Metal organic frameworks of lanthanum and iron using BDC linker as catalysts for glucose conversion into 5-hydroxymethylfurfural (5-HMF)

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Abstract. Lanthanum and Iron-Metal Organic Frameworks (La-MOFs, Fe-MOFs) have been successfully synthesized through solvothermal method and applied as catalysts to convert glucose into 5-Hydroxymethylfurfural (5-HMF). 5-HMF is a very promising energy source which extensively used in chemical industries and polymer materials. MOF is used as source of Lewis and Brønsted acid that can improve the conformation of 5-HMF in glucose transformation. The XRD pattern, surface morphology, chemical composition, absorption spectra, and surface area were characterized by X-Ray Diffractometer (XRD), Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), Fourier Transform Infrared (FTIR) and Brunauer-Emmelt-Tellers (BET). The specific peaks of La-MOF on XRD pattern corresponded at 2θ = 8° respectively, while Fe-MOF corresponded to MIL-88B structure at 2θ = 9°. SEM analysis of La-MOF and Fe-MOF revealed the catalysts morphology were rod-like and rhombic. The FTIR spectrum of La-MOF showed the broadening peak at 3526 cm$^{-1}$ for O-H stretching vibrations while Fe-MOF had sharp peak intensity at 749 cm$^{-1}$ for C-H bending vibrations. The surface area of the La-MOF and Fe-MOF were 107.107 m$^2$/g and 215.435 m$^2$/g, respectively. The activity of La-MOF and Fe-MOF as catalysts was performed in 10 mL vial glass reactor at T = 403 K with varied time from 0–8 h and catalyst loading were varied from 8–12 mg. The product analysis was carried out using High Performance Liquid Chromatography (HPLC) in which Fe-MOF showed higher activity giving yield 26.79% rather than La-MOF with 19.2% yield of 5-HMF in 6 h reaction time using 10 mg catalyst in DMSO as solvent.

Keywords: Fe-MOF, La-MOF, glucose conversion, BDC, 5-HMF production

1. Introduction

In the past few years, lignocellulose biomass conversion has been the center of interest to develop by the academics or industry. Lignocellulose biomass can be used as an alternative energy sources which can reduce the use of fuel cells [1]. This biomass contains such as cellulose, hemicellulose and lignin with glucose as the main component. Glucose can be converted into 5-hydroxymethylfurfural (5-HMF) as important precursor to other chemicals, polymer industry, and also biofuel as renewable energy [2]. 5-HMF can be formed by glucose dehydration using homogenous acid, metal ion, zeolite or heterogeneous catalysts [3, 4]. Metal Organic Framework (MOF) as one of the heterogeneous catalyst for glucose conversion has attracted a great attention because their properties, such as high
surface area [5], interested structure, gas storage [6], and photo reactive materials. MOFs consist of metal ion as “nodes” and organic ligand as “bridges” which can be synthesized using various metal ion and organic linker. MOF, as a new class of porous materials has been reported successfully for biomass conversion which HMF yield 90 % for a full fructose conversion by using MIL-101(Cr)-SO3H (15 %) as catalyst [7]. Based on previous report [8], in this study MOF was synthesized using Lanthanum (La) and Iron (Fe) as metal ions and benzenedicarboxylic acid (BDC) as linker. The catalysts were used for glucose conversion into 5-hydroxymethylfurfural (5-HMF). The used of MOFs as catalysts will increase the activity of glucose dehydration to 5-HMF because the amount of Lewis acid and Brønsted acid site should be significant. La-MOF and Fe-MOF were characterized to obtain information on crystal size, surface morphology, thermal stability, functional group and surface area, so it can give the best performance to convert glucose into 5-HMF.

2. Materials and method

2.1. Materials

The entire chemicals were analytical grade and used directly without further purification. The chemicals and reagents used were: lanthanum nitrate (La(NO3)3.6H2O) 99 % (Sigma Aldrich), iron chloride (FeCl3.6H2O) 99 % (Sigma Aldrich), 1,4-benzenedicarboxylic acid (C8H6O4) 99 % (BDC) (Sigma Aldrich), N,N-dimethylformamide (C3H7NO) (Merck Co), D-glucose monohydrate (C6H14O7) 99 % (Merck Co), dimethyl sulfoxide 99 % (DMSO) from Sigma Aldrich and ethanol.

2.2. Synthesis of La-BDC MOF and Fe-BDC MOF

La-BDC and Fe-BDC MOF was synthesized using solvothermal method based on previous works [9]. Lanthanum nitrate (1 mmol) with 1,4-benzenedicarboxylic acid (1.5 mmol) was diluted in a solution of 5 mL DMF and a mixture of 0.25 mL H2O [10] under vigorous stirring for 30 min and transferred into a Teflon lined stainless steel autoclave and heated over 120 °C for 20 h. Afterward, the crystals formed was separated and washed with 5-10 mL DMF and acetone, then dried at 60 °C for 24 h. Fe-BDC MOF was also synthesized using the same method and washed with ethanol. MOFs were characterized using FTIR, XRD, BET and SEM. Powder X-ray diffraction (PXRD) was registered on a Shimadzu 6000 with Cu-Kα 1/2 radiation (λ = 1.54184 Å) and 2θ = 2–30° (step width 0.02° in 2θ) and operated at 40 kV and 40 mA. FTIR analysis was also carried out at room temperature at wavelengths of 400–4000 cm⁻¹ using FTIR Prestige 21 Shimadzu's. Scanning electron microscope (SEM) image taken on JEOL JSM-G510LA SEM emission field with lens semi-detector using a working distance of 3 mm and an acceleration voltage of 20 kV. The surface area and pore size were measured using the Quantachrome QuadraWin 2000–16 with the adsorption/desorption method.

2.3. Application of La-BDC and Fe-BDC MOF as catalyst to convert glucose into 5-hydroxymethylfurfural

La-BDC and Fe-BDC MOF were used as catalysts for the glucose conversion into 5-hydroxymethylfurfural (5-HMF). The catalytic tests were performed in 10 mL vial glass reactor at T = 403 K with varied time from 0, 3, 6 and 8 h and also varied amount of catalysts (0, 8, 10 and 12 mg). Then, 2 mL of 10 % wt. glucose solution in H2O or DMSO were added to the reactor and mixed with catalyst. Blank experiment was carried out without catalyst. After heated for various reaction times, the vial was immediately placed into an ice bath at 5 °C to stop the reaction. The solution was filtered and then the product was analyzed with High Pressure Liquid Chromatography using LC200 Quantine Isochratic Pump with Inertsil ODS column packaged, UV detector with 285 cm⁻¹ wavelengths (for 5-HMF) was used.
3. Results and discussion

Metal organic framework MIL-88B of La-BDC and Fe-BDC MOF were produced via solvothermal method based on Zhu et al. [9]. Figure 1 shows the XRD pattern of La-BDC MOF and Fe-BDC MOF. Based on figure 1, it can be seen that there were peaks with high intensity which indicated the crystallinity of La-BDC MOF and Fe-BDC MOF. The diffractogram of La-BDC MOF (figure 1) exhibits clear specific peaks in $2\theta = 9.54^\circ$ and $10.62^\circ$. The small impurity was observed at $2\theta$ at $16.37^\circ$, $28.84^\circ$, $26.75^\circ$ and $35.09^\circ$. Meanwhile, the Fe-MOF shows peaks at $9.36^\circ$, $10.01^\circ$, $16.74^\circ$, $20.30^\circ$ and $24.25^\circ$ which are in good agreement with the simulated MIL-88B structure [10].

SEM analysis of La-BDC and Fe-BDC materials are represented in figure 2, in which La-BDC shows morphology of rod-like with larger and agglomerated particles, while Fe-BDC was rhombic and quite uniform in small particles. It is suggested that Fe-BDC MOF with smaller particles will have a higher surface area, which confirmed by BET analysis in figure 3. La-BDC particles were agglomerated and are not uniform compared to rhombic shape Fe-BDC particles [11].

EDX analysis of La-BDC MOF and Fe-BDC MOF is confirmed by the previous research [12]. The element content of La-BDC are C 48.95 %, O 16.91 % and La 34.14 %, while the Fe-BDC consists of C 59.29 %, O 16.50 %, Cl 7.02 % and Fe 17.18 %.

![Figure 1. XRD pattern of La-BDC MOF and Fe-BDC MOF.](image1)

![Figure 2. SEM images of A. La-BDC and B. Fe-BDC for 10,000x magnitude.](image2)
Functional groups and vibrational spectra were determined using FTIR as described in figure 4. La-BDC spectrum has a broad band at 3526–2666 cm$^{-1}$ with low intensity, assigned for O–H stretching vibration of coordinated and uncoordinated water molecules, indicating that complex interaction between metal and linker was formed. There was low intensity peak at 1593 and 1395 cm$^{-1}$ region which indicated the symmetry and asymmetry C=O stretching vibration from carboxylic in the coordinated framework with $\Delta \nu = 198$ cm$^{-1}$. This difference indicated that the bridging mode of the carboxylic groups are found in this compound. C=C stretching vibration appears in 1400–1564 cm$^{-1}$ area with medium intensity peak from aromatic groups [13].

Fe-BDC spectra show that at 556 cm$^{-1}$ peak belongs to Fe-O symmetric stretching and in area 1434–1391 cm$^{-1}$ indicated the asymmetric and symmetrical O–C–O. The asymmetric C–H bending appeared at 1505 cm$^{-1}$ while at 1652 cm$^{-1}$ the peak from C=O vibration from carboxylic groups appeared with weaker peak. The characteristic peaks shown at 748 cm$^{-1}$ and 461 cm$^{-1}$ represent the C–H bending vibrations form benzene [14].

![Figure 3](image.png)

Figure 3. Graph of (a) isotherm absorption and desorption of La-BDC MOF and Fe-BDC MOF, (b) pore size distribution of La-BDC and Fe-BDC MOF.

![Figure 4](image.png)

Figure 4. FTIR spectra of BDC, La-BDC MOF and Fe-BDC MOF.
BET analysis was determined to show the surface area by using Bernaeur Emmert Teller (BET) equation.

In this experiment, the surface area for La-BDC MOF was 107.107 m$^2$/g and for Fe-BDC MOF was 215.435 m$^2$/g. Lower surface area of La-BDC MOF rather than of Fe-BDC MOF indicated that the form of La-BDC MOF was a closed pore system [15]. Both La-MOF and Fe-MOF pore radius were 16-18 Å, while the pore volume of La-BDC and Fe-BDC were 0.103 cm$^3$/g and 0.152 cm$^3$/g, respectively. Based on the isotherm absorption and desorption curves, it can be suggested that the MOFs were Type I materials (microporous) which shown in figure 3. The difference of synthesis condition would give a different specific surface area, in which more irregular shape of particles will give lower surface area [16]. The higher surface area of Fe-BDC has confirmed the uniformity and smaller size of particles observed by SEM, which was expected to become a better catalyst to convert the glucose into 5-HMF rather than La-BDC MOF.

The catalytic activity of La-BDC MOF and Fe-BDC MOF was performed in 10 mL vial glass reactor by using glucose solution in water and DMSO. The first optimization was carried out by varying the reaction time, and the results are shown in figure 5a. The yield of 5-HMF shown in figure 5a with Fe-BDC MOF give a higher activity than La-MOF and blank. When the time reaction increased from 3 h to 6 h there was an increasing yield of 5-HMF from 0.04 % to 1.81 % for La-BDC MOF while Fe-BDC MOF increased from 0.97 % to 11.06 %. Thereafter, as the time reaction increased to 8 h, the yield of 5-HMF were decreased significantly to 0.57 % and 2.78 % for La-BDC MOF and Fe-BDC MOF, respectively, which is similar as the report in [16]. This may due to the decomposition of 5-HMF after 6 h and also because of the reaction pathways for 5-HMF decomposition to form levulinic and humin as by-product of this dehydration reactions as shown by the color change from clear to black [8].

The second optimization was the variation of catalyst loading. There was a significant increase in the yield of 5-HMF as the catalyst loading increased from 8 mg to 10 mg, but as the catalyst loading increased to 12 mg the yield of 5-HMF was decreased. We assumed that 10 mg is the optimum catalyst loading to produce 5-HMF. Fe-BDC also consistently has a greater yield than La-BDC MOF which only 11.22 % while compared with 1.78 % in La-BDC MOF as shown in figure 5b. It was influenced by its material characteristics such as surface area and morphology, in which the Fe-BDC MOF surface area is greater than La-BDC MOF. As the catalyst loading increased, the amount of embedded Lewis acid cites will be increased leading to more of 5-HMF production. However, the 5-HMF produced using 12 mg catalyst loading was decreased, we assumed that this is due to the compounds (including humin) were produced as the catalyst loading increased.

![Figure 5](image.png)

**Figure 5.** Catalytic activity of La-BDC MOF and Fe-BDC MOF in glucose conversion to 5-HMF in water solution: (a) variation of reaction time and (b) variation of catalyst loading.
Figure 6. Catalytic activity of La-BDC MOF and Fe-BDC MOF in glucose conversion to 5-HMF in DMSO solution: (a) variation of reaction time and (b) variation of catalyst loading.

The last optimization process was solvent variation by using DMSO as glucose solvent to determine the stability of MOFs as shown in figure 6. DMSO as glucose solvent was employed in the reaction with variation of reaction time and different catalyst loading. The percentage yield of 5-HMF was increased for La-BDC MOF from 5.17 % to 19.21 % while when using Fe-BDC MOF, the yield was significantly increased from 9.79 % to 26.79 % as the reaction time increased from 3 h to 6 h, but decreased after 6 h reaction time. There was no significant change of % yield over time in the blank experiment. Similarly, the experiments were carried out using water as solvent, the % yield of 5-HMF reached maximum at 10 mg catalyst loading then decreased as the catalyst loading increased.

It is suggested that water can facilitate the conversion of glucose into 5-HMF because of the increase in their solubility of the substrate. On the other hand, the use of DMSO as solvent has given a higher % yield of 5-HMF compared to water, because it can reduce the formation of by-products from the mechanism of glucose dehydration [17]. Also, DMSO will increase the formation of β-D-fructofuranose so it will increase the isomerization of glucose into fructose and also increase the yield of 5-HMF [18].

4. Conclusion
La-BDC and Fe-BDC have been successfully synthesized using DMF and H₂O as solvent via solvothermal method. Based on the results, XRD pattern of materials shows the similarity peaks with MIL-88B. SEM images show that La-BDC was a rode-like and the Fe-BDC was rhombic, while the specific surface area was 107.107 m²/g for La-BDC and 215.28 m²/g for Fe-BDC. Based on this work, the optimum condition for glucose conversion to 5-HMF is 10 mg of catalysts mixed with glucose in 10 mL of DMSO (10% w/v solution) and heated until 403 K for 6 h which give % yield of 19.21 % and 26.79 % for La-BDC MOF and Fe-BDC MOF, respectively. To conclude, Fe-BDC MOF is a more active catalyst for glucose conversion to form 5-HMF.

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References
[1] Li X et al. 2019 *Ind. Crops Prod.* **130** 184-97
[2] Herbst A and Janiak C 2016 *New J. Chem.* **40** 7958-67
[3] Qi X, Guo H, Li L and Smith R L. 2012 *ChemSusChem* **5** 2215-20
[4] Su Y et al. 2016 *Am. Inst. Chem. Eng.* **62** 4403-17
[5] Pertiwi R et al. 2019 *Catalysts* **9** 1-20
[6] Li H et al. 2019 *EnergyChem* **1** 100006
[7] Chen J et al. 2014 *Green Chem.* **16** 2490-9
[8] Gong J, Katz M J and Kerton F M 2018 *RSC Adv.* **8** 31618-27
[9] Zhu T-T, Zhang Z-M, Chen W-L, Liu Z-J and Wang E-B 2016 *RSC Adv.* **6** 81622-30
[10] Shi L et al. 2015 *Adv. Sci.* **2** 1500006
[11] Pertiwi R 2017 *Investigation of Metal Organic Frameworks (MOFs): MIL-101 and MB2 as Potential Catalyst for Biomass Derived Transformation* Master Thesis (Depok: Universitas Indonesia)
[12] Wu Z et al. 2016 *Energy Fuels* **30** 10739-46
[13] Abdelbaky M S M, Amghouz Z, García-Granda S and García J R 2016 *Polymers* **8** 1-15
[14] Nehra M 2019 *Environ. Res.* **169** 229-36
[15] Pu M et al. 2018 *Appl. Catal. A Gen.* **549** 82-92
[16] Kuster B F M 1990 *Starch* – *Stärke* **42** 314-21
[17] Baslyman W 2015 *Microwave-assisted Dehydration of Fructose into 5-Hydroxymethylfurfural (5-HMF) over Acidic Porous Catalysis* Master Thesis (Ottawa, Ontario: University of Ottawa)
[18] Mirzaei H M and Karimi B 2016 *Green Chem.* **18** 2282-6