4th International Conference on Process Engineering and Advanced Materials

Effect of Synthesis Parameters on the Formation of ZIF-8 Under Microwave-assisted Solvothermal

Li Sze Lai, Yin Fong Yeong, Kok Keong Lau, Azmi Mohd Shariff

Abstract

In this paper, the effect of synthesis parameters including temperature, pressure and volume of the synthesis solution towards the formation of ZIF-8 under microwave-assisted solvothermal synthesis was investigated. The resultant ZIF-8 samples were characterized using X-ray diffraction and nitrogen physisorption. The surface morphology was examined via scanning electron microscopy. The results exhibited that, highly crystalline ZIF-8 was successfully synthesized within 0.5 hours at 120 ºC, with the BET surface area up to 690.75 m²/g and micropore volume of 0.32 cm³/g. It was found that, at higher temperature and pressure, the formation of ZIF-8 can be affected by the expansion of solvent, which reduced the initial concentration of the reactant ions. Hence, further increased of the temperature did not cause higher crystallinity and larger size of ZIF-8 particles.

Keywords: ZIF-8; microwave synthesis; crystallinities; BET surface area; surface morphology

1. Introduction

Zeolitic imidazolate frameworks-8 (ZIF-8) is one of the typical materials for gas separation due to its excellent chemical and hydrothermal stability, high surface area, microporosity and frameworks flexibility [1]. It possesses large pore sizes of 11.6 Å and small apertures of 3.4 Å with the zinc metal center coordinated by the imidazole-type of organic linkers and resembles neutral zeolithic sodalite (SOD) topology [2]. Since last decade, microwave technology has provoked a great interest in chemical synthesis of nanoporous materials [3]. Microwave irradiation

* Corresponding author. Tel.: +05-368-7564; fax: +05-365-6176.
E-mail address: yinfong.yeong@petronas.com.my
with uniform, rapid heating and controllable ramp rate [4], has successfully reduced the synthesis duration and enhanced the product yield [3]. To date, few literatures have been reported on the microwave-assisted synthesis of ZIF-8. As reported by Bao et al (2013) [5], ZIF-8 has been successfully synthesized in water medium using reaction mixture with the molar ratio of ligand to zinc ion (Hmim/Zn²⁺) of 10 via microwave irradiation at 120 °C for 0.5 h. Well-intergrown ZIF-8 crystals were obtained. Besides, Yang and Lu (2012) [6] has incorporated ionic liquid, which acted as the structural directing agent, into the reaction mixture with Hmim/Zn²⁺ ratio of 4 for the synthesis of ZIF-8. Stable and uniform ZIF-8 was produced under the microwave-assisted ionothermal synthesis at 140 °C for 1 h. However, formation of ZIF-8 using water as the medium causes higher chemical consumption with higher Hmim/Zn²⁺ ratio. Furthermore, ionic liquid is expensive although it can reduce the amount of reactants used.

On the other hand, formation of ZIF-8 particle involves nucleation and crystallization, which is initiated by the presence of unstable clusters under supersaturation condition [7]. Several factors such as the temperature of the system, evaporation of solvent and the molar composition of the solution will affect the particles formation [8] during microwave-assisted synthesis process. In our previous work [9], pure phase and high crystallinities ZIF-8 particles has been successfully synthesized under microwave irradiation at temperature of 120 °C and 140 °C within 0.5 h. However, the effects of the synthesis parameters on the formation of ZIF-8 have not been studied and are rarely reported in the literature.

Therefore, in the present work, a series of ZIF-8 particles were synthesized at different temperatures, ranged from 80 °C to 140 °C, via microwave-assisted solvothermal synthesis by using methanol as the medium. The resultant particles were characterized using X-ray diffraction (XRD), nitrogen physisorption and scanning electron microscopy (SEM). The reaction profile of the microwave reactor was studied based on the temperature, pressure and the actual volume involved under constant initial molar composition and volume of the solution. Their effects on the formation of ZIF-8 were discussed.

2. Methodology

2.1. Chemicals

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 99%) as the zinc source, 2-methylimidazole (meIm, 99%) as the organic ligand and sodium formate (HCOONa, >95%) as the deprotonator were purchased from Sigma-Aldrich. Methanol (99.8%) purchased from Merck was used as the polar solvent. All the chemicals were utilized as received without further purification.

2.2. Preparation of ZIF-8

The precursor solution was prepared by fully dissolving 0.59 g of Zn(NO₃)₂·6H₂O, 1.28 g of meIm and 0.08 g of HCOONa in 80 mL of methanol. Then, the solution was poured into a Teflon-lined vessel. The vessel containing solution was subjected to heating in a microwave oven (MARS 6, CEM Corporation) for 0.5 h. After solvothermal synthesis, the milky solution was cooled down to room temperature. Subsequently, the ZIF-8 particles were recovered from the solution using centrifugation at 7800 rpm for 5 min. The resultant particles were then washed with fresh methanol for three times and dried in the oven overnight at 80 °C. The procedure was repeated by varying the synthesis temperature from 80 °C to 140 °C.

2.3. Characterization

The ZIF-8 was characterized using X-ray diffraction (XRD), which was performed using CuKα radiation on Bruker D8 Advance diffractometer at room-temperature. Step size of 0.02 ° was used for scanning at 2θ ranged from 2 ° to 50 °. The nitrogen adsorption-desorption isotherm was measured using Micromeritics ASAP 2020 adsorption porosimeter equipped with liquid nitrogen as coolant at 77 K. The surface areas were determined using Brunauer-Emmett-Teller (BET) method and the micropore volume was estimated using t-plot method. The
morphology of the ZIF-8 was observed with scanning electron microscopy (SEM). The testing was carried out on Hitachi model TM 3030 at magnification of 5000.

3. Results and discussion

3.1. X-ray diffraction (XRD)

Fig. 1 shows the XRD patterns of the ZIF-8 samples synthesized at different temperatures in 0.5 h. It can be seen that all the samples show the characteristic peaks of ZIF-8 [1, 10, 11]. The intensities of the ZIF-8 peaks increase as the synthesis temperature increases. This is due to the enhanced rate of ZIF-8 formation under higher temperature. However, the crystallinities based on (110) plane for the ZIF-8 synthesized under 80 °C and 100 °C are relatively weak as compared to the ZIF-8 synthesized at 120 °C and 140 °C. This result shows that, synthesis temperature of 120 °C and above is required for the formation of ZIF-8 with high crystallinities within a very short duration of 0.5 h under rapid microwave irradiation. In fact, lower temperature of 100 °C is not sufficient to create a supersaturation condition for the formation of ZIF-8 within a short period of time. However, higher temperature of 140 °C did not further enhance the crystallinity of the particles, as reported in our previous work [9]. Thereafter, highly crystalline ZIF-8 synthesized at 120 °C and 140 °C was selected for the following characterization study.

Fig. 1. XRD patterns of ZIF-8 synthesized at (a) 80 °C; (b) 100 °C; (c) 120 °C and (d) 140 °C within 0.5 h under microwave irradiation.
3.2. Scanning electron microscopy (SEM)

Fig. 2 shows the surface morphology of ZIF-8 synthesized at 120 °C and 140 °C, which has been reported in our previous work [9]. The ZIF-8 particles display well-defined rhombic dodecahedron facets, which is in consistent with those SEM morphologies for ZIF-8 particles reported in the literature [11, 12]. However, the average particles size of the ZIF-8 formed at 140 °C is slightly larger than the particles synthesized at 120 °C, which shows ~175 nm and ~100 nm, respectively. The result is consistent with the XRD pattern shown in Fig. 1, with the particle size estimated based on Scherrer Equation shows ~172 nm and ~157 nm for ZIF-8 synthesized at 140 °C and 120 °C, respectively. The effect of the temperature on the ZIF-8 formation can be correlated with the fact that, higher temperature causes higher total free energy and thus inducing larger size of critical nucleus for the crystallization [13]. Besides, the nucleation and crystallization rates are enhanced with the increasing temperature [14]. Therefore, ZIF-8 synthesized at 140 °C is generally larger in the particle size. The uniform heating with the controllable ramping rate induced by microwave irradiation enables the formation of ZIF-8 rapidly. Hence, the ZIF-8 particles are well-intergrown and uniform although the synthesis duration is relatively short.

![Fig. 2. SEM images of ZIF-8 synthesized at temperature of (a) 120 °C and (b) 140 °C within 0.5 h [9].](image)

3.3. Nitrogen physisorption

The nitrogen isotherms of ZIF-8 shown in Fig. 3 are in good agreement with the reported isotherm [1, 11] for ZIF-8, which is type I isotherm. A hysteresis loop is observed at larger relative pressure ($P/P_0 > 0.8$) due to the presence of large mesopores between the adjacent of the ZIF-8 particles. The BET surface area and micropore volume for ZIF-8 synthesized at 120 °C are 690.75 m$^2$/g and 0.32 cm$^3$/g respectively. Meanwhile, ZIF-8 synthesized at 140 °C shows higher BET surface area of 975.55 m$^2$/g and micropore volume of 0.45 cm$^3$/g. The result was higher than the BET surface area reported for ZIF-8 particles synthesized at room temperature for 24 h, which was 798 m$^2$/g [12]. The lower BET surface area of the ZIF-8 synthesized at 120 °C could be due to the lower amount of micropore volume, regardless of the smaller particles sizes compared to ZIF-8 synthesized at 140 °C. Besides, the presence of amorphous intermediates or solvated secondary building units in the ZIF-8 synthesized at 120 °C could result in a lower BET surfaces and the result is consistent with the XRD pattern shown in Fig. 1 (c), with lower crystallinity observed for ZIF-8 particles synthesized at 120 °C as compared to the particles synthesized at 140 °C within 0.5 h.
3.4. Effects of temperature, pressure and volume

The effect of the actual condition in the vessel of the microwave reactor on the formation of ZIF-8 is studied, including temperature, actual pressure and the volume of the solvent (methanol) used. The temperature was set accordingly while the pressure data was retrieved from the microwave system. Fig. 4 shows the schematic diagram of the volume condition in the vessel. The evaporation of methanol under elevated temperature in the reactor caused the expansion of the total volume of the solution.

By assuming the condition to be non-leakage, the total volume of the reactor ($V_T$) is equal to the total volume of methanol in the reactor in the form of vapor and liquid phase as shown in Equation 1.

$$V_T = V_g + V_L$$  \hspace{1cm} (1)

Where $V_g$ refers to the volume of the methanol in vapor phase and $V_L$ refers to the volume of methanol in liquid phase. $i$ refers to initial condition of the reaction. By neglecting the presence of the existing atmospheric air in the
reactor, the initial number of moles for the methanol liquid in the reactor \(n_{IL}\) is equal to the total number of moles of methanol in the reactor \(n_T\). Thus,

\[
n_{IL} = n_g + n_L
\]

(2)

Where \(n_g\) refers to the number of moles of methanol in the vapor phase and \(n_L\) refers to the number of moles of methanol in the liquid phase.

The actual volume of the methanol in the vessel was changed under an elevated temperature and pressure with the evaporation of the solvent. Therefore, real gas model, as shown in Equation (3) [15], is applied to correlate among the temperature, pressure and the volume for the real condition.

\[
P_s V_g = n_g ZRT
\]

(3)

Where \(P_s\) refers to the saturation pressure of methanol, \(Z\) refers to the gas compressibility factor, \(R\) refers to the ideal gas constant and \(T\) refers to the temperature.

Where,

\[
n_g = \frac{P_s V_g}{ZRT}
\]

(4)

On the other hand, the number of moles for methanol in liquid phase is defined in Equation (5) as follows,

\[
n_L = \frac{V_L D_L}{MW}
\]

(5)

Where \(D_L\) refers to the density of the methanol in liquid phase and \(MW\) refers to the molecular weight of the methanol.

Equation (6) is thus derived based on Equation (2).

\[
\frac{V_L D_L}{MW} = \frac{P_s (V_T - V_L)}{ZRT} + \frac{V_L D_L}{MW}
\]

(6)

Where,

\[
Z = \frac{P_s MW}{D_g RT}
\]

(7)

Where \(D_g\) refers to the density of the methanol in vapor phase and \(V_{IL}\) refers to the initial volume for the methanol in liquid phase.

In this case, the molar ratios of the reactants (Zn, Hmim and HCOONa) are in a very small composition as compared to the methanol (1: 8: 1002: 0.6 for Zn\(^{2+}\): Hmim: MeOH: HCOONa). Therefore, their effect on the thermophysical properties of the methanol is assumed to be negligible.

Table 1 shows the actual synthesis condition in the microwave reactor. According to Table 1, when the temperature increases gradually, the actual pressure in the reactor also increases. The pressure measured by the pressure sensor is close to the saturation pressure data for methanol, which retrieved from the NIST chemistry web book [16]. This observation indicates the non-leakage condition in the microwave system. As shown in Table 1, the actual volume of the methanol in liquid phase, \(V_L\), which is calculated based on Equation (6), has been expanded in the microwave system under elevated temperature and pressure, while the initial volume, \(V_{IL}\) was only 80 ml. The changes of the volume of the solvent will thus affect the concentration of the reactant ions. According to our previous reported data [17], higher concentration of the reactant ions resulted in higher crystallinity and larger size of ZIF-8 particles under room temperature synthesis. However, in solvothermal synthesis, ZIF-8 formed at lower
temperature (80 ºC and 100 ºC) shows lower crystallinities although the concentration of the reactant ions is higher based on the calculated $V_L$ value. This means that, temperature and pressure are the main factors that significantly affect the nucleation and growth rate of ZIF-8. The slight changes of the concentration of the reactant ions attributed to the solvent expansion do not significantly affect the formation rate of ZIF-8. Nonetheless, when the temperature is sufficient for the formation of ZIF-8 with high crystallinities (120 ºC and above), the changes on the supersaturation ratio of the solution that depended on the concentration of the reactant ions play as a key factor in affecting the ZIF-8 formation. Therefore, the crystallinities of ZIF-8 synthesized at higher temperature of 140 ºC with lower concentration of reactant ions did not further increase (Fig. 1). Moreover, there is only a slight increase in the particles size as shown in Fig. 2.

| Temperature, $T$ (ºC) | Actual Reactor Pressure, $P$ (psig) | Saturation Pressure, $P_s$ (psig)* | Actual Solvent Volume, $V_L$ (ml) |
|-----------------------|------------------------------------|-----------------------------------|---------------------------------|
| 80                    | 11                                 | 11                                | 85.3                            |
| 100                   | 34                                 | 37                                | 87.3                            |
| 120                   | 72                                 | 78                                | 89.4                            |
| 140                   | 139                                | 143                               | 91.3                            |

* - Data retrieved from NIST chemistry web book; $P_s$ (psig) = $P_s$ (psia)-14.7.

4. Conclusion and future direction

In conclusion, highly crystalline ZIF-8 was successfully synthesized at 120 ºC within 0.5 h, with the BET surface area of 690.75 m²/g and micropore volume of 0.32 cm³/g using microwave-assisted solvothermal method. Besides, synthesis temperature and pressure have found to be the main factors in the formation of ZIF-8. Nonetheless, the concentration of the reactant ions can affect the crystallinity and particle size of ZIF-8 under higher temperature of 120 ºC and above with the expansion of solvent. On the other hand, the significant effect of the concentration of the reactant ions has been found to be depended on the total volume of vessel and solution. Since the effects of the volume on the nucleation and the growth of particles are rarely reported on the literature, this can be an interesting finding for the study of microwave-assisted synthesis of ZIF-8. Based on the study, formation of ZIF-8 can be enhanced and large scale production of ZIF-8 can be optimized.

Acknowledgements

The financial and technical supports provided by CO₂ Management (MOR) research group, Universiti Teknologi PETRONAS are duly acknowledged.

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