend to have smaller crystal size.

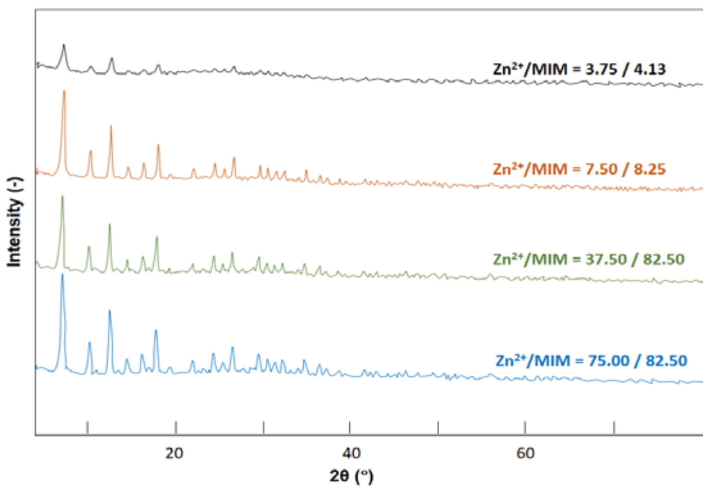

Fig. 4. XRD analysis results of particles prepared with various concentrations of metal ions and ligands.

4. Discussion

Experimental data confirmed that all variations in the concentrations of metal ions and ligands gave great impacts on the final particle size. The change in these variations did not alter the change in the physicochemical properties of the product, verified by the identical FTIR and XRD patterns. Although there is a change in the XRD intensities, this is because of the crystallite size in the material. Indeed, the smaller particle sizes correlate to the containment of smaller crystallite sizes. The phenomena in the unchanged XRD phase and pattern is because metal ions and ligands are very reactive to form ZIF-8 and the unreacted components did not form other types of by-products.

The fundamental reason for the change in the final particle outer diameter as a function of concentrations of reactants is due to the different nucleation and growth rate during particle formation [19, 20]. In short, the particle formation is followed the Lamer and Dinegar's theory, which is detailed explained in previous literature (see Fig. 5) [21]. In short, the reactants (i.e., metal ions and ligands) gave impacts on the formation of smaller molecules of product, namely monomer of ZIF-8. Indeed, this can bring more collateral formation of nuclei and further growth processes of ZIF-8 [2, 8].

When the high concentration of metal ions and ligands are used, there is no problem in the nucleation and growth process, giving positive consequences to the formation of larger particles (see Fig. 5). As shown in nuclei condition 1 in Fig. 5, the more concentrations of reactants can allow the more formation of nuclei. However, when the concentration of metal ions and ligands are limited, it can disturb in the formation of nuclei and/or growth process (see nuclei condition 2 in Fig. 5. This analysis can be found clearly in Fig. 2 that was completed with calculated line based on statistical analysis (see dashed lines). To clarify the analysis, the explanation is divided based on the type of reactant: i.e., metal ion (Zn^{2+}) and ligand (MIM), corresponding to Figs. 2(a) and (b), respectively.

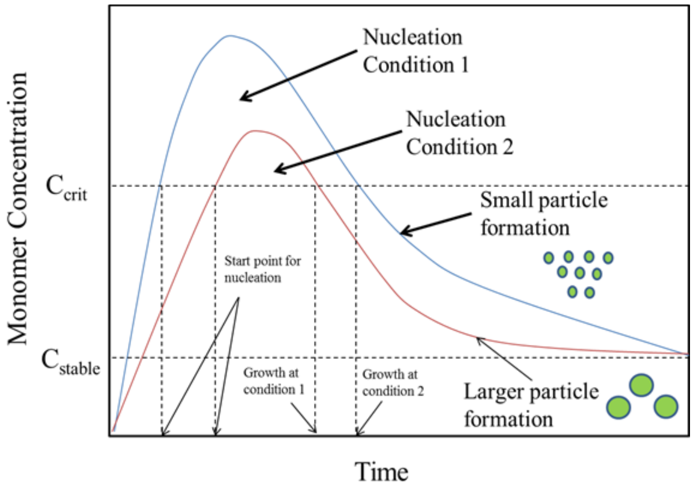

Fig. 5. Illustration of Lamer and Dinegar's theory as a function of reaction time [21].

As shown in Fig. 2(a), when using a high concentration of metal ions, the trend was positive, in which the more concentrations related to the formation of larger particles (see curves for MIM with concentrations of 37.50 and 75.00 g/L). However, when using less concentrations of reactant, especially less amount of ligands, the logarithmic curves were obtained. The more additional concentration of metal ions has no effect on the further growths of particles (see curves for MIM with concentrations of 4.13 and 8.25 g/L). This can be also found in Fig. 2(b) (see red arrows in this figure). The correlation of metal ions is in opposite trend in the ligands (see Fig. 2(b)). All curves were in a good agreement with the fact that the more additional ligands led to the formation of smaller particles. The more additions of ligands concentrations have no impact on the formation of larger particles. Based on these results, ligands give faster nucleation rate. All metal ions were consumed during the initial formation of nuclei, disturbing the growth process. However, excess amounts of ligands have no impact. Regarding the metal ions, they can promote more growth process. In short, when nuclei are formed, metal ions provide more electrostatic phenomena to make the formed nuclei to adsorb more reactants. Thus, the more additional metal ions lead to the formation of larger particles.

5. Conclusions

The present study investigates the effects of concentrations of metal ions and ligands on the formation of ZIF-8 particles. Experiment results showed that concentrations of metal ions and ligands gave great impacts on the formation of ZIF-8 particles, shown by different outer diameters. No change in the XRD phase and pattern when changing the concentrations of metal ions and ligands, bringing information that metal ions and ligands are very reactive to form ZIF-8 and the unreacted components did not form other types of by-products. In short, metal ions can permit a faster growth rate, whereas ligands can allow the more formation of nuclei. This study demonstrates the important consideration of the concentrations of metal ions and ligands for the production of the metal-organic framework with controllable sizes and morphologies.

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