Synthesis of Metal-organic Frameworks Based on Zr$^{4+}$ and Benzene 1,3,5-Tricarboxylate Linker as Heterogeneous Catalyst in the Esterification Reaction of Palmitic Acid

Larasati, I D Winarni, F R Putri, Q A Hanif, W W Lestari*

Research Group of Porous Material for Sustainability, Chemistry Department, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Jl. Ir Sutami No.36A, Kentingan-Jebres, Surakarta, Central Java, Indonesia, 57126
Fax: +62 271 663375; Tel: +62 271 663375

*Email : witri@mipa.uns.ac.id

Abstract. The conversion of the biomass into biodiesels via catalytic esterification and transesterification became an interesting topic due to the depletion of fossil-based energy. Homogenous catalysts such as HCl, H$_2$SO$_4$ and NaOH commonly used as catalyst, however, the use of this kind of catalyst causes more problems, such as the difficulties on the separation from the product and the pollution effect on the environment. Heterogeneous catalysts, such as Metal-Organic Frameworks (MOFs) give an alternative promising way to substitute these limitations due to their strong catalytic site, porosity, high specific surface area, and easy-separation and reusable properties. Herein, we reported the synthesis of MOFs based on zirconium(IV) and H$_3$BTC linker (H$_3$BTC= benzene-1,3,5-tricarboxylic acid) by solvothermal and reflux method. Solvothermal reaction at 120 °C was found to be the optimum method, that was indicated by most crystalline product compared to the simulated pattern in XRD analysis. The formation of the framework was characterized by FTIR analysis, which showed a significant shift from 1722 cm$^{-1}$ to 1620 cm$^{-1}$. The synthesized Zr(IV)-BTC was thermally stable up to 322°C as shown by TG/DTA analysis. This high thermal stability was related to the high oxidation state of Zr(IV), which give a significant covalent character to the Zr-O bond.

1. Introduction
The development of alternative renewable energy source became an important and interesting issue to be evaluated and developed due to the depletion of fossil-based energy [1–3]. One of the interesting topics is the conversion of biomass into biodiesels via esterification and trans-esterification reaction. The production of biodiesel from biomass by esterification reaction frequently needs homogenous acid catalyst, such as H$_2$SO$_4$ and HCl due to its high selectivity and thermal stability [4, 5]. However, the use of this kind of catalyst causes more problems, such as the difficulties on the separation from the product and the pollution effect on the environment. [6]

Heterogeneous acid catalysts can be an alternative promising way to substitute the homogeneous catalyst and solve the separation and environmental problems [7,8]. One of the interesting heterogeneous catalysts is Metal-organic frameworks (MOFs). MOFs are porous crystalline materials constructed from metal cation or metal-oxide cluster as the node and organic ligand as the linker form an infinite three dimensional structure. Their high specific surface area, volume and active sites both of on the node and the linker enable them to be used as catalysts [9,10]. Their most adorable advantage...
is that their properties are tunable by modification of the node and the linker. The Lewis acid character of the MOFs come from the creation of vacant orbitals in the nodes by solvent removal, and this character can be raised by activation through heating [11, 12]. The only limitation of the use of MOFs in the catalysis is their low thermal stability.

Zirconium-based MOFs, with Zr$^{4+}$ as the metal node can be an alternative to solve this problem with their chemical, mechanical and hydrothermal stabilities. They have the most stable construction with the contribution of the carboxylate-bridge ($\text{Zr}_6\text{O}_{12}\text{(OH)}_4\text{(A)}_6\text{(CO}_2)$ building units which raise the significant covalent character [13, 14]. The first synthesized zirconium(IV) based MOFs was UiO-66, with BDC as the linkers by solvothermal method [15]. The structural variety and synthetic strategy of zirconium(IV) based MOFs are progressively developed by modifying the linkers such as aminoterephthalate [16], metallophophyrin [17] and BTC [18], and modifying the synthetic method such as microwave assisted synthesis [19] electrochemical deposition [20], reflux [11] and mechanochemical free solvent assembly [21, 22], or by embedding metal cation like copper(II) and iron(III) [23].

The application of zirconium(IV) based MOFs as catalyst has been evaluated in many kinds of reactions, including cyanosilylation of carbonyl [24], Knoevenagel condensation [25], cyclization of citronellal [26] and biomimetic reaction [17]. Herein, we report the comparison synthetic method of MOFs based on zirconium(IV)- and H$_2$BTC linker through reflux and solvothermal reaction, their characterization as well as their catalytic properties on the esterification reaction of palmitic acid with ethanol.

2. Experimental Section

2.1. Materials

Anhydrous zirconium tetra chloride ($\text{ZrCl}_4$, Merck, 98.0%), benzene 1,3,5-tricarboxylic acid (H$_3$BTC, Sigma Aldrich, 95%), acetic acid (CH$_3$COOH, Merck, 99%), ethanol (EtOH, Merck, 99.9%), methanol (MeOH, Merck, 99.9%), N,N’-dimethyl-formamide (DMF, Merck, 99.8%), acetone were used without any further purification.

2.2. Synthesis of MOFs based on Zr$^{4+}$-BTC

2.2.1. Solvothermal Method

Two different trials were conducted using reported procedure [18]. Briefly, the first trial was synthesized by dissolving 0.1165 g (0.50 mmol) of ZrCl$_4$ and 0.0353 g (0.168 mmol) of 1,3,5-benzenetricarboxylic acid in 2.8 mL of acetic acid and 5 mL of N,N’-dimethylformamide in a closed teflon line. The mixture was stirred without heating by magnetic stirring for 15 minutes before being sealed and heated at 120 °C for 24 hours. The mixture was cooled to the room temperature in the oven and then the resulting materials were recovered by filtration and washed with 5 mL of N,N’-dimethyl formamide, 5 mL of acetone and 5 mL of methanol. Finally, the resulting precipitate was dried at room temperature and activated at 200 °C for 2 hours. The second trial batch was synthesized by simply changing the heating temperature from 120 °C to 135 °C with the same procedure.

2.2.2. Reflux Method

Synthesis was carried out using reported procedure [11], by dissolving 0.1 g of ZrCl$_4$ (1 mmol) and 0.09 g (1 mmol) 1,3,5-benzenetricarboxylic acid in 7.31 mL (220 mmol) of N,N’-dimethyl-formamide in a closed round bottom flask. The mixture was heated at 80 °C for 6 hours without stirring, and followed by heating at 100 °C for 24 hours with stirring. The resulting materials were recovered by filtration and washed with 5 mL of N,N’-dimethyl-formamide. The solids were then soaked in dichloromethane for 3 hours, followed by filtration and drying in air at room temperature.

2.3. Characterization

XRD diffractograms were obtained from JEOL JDX-3530 diffractometer using Cu–Kα radiation ($\lambda = 1.5406$ Å) to confirm the expected structure, phase purity and the crystallinity of MOFs based on Zr$^{4+}$-BTC. TG and DTA curves were recorded from STA Linseis PT-1600 over the temperature range 25
°C up to 800 °C at heating rate 10 °C min⁻¹ under a flow of nitrogen to analyze the thermal stability. Scanning Electron Microscopy (SEM) were carried out on FEI type Inspect S50 to determine the morphology and surface area analysis were performed using a static volumetric apparatus Micrometries, NOVA 1200e to provide the BET specific surface area.

2.4. Catalytic Test
The solvothermal synthesized Zr⁴⁺-BTC MOFs at 120 °C was tested in a catalytic reaction on esterification reaction of palmitic acid with ethanol according to reported procedure [27]. The reaction was performed as follows: one mmol of palmitic acid and 60 mmol of ethanol were contacted with the MOF based on Zr⁴⁺-BTC with variation 0; 0.6 and 1.8% mol of total weight) in a reflux reactor at 78 °C for 2 hours. At the end of reaction, the GC-MS analysis was carried out to determine the conversion of palmitic acid into palmitate ester as a model reaction in biodiesel production.

3. Results and Discussion

3.1. Material Characterization
The MOF based on Zr⁴⁺-BTC was prepared through two different methods, the solvothermal and reflux method, to determine the optimum method and condition for the synthesis. The comparison of the diffraction pattern of the synthesized materials are presented in figure 1.

![XRD diffractogram of synthesized MOFs based on Zr⁴⁺-BTC compared to standard pattern.](image)

Figure 1. XRD diffractogram of synthesized MOFs based on Zr⁴⁺-BTC compared to standard pattern.

The solvothermal method products show the higher crystallinity than the product synthesized by reflux method. Compared to the products obtained from reflux and solvothermal method at 135 °C, material prepared by solvothermal at 120 °C has the sharpest and similar peaks with the standard pattern with 20 of the mean peak recorded on 8.6° and 8.3°.

Functional group analysis by FTIR (Fourier Transform Infra-Red) shows the significant absorption bands shifts of carbonyl (C=O) and hydroxyl (-OH) groups, as depicted in figure 2.
Figure 2. FTIR spectra of H$_3$BTC ligand and Zr$^{4+}$-BTC MOF synthesized under solvothermal reaction at 120 °C.

Significant shift was observed from 1722 to 1620 cm$^{-1}$ corresponds to C=O stretching band, and peak at 1365 cm$^{-1}$ is assigned as stretching vibration of C-O group, indicating the deprotonation of carboxylate group (from H$_3$BTC ligand) and coordination with zirconium(IV) metal ion to form [Zr$_6$O$_4$(OH)$_4$(A)$_6$(BTC)$_2$]·nH$_2$O[18]. In addition, the absorptions bands of hydroxyl groups (O-H stretching) from the ligand clearly shifted from 2663; 2878 and 2984 cm$^{-1}$ into 2779; 2983 and 3382 cm$^{-1}$. Broad band observed either in the ligand or in synthesized MOF correspond to the formation of hydrogen bonding either in the ligand or in MOFs. Moreover, broad peak observed in MOFs indicates that the zirconium ion was also coordinated with water molecules and associated with the formation of zirconium oxide cluster (Zr$_6$O$_4$(OH)$_4$(A)$_6$(CO$_2$)). The C–H aromatic vibration bands from the synthesized Zr-BTC MOF are shown at 3004 cm$^{-1}$. The peak at 1578 cm$^{-1}$ is assigned with C=C bond in the aromatic ring, while the band at 658 cm$^{-1}$ the characteristic absorption of Zr-O symmetric bond.

The thermal stability of the Zr$^{4+}$-BTC based MOF was measured with TG/DTA (fig. 3). According to thermogravimetric curves, there are three mass loss regions, which occurred at 37.8-147.7 °C; 147.7-321.7 °C and 321.7-541.1 °C. The first (53.3%) and the second (79.6%) mass losses were attributed to the removal of superficial solvents in the pore or surface of the material and the coordinated solvent in the material, respectively. The third mass loss occurred at 321.7 °C, where the framework started to decompose, and at 541.1 °C the frameworks was completely collapse. These mass loss confirmed by the DTA curves, which had endothermic peak, followed by sharp exothermic peak and the other endothermic peak. The high thermal stability of the Zr$^{4+}$BTC MOFs was confirmed to be related to the strong Zr-O bonds. The high oxidation state and high charge density of zirconium(IV) polarize the oxygen atoms from the carboxylate groups, to result the high covalent character of Zr-O bonds [14].
Figure 3. TG/DTA curves of synthesized Zr$^{4+}$-BTC MOFs.

![TG/DTA curves of synthesized Zr$^{4+}$-BTC MOFs](image)

Figure 4. (a) SEM image and (b) particle size distribution of synthesized Zr$^{4+}$-BTC MOFs.

![SEM image and particle size distribution](image)

According to SEM analysis, the synthesized Zr$^{4+}$-BTC based MOF has irregular shape with the average particle size ca. 2.738 ± 1.632 μm (Figure 4). The bigger particles were assumed as the result of agglomeration from the smaller particles. The histogram (Figure 4b) shows the less homogenous of the grain, with size range 1-7 μm. Nitrogen sorption isotherm revealed this compound has the BET surface area of 223.766 m$^2$/g.
3.2. Catalytic Activity on Esterification Reaction
Catalytic activity of the Zr\textsuperscript{4+}-BTC based MOF was evaluated on esterification reaction of palmitic acid with ethanol. Concentration variation of the catalyst were 0, 0.6 and 1.8%. The resulting analysis carried out by GC-MS as given on Table 1 and shows that catalyst loading at 0.6% was the optimum condition for the esterification reaction.

Table 1. Esterification of palmitic acid and ethanol with percent variation of Zr\textsuperscript{4+}-BTC based MOF as catalyst

| Condition        | Conversion (%) |
|------------------|----------------|
| Without catalyst | 38.61          |
| 0.6 % catalyst   | 69.20          |
| 1.8 % catalyst   | 54.82          |

4. Conclusions
The synthesis of Zr\textsuperscript{4+}-BTC based Metal-Organic Frameworks (MOFs) has been evaluated by various method. The solvothermal at 120 °C gives the most optimum resulting material as characterized in the terms of crystallinity, functional groups absorption bands shift, thermal stability, morphology and surface area. Based on the catalytic test the compound is effective as the catalyst for esterification reaction of palmitic acid and ethanol with catalyst loading of 0.6 % to give maximum conversion at 69.20 %, as shown by GC-MS analysis.

5. References
[1] Dincer I 2000 Renew. Sustain. Ener. Rev 4(2) 157–175
[2] Bu Q, Lei H, Zacher A H, Wang L, Ren S, Liang J, Wei Y, Liu Y, Tang J, Zhang Q, and Ruan R 2012 Bioresour. Technol 124 470–477
[3] Hassan M H and M A Kalam 2013 Procedia Eng 56 39–53
[4] Ejikeme P M, Anyaogu I D, Ejikeme C L, Nwafor N P, Egbuonu C A C, Ukogu K, and Ibemesi J A 2010 E-Journal Chem 7(4) 1120–1132
[5] Basha S A, Gopal K R, and Jebraaj S 2009 Renew. Sustain. Ener. Rev 13(6–7) 1628–1634
[6] Marchetti J M, Miguel V U, and Errazu A F 2007 Renew. Sustain. Ener. Rev 11(6) 1300–1311
[7] Lee A F, Bennett J, Manayi J C, and Wilson K 2014 Chem. Soc. Rev 43 7887–7916
[8] Thanh L T, Okitsu K, Van L B, and Maeda Y 2012 Catalysts 2(1) 191–222
[9] Zhou H C, Long J R, and Yaghi O M 2012 Chem. Rev 112 673–674
[10] Čejka J 2012 Angew. Chem. Int. Ed 51(20) 4782–4783
[11] Cirujano F G, Corma A, and Xamena F X L 2015 Chem. Eng. Sci 124 52–60
[12] Lee J, Farha O K, Roberts J, Scheidt K A, Nguyen S T, and Hupp J T 2009 Chem. Soc. Rev 38(5) 1450–1459
[13] Kim M and Cohen S M 2012 Cryst. Eng. Comm 14(12) 4096–4104
[14] Bai Y, Dou Y, Xie L H, Rutledge W, Li J R, and Zhou H C 2016 Chem. Soc. Rev 45(8) 2327–2367
[15] Cavka J H, Jakobsen S, Olsbye U, Guillou N, Lamberti C, Bordiga S, and Lillerud K P 2008 J. Am. Chem. Soc 6 13850–13851
[16] Kandiah M, Nilsen M H, Usseglio S, Jakobsen S, Olsbye U, Tilset M, Larabi C, Quadrelli E A, Bonino F, and Lillerud K P 2010 Chem. Mater 22(24) 6632–6640
[17] Feng D, Gu Z Y, Li J R, Jiang H L, Wei Z, and Zhou H C 2012 Angew. Chemie - Int. Ed. 51(41) 10307–10310
[18] Liang W, Chevreaux H, Ragon F, Southon P D, Peterson V K, and D’Alessandro D M 2014 Cryst. Eng. Comm. 16(29) 6530
[19] Ren J, Segakweng T, Langmi H W, Musyoka N M, North B C, Mathe M, and Bessarabov D 2014 Int. J. Mater. Res. 105(5) 516–519
[20] Stassen I, Styles M, Assche T V, Campagnol N, Fransaer J, Denayer J, Tan J C, Falcaro P, Vos D D, and Ameloot R 2015 Chem. Mater 27(5) 1801–1807
[21] Užarević K, Wang T C, Moon S Y, Fidelli A M, Hupp J T, Farha O K, and Friščić T 2016 Chem. Commun 52 (10) 2133–2136
[22] Reinsch H, Bueken B, Vermoortele F, Stassen I, Lieb A, Lillerud K P, and Vos D D 2015 Cryst. Eng. Comm. 17 (22) 4070–4074
[23] Morris W, Volosskiy B, Demir S, Gándara F, McGrier P L, Furukawa H, Cascio D, Stoddart J F, and Yaghi O M 2012 Inorg. Chem 51(12) 6443–6445
[24] Xi F G, Yang Y, Liu H, Yao H F, and Gao E Q 2015 RSC Adv. 5(97) 79216–79223
[25] Yang Y, Yao H F, Xi F G, and Gao E Q 2014 J. Mol. Catal. A Chem 390 198–205
[26] Vermoortele F, Bueken B, Voorde B V D, Vandichel M, Houthooft K, Vimont A, Daturi M, Waroquier M, Speybroeck V V, Kirschhoek C E, and Vos D E D 2013 J. Am. Chem. Soc 66 0–3
[27] Carmo A C, Souza L K C., Costa C E F, Longo E, Zamian J R, and Filho G N R 2009 Fuel 88 (3) 461–468

Acknowledgements

The authors thank the Ministry of Research, Technology and Higher Education of the Republic of Indonesia (Student Creativity Program/ PKM Grant 2016 and KI 2017) for the financial support.