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Fast Synthesis of Highly Crystalline ZIF-8 using Microwave-assisted Solvothermal Method

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Abstract. This paper presents the formation of highly crystalline ZIF-8 using microwave-assisted solvothermal method. The crystallinity of the ZIF-8 particles was characterized using X-ray diffraction. The lattice vibrations of the structure in the ZIF-8 framework were determined through Fourier transforms infrared spectroscopy. The morphology of the ZIF-8 particles was observed through scanning electron microscopy. The results showed that, 0.5 hour was sufficient for the formation of highly crystalline ZIF-8 particles using microwave-assisted solvothermal method under temperature 120 ºC.

Introduction

Zeolitic Imidazolate Framework (ZIF) -8 is one of the most studied prototypical MOF materials owing to its high CO_2 permeance [1], surface area and the exceptional thermal and chemical stability [2]. It is a hybrid organic-inorganic material with zinc ions linked by 2-methylimidazolates ions, forming neutral frameworks with the diameter of 11.6 Å and small windows with the diameter of 3.4 Å [3]. Microwave is a remarkable technology in particles synthesis since 1988 with the first patent filed by Mobil [4]. The rapid heating induced by microwave irradiation and the uniformity of the microwave field has successfully reduced the synthesis duration of the particles [5]. To date, there are few literatures reported on the formation of ZIF-8 using microwave irradiation method. For instance, Bux et al (2009) [6] has successfully synthesized ZIF-8 using methanol solution under microwave irradiation with the Hmim/Zn^{2+} ratio of 1.5. Pure phase ZIF-8 was obtained after 4 h at 100 ºC. On the other hand, Yang and Lu (2012) [7] has synthesized ZIF-8 using microwave irradiation in the presence of ionic liquid (1-butyl-3-methyl-imidazolium) as the structure directing agent with the Hmim/Zn^{2+} ratio of 4. Highly crystalline ZIF-8 particles were obtained after 1 h at 140 ºC. During microwave irradiation, heterogeneity of the solution caused different energy-loss mechanism in the bulk phase of particles, which induced the local superheating of the solution and thus enhancing the digestion of the reagents for the crystallization. Besides, Bao et al (2013) [8] has synthesized ZIF-8 in the aqueous system under microwave irradiation with the Hmim/Zn^{2+} ratio of 10. The ZIF-8 particles synthesized were pure phase, with the absence of *dia* frameworks, which usually shown by the ZIF-8 particles synthesized using hydrothermal methods. In this paper, we have successfully synthesized highly crystalline and pure phase ZIF-8 under microwave irradiation at 120 ºC for only 0.5 h in methanol solution with the Hmim/Zn^{2+} ratio of 8. We have synthesized ZIF-8 at higher temperature of 140 ºC in 0.5 h as comparison. The resultant ZIF-8 particles were characterized using X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

Experimental

Chemicals. Zinc nitrate hexahyrate ($Zn(NO_3)_2.6H_20$, 99% ,Sigma-Aldrich) was used as the zinc source and 2-methylimidazole (meIm, 99%, Sigma-Aldrich) was used as organic ligand. Sodium formate (NaCOOH, >95 %) was purchased from Sigma-Aldrich and methanol (99.8 %) was obtained from Merck. All chemicals were used as received without further purification.

Preparation of ZIF-8. The synthesis precursor was prepared by dissolving 0.59 g of $Zn(NO_3)_2.6H_2O$, 1.28 g of meIm and 0.08 g of NaCOOH in 80 mL of methanol. The synthesis precursor was poured into the vessel and heated in a microwave oven (MARS 6, CEM Corporation) at 120 ºC and 140 ºC for 0.5 h. After heating, the resultant particles were recovered through centrifugation at 7800 rpm for 5 min and washed with methanol before drying in oven at 80 ºC.

Characterization Techniques. XRD patterns were recorded on a Bruker D8 Advance diffractometer using CuKα radiation. The 2θ values ranged from 2 ° to 50 ° were scanned at a step size of 0.02 °. The morphology and the elements of the ZIF-8 were determined through SEM and EDX (model: Hitachi TM 3030). The images were taken at magnification of 5000 X at 15 kV accelerating voltage. Meanwhile, EDX analysis was done at magnification 100 X at 15 kV. The functional groups and the lattice vibration of ZIF-8 were determined through FTIR (model: Spectrum One/BX) over the scan range of 400-4000 cm^{-1}.

Results and Discussion

Fig. 1 shows the XRD pattern of the ZIF-8 particles synthesized at 120 ° C and 140 ° C under microwave irradiation of 0.5 h. All the significant peaks of ZIF-8 are shown [1, 9-11], indicating the presence of the pure phase of ZIF-8. The well-resolved peaks demonstrate the high crystallinity of the particles. The main peak at (110) indicates the relative crystallinity of ZIF-8. These results show that, high temperature of crystallization (140 ° C) do not enhance the relative crystallinity of the particles.

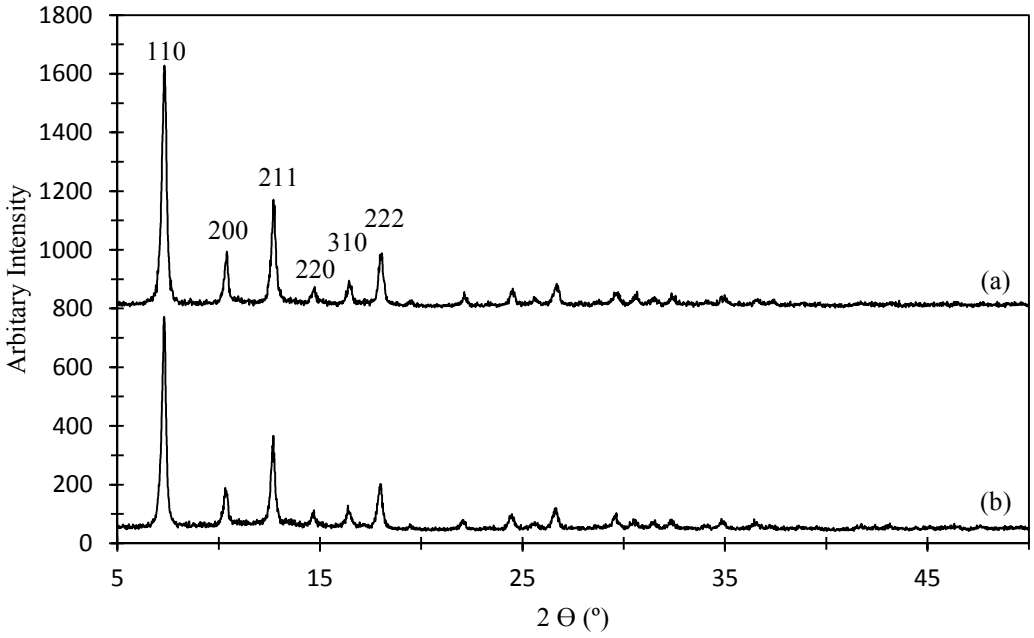

Fig. 1. XRD pattern of ZIF-8 synthesized at (a) 120 ºC, 0.5 h and (b) 140 ºC, 0.5 h.

The FTIR spectra for the ZIF-8 particles synthesized at different temperature within 0.5 h is shown in Fig. 2. All the peaks observed are comparable with those peaks reported in the literature [12, 13]. The Zn-N stretch mode is observed at 423 cm^{-1}, C-N stretch at 999 cm^{-1} and 1148 cm^{-1} respectively. The bands below 800 cm^{-1} is caused by the out-of-plane bending meanwhile the peaks in the region 900-1350 cm^{-1} is due to the in-plane bending. The peaks at 1350-1500 cm^{-1} is attributed to the entire ring stretching whereas the peak at 1600 cm^{-1} is due to the C=N stretching. The adsorptive peaks at 2959 cm^{-1} and 3169 cm^{-1} are assigned as the aromatic and aliphatic C-H stretch mode of the imidazole ring. The intensity of the peaks is slightly icreased with the increased of the crystallization temperature. This indicates that, higher temperature can affect the vibration of

the frameworks of the ZIF-8. Nonetheless, these results show that, a highly crystalline and pure phase ZIF-8 can be synthesized in 0.5 h at lower temperature of 120 ºC, which is consistent with the XRD results.

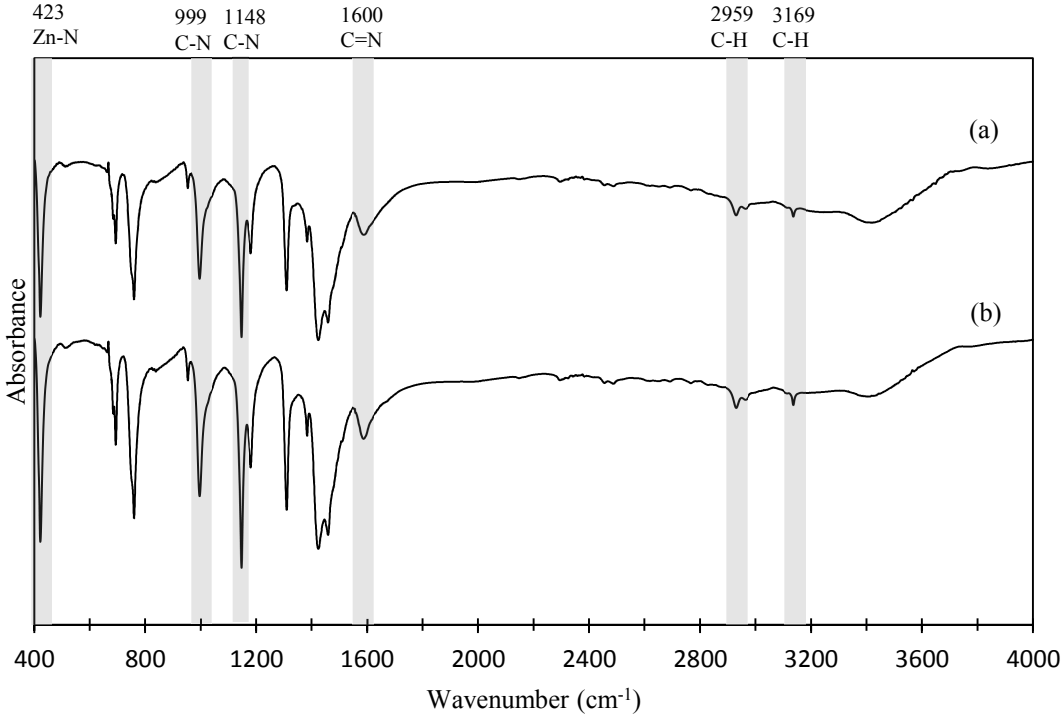

Fig. 2. FTIR spectra of ZIF-8 synthesized at (a) 120 ºC, 0.5 h and (b) 140 ºC, 0.5 h.

The morphology of the ZIF-8 particles was comparatively examined by SEM, as shown in Fig. 3. The rhombic dodecahedron shapes exhibited by the ZIF-8 particles are consistent with the XRD pattern. The particles size of the ZIF-8 synthesized at 140 ºC is slightly larger than the ZIF-8 synthesized at 120 ºC, which is ~175 nm and ~100 nm, respectively. However, the particles synthesized under both conditions show fully crystalline phase regardless of the temperature induced.

Fig. 4 shows the EDX analysis of ZIF-8 synthesized at 120 ºC and 140 ºC within 0.5 h corresponding to the SEM images shown in Fig. 3. The EDX spectrum is similar with the typical spectrum of ZIF-8 [14]. High intensity of zinc indicates the absence of amorphous phase of ZIF-8. Besides, the quantification analysis of the EDX spectra shows the content of C- 47% ; N-22% and C- 45%; N-25% for ZIF-8 synthesized at 120 ºC and 140 ºC, respectively. The results obtained were close to the theoretical amounts for the ZIF-8 according to its molar ratio (C-42.22% and N-24.62%) [15, 16]. Therefore, a short duration of time would not affect the formation of a pure phase ZIF-8 particles.

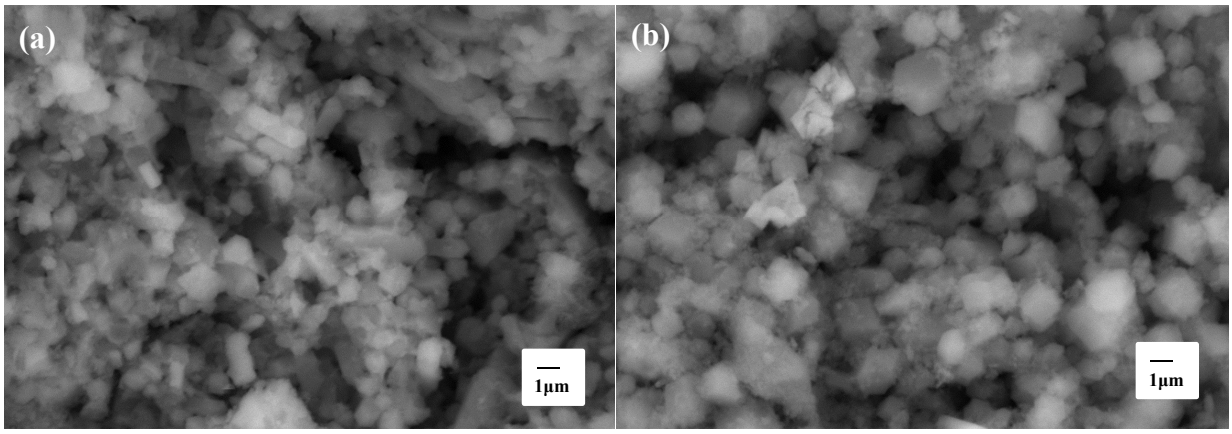

Fig. 3. SEM micrographs of ZIF-8 prepared at (a) 120 ºC, 0.5 h and (b) 140 ºC, 0.5 h.

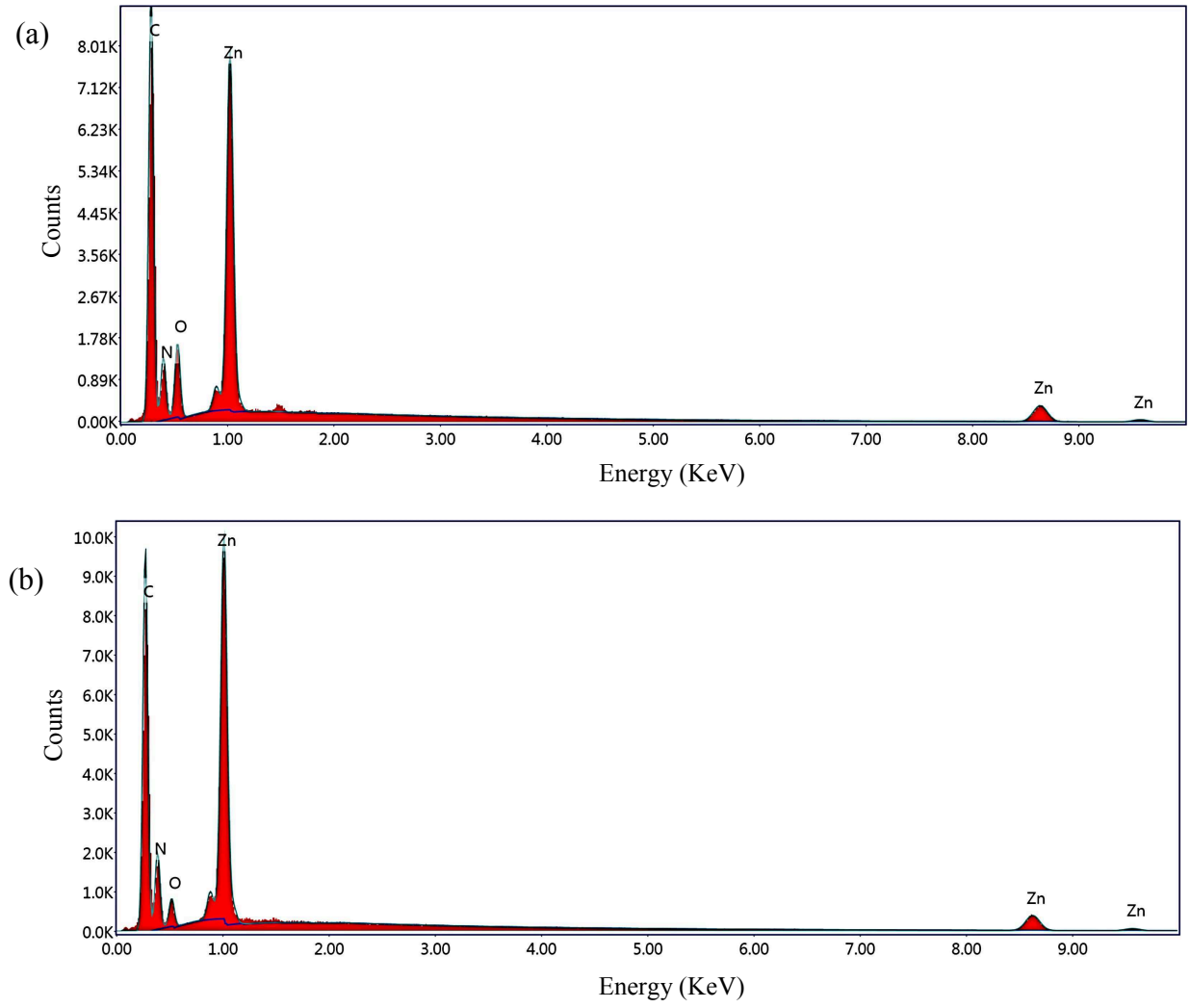

Fig. 4. EDX analysis for ZIF-8 synthesized at (a) 120 ºC, 0.5 h and (b) 140 ºC, 0.5 h.

Conclusion

In conclusion, pure and highly crystalline ZIF-8 particles have been synthesized in a very short duration of time (0.5 h) at 120 ºC under microwave irradiation. This finding has successfully reduced the synthesis duration of ZIF-8, which provided a faster and feasible way for the formation of highly crystalline ZIF-8 membrane. Hence, the energy consumption for the formation of ZIF-8

particles and membrane could be reduced. For future development, the synthesis parameters, such as the duration and temperature can be optimized to make microwave technology feasible.

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