Effect of Synthesis Methods Using Renewable PODFA on Structural Characteristics of Metal-Organic Framework (MOF-5)

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Abstract. In this work, metal-organic framework (MOF-5) syntheses were successfully synthesized with three different methods namely i) modified direct-mixing method ii) microwave assisted method and iii) autoclave assisted method without using surfactants. Palm oil derived fatty alcohol (PODFA), dodecyl alcohol (C8) was used as renewable non-surfactant template. Four prominent peaks were observed in all three samples attributable to the reflection planes of (200), (220), (400) and (420) of a cubic structure at ca. 2θ =6.9°, 9.6°, 13.7° and 15.2°. The morphology of MOF-5 produced using modified direct-mixing method was faceted structure with average size of ca. 1 µm. In addition, the morphology of MOF-5 produced using microwave assisted synthesis was cubic structure with average size of ca. 8.34 µm. However, the morphology of MOF-5 using autoclave assisted method was interpenetrated cubic with average size of ca. 22.65 µm.

1. Introduction

Metal-organic frameworks (MOF) are a class of microporous organic-inorganic hybrid materials made of metal clusters interconnected with organic linkers with a geometrically well-defined structure [1]. The organic linkers were typically a single, di-benzene or tri-benzene rings. MOF materials has unique structure with permanent but flexible porosity. It has extremely high surface area and large pore volume compared to other mesoporous materials such as mesoporous silica [1, 2]. MOF materials are gaining extensive interest in recent years due to these advanced characteristics that were making them suitable materials in gas-storage, gas separation, gas sensing and as catalysts [2]. In particular, the research of MOF-5 materials are gaining increasing interest because it was relatively easy to be produced among all other MOFs and has simple cubic structure. This is because of its organic linker that consists of only a single benzene ring [1]. The compound serves as a prototype for an extensive family of metal-organic frameworks in which oxocentered Zn_4 tetrahedra (similar to the type encountered in basic zinc acetate) that were connected through linear organo-dicarboxylates to give a cubic network structure. As the synthesis were carried out in a solution assembly reaction, the pores within the structure are filled with guest solvent molecules. The studies on various and efficient synthesis methods of MOF materials suggested to be the major role in advancing MOF materials by improving their structural properties, surface area, and single crystals size as well as overall time duration in the synthesis process. The synthesis method of MOFs includes direct-mixing method [3],

diffusion method, liquid-crystal templating (using surfactant) method [4], ultrasonic-assisted method and microwave-assisted method [5].
Therefore, this paper attempts on various synthesis approach using renewable nonsurfactant template of fatty alcohol derived from biomass, namely palm oil with C12 carbon chain (dodecyl alcohol). The methods include modified direct-mixing method, microwave-assisted and autoclave-assisted method. Then, the effect various synthesis methods on the structural characteristics of MOF-5 were investigated and studied.

2. Materials and Method

2.1 Materials
Zinc nitrate (98% $Zn(NO_3)_2.6H_2O$, Sigma-Aldrich), 1,4-benzenedicarboxylic acid (98% H_2BDC, Merck), N,N dimethylformamide (99.8% DMF, Merck), triethylamine (99% TEA, Merck) were used. Palm oil derived fatty alcohol (PODFA) dodecyl alcohol ($C_{12}H_{26}O$) was purchased from Emery Oleochemicals. All materials were used in the as-received condition.

2.2. Synthesis Approach
i) Direct-Mixing Method
$Zn(NO_3)_2.6H_2O$ and H_2BDC were dissolved in DMF under mild stirring condition for 10 minutes. Next, the dodecyl alcohol and TEA were added into the solution. Then, the solution was stirred for four hours. After that, the solution was centrifuged and washed twice with DMF. The sample was aged for two days, prior to drying. The resultant powder was dried overnight and denoted as DMOF-5.[6]
ii) Microwave-Assisted Synthesis
$Zn(NO_3)_2.6H_2O$ and H_2BDC were dissolved in DMF under mild stirring condition for 10 minutes. Next, the dodecyl alcohol was added into the solution. The solution was stirrer for another 10 minutes. Then, the solution was poured into microwave digestive bomb and heated in microwave (Sharp, Model R290HS) for 15 minutes. After that, the digestive bomb was cooled in room temperature. Then, the solution were centrifuged and washed twice with DMF. The sample was aged for two days, prior to drying. The resultant powder was dried overnight and denoted as MMOF-5.
iii) Autoclave-Assisted Synthesis
$Zn(NO_3)_2.6H_2O$ and H_2BDC were dissolved in DMF under mild stirring condition for 10 minutes. Next, the dodecyl alcohol and TEA were added into the solution. The solution was poured into Teflon autoclave. The autoclave was heated at 100°C for 24 hours. Then, the solution was heated in oven at 100°C in oven for 24 hours. After that, the autoclave was cooled in room temperature. Later, the solution was centrifuged and washed twice with DMF. The sample was aged for two days, prior to drying. The resultant powder was dried overnight and denoted as AMOF-5.

2.3. Characterizations
The X-ray diffraction analyses were conducted using Shimadzu XRD-6000 with CuK_α radiation at 2θ = 5°- 40° with 30 kV and 20 mA. The scan speed was 2°/min with scan step of 0.02°. SEM images were obtained with LEO 1455 VP SEM with 20 kV. Nitrogen adsorption were done on a Quantachrome Autosorb iQ at 77 K. Samples were degassed at 373 K overnight prior to adsorption.

3. Results and Discussion
Figure 1 shows the X-ray diffraction patterns of MOF-5 synthesized with three different methods. All samples exhibited four prominent peaks attributable to the reflection planes of (200), (220), (400) and (420) at 6.9°, 9.6°, 13.7° and 15.2° of a cubic crystal structure. These peaks were also observed in MOF-5 prepared by previous groups [1, 7]. These results suggested the successful formation of MOF-5 using PODFA with 12 carbon chains. Moreover, higher relative intensity of (220) reflection peaks compared to (200) reflection peaks suggested the pore filling effect given rise from the effect of DMF

molecules inside the pore framework during washing by solvent-lattice interactions [7,8]. This interactions was weaker than those observed in zeolitic materials [7, 8].

The results suggested that oven-drying in 24 hours at 373 K was not able to remove the solvent. The peak splitting at 9.7° was due to distortion of the cubic symmetry and resulting with tetragonal crystal formation [8]. Small peaks were observed at ca. 2θ = 32°, 34° and 36° attributable to the ZnO crystals originating from the starting precursor [9]. Additional peak at ca. 8.9° (starred) was observed for samples prepared using direct-mixing method and autoclave-assisted method suggesting that the partial hydrolysis of metal clusters and organic linkers with water molecules during the synthesis or due to exposure to water molecules in the environment [10]. Therefore, samples prepared with microwave-assisted method exhibited better stability compared to other methods. Figure 2 shows the SEM images of dried MOF-5 synthesized using different methods. The SEM image of DMOF-5 suggested faceted crystal structure. The microwave assisted resulted with cubic crystal structure. The autoclave assisted method resulted with interpenetrated cubic structure. The non-interpenetrated structure offer larger pores, larger total pore volume and lower density [11]. The average crystal sizes were ca. 1 µm for DMOF-5, 8.34 µm for MMOF-5 and 22.6 µm for AMOF-5 respectively. The modified direct-mixing synthesis suggested smallest crystals size compared to other methods. The

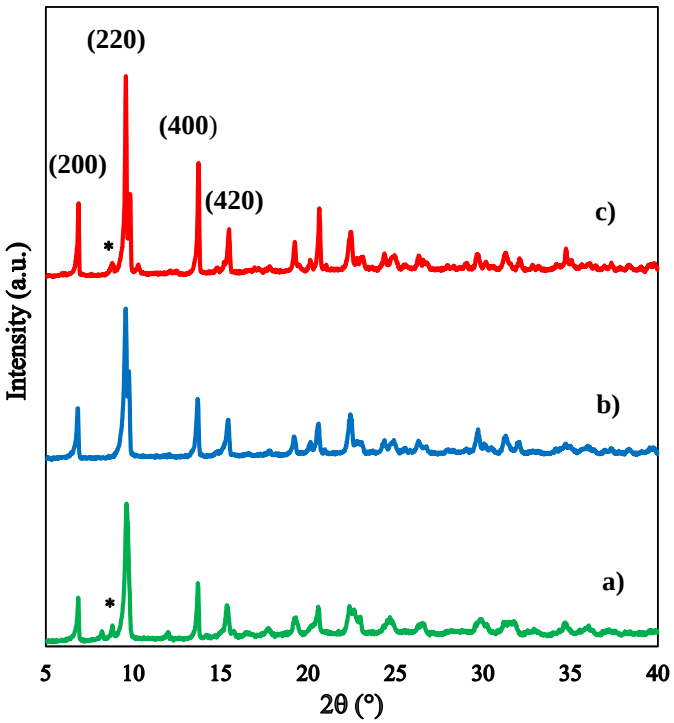

Figure 1. X-ray diffraction analyses of MOF-5 synthesized at different condition a) DMOF-5, b) MMOF-5 and c) AMOF-5.

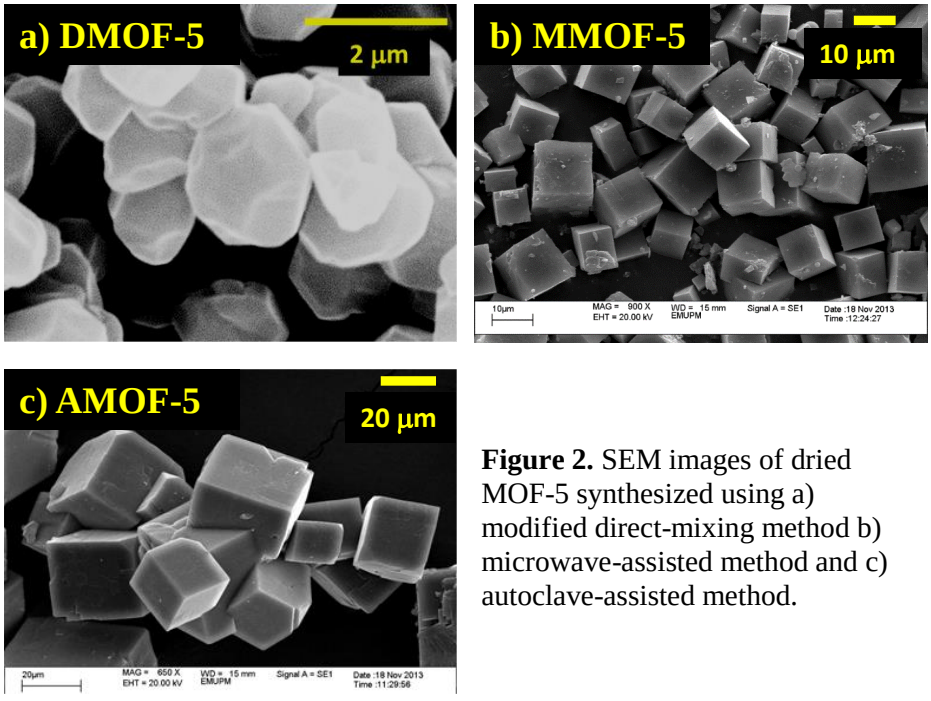

Figure 2. SEM images of dried MOF-5 synthesized using a) modified direct-mixing method b) microwave-assisted method and c) autoclave-assisted method.

autoclave assisted technique resulted with largest MOF-5 crystal with interpenetrated structure because longer heating duration at 100° for 24 hours. The long heating duration allowed crystal growth to larger size for AMOF-5. The microwave heating allowed uniform and faster nucleation which lead to homogeneous nucleation and reducing the crystallization time compared to conventional oven heating [5]. Figure 3 shows the nitrogen adsorption isotherm and its corresponding Horwath-Kawazoe (HK) pore size distribution of DMOF-5. The isotherm was Type 1 typical of microporous materials with Langmuir surface area of ca. 348 m2/g and HK pore size distribution of ca. 0.52 nm suggesting successful formation of MOF-5 with microporous structure.

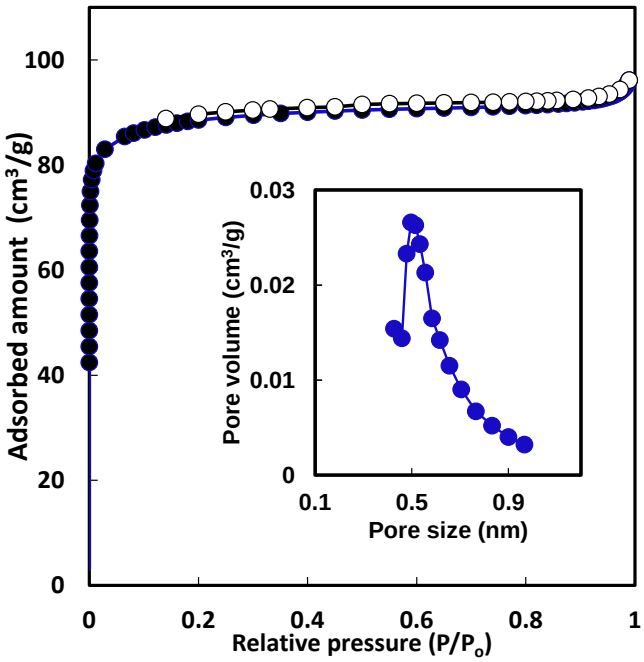

Figure 3. Nitrogen adsorption isotherm of MOF-5 prepared using microwave-assisted method and the corresponding H-K pore size distribution (inset).

2. Conclusions

All three syntheses methods were applicable to synthesis MOF-5 with dodecyl alcohol as non-surfactant template. The syntheses methods influenced crystallite formation. The microwave assisted technique resulted with cubic crystals with average crystal size of 8.34 μm, while interpenetrated cubic was obtained using autoclave assisted technique. The smallest average crystal size was obtained by modified direct-mixing technique with faceted morphology.

3. References

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