SYNTHESIS AND CHARACTERIZATION OF ZEOLITIC IMIDAZOLATE FRAMEWORK-8 (ZIF-8)/Al₂O₃ COMPOSITE

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Abstract

Metal-organic framework (MOF) such as ZIF-8 is the tremendous porous material applied in many fields due to high specific surface area and excellent regularity of pores. One technique to improve the physical properties of ZIF-8 with the formation of a composite between a metal oxide and MOF. ZIF-8 and ZIF-8/Al₂O₃ were successfully synthesized by the solvothermal method with an Al variation of 19%, 38%, and 76%. The ZIF-8/Al₂O₃ were characterized by XRD, FTIR, SEM, and N₂ Physisorption. The diffractogram shows that the appearing of ZIF-8’s peak on 2θ = 7.26; 10.41, 12.66, 16.41, and 17.95°. The morphological of ZIF-8 crystals had a cubic shape. Then the ZIF-8/Al₂O₃ had different shapes with ZIF-8. Based on the FTIR result, the Zn-N peak appears on 420 cm⁻¹, which indicates the bonding between metal and organic ligand for ZIF-8/Al₂O₃ has an additional spike on 825 cm⁻¹ due to the vibration of Al − O − Al.

KEYWORDS:
Synthesis, ZIF-8, Al₂O₃, Metal-Organic Framework

1 | INTRODUCTION

Metal-Organic Framework (MOF) is a tremendous crystalline and porous material with a large specific surface area, where the MOF structure was formed by coordination bonding between metal and organic ligand. In this era, MOF used in many fields and applications such as adsorbent, catalyst, porous support, hydrogen storage material, etc. Zeolitic Imidazolate Framework(ZIF) is a porous material which contains divalent metal and connected with imidazole ligand. ZIF has properties such as better thermal stability compared to other types of zeolite.

ZIF-8 is one type of ZIF that catches the attention of researchers in the world due to SOD of crystal topography(SOD means Sodalite framework), then the pore size is 11.6 Å. In this framework, ZIF-8 has lewis acid-base properties such as lewis acid..
from Zn$^{2+}$ and Lewis base from N in imidazole structure. This is why ZIF-8 has potency as a heterogeneous catalyst, and it was well-known as a catalyst in Knoevenagel reaction \[5, 6\].

Some researchers modified ZIF-8 to improve their properties. Li et al. \[7\] used Ni nanoparticles and ZIF-8 to enhance the catalytic activity in the hydrolysis reaction of Ammonia boran. Zahmarikan et al. \[8\] used a combination of Iridium nanoparticles and ZIF-8 to increase the rate of catalytic reaction for hydrogenation of cyclohexane. Based on the previous study, ZIF-8 has excellent catalytic activity if it is combined with another metal that has strong lewis acid cite. Another promising material that has excellent properties is Al$_2$O$_3$. It has very high thermal stability, and it can be used as one of the precursors to form a composite with ZIF-8.

Alumina is a metal oxide applied in many fields on the fabrication of thin layer, membrane, and catalyst. It was used in many areas due to excellent thermal and hardness stability and their amphoteric properties \[9\]. Zhang et al. \[10\] used PtSn as an active site supported on Al$_2$O$_3$ on the hydrogenation reaction of acetic acid. On the other hand, Zhou et al. \[11\] also used Al$_2$O$_3$ as support material for the synthesis of Au/Al$_2$O$_3$ for hydrogenation of acetylene. This research aims to synthesize the ZIF-8/Al$_2$O$_3$ composite and identity of structural, morphological, functional groups, and surface as well as pores of ZIF-8/Al$_2$O$_3$.

### 2 MATERIAL AND METHOD

#### 2.1 Materials

All percursors and Al$_2$O$_3$ from Merck were used to synthesis ZIF-8/Al$_2$O$_3$. The precursors such as Zn(NO$_3$)$_2$, 4H$_2$O, 2-methyl-imidazole, DMF, Al$_2$O$_3$, and methanol.

#### 2.2 Synthesis of ZIF-8 and ZIF-8/Al$_2$O$_3$

ZIF-8 was synthesized by solvothermal method, i.e. 2.091 g of Zn(NO$_3$)$_2$, 4H$_2$O as a source of Zn$^{2+}$ dissolved into 15 mL of DMF’s stirred for 30 minutes until homogenous, this solution denoted as A solution. Then, 1.3138 of 2-MeIM was dissolved into 15 mL of DMF and stirred for 15 minutes. It was denoted as B solution. The A and B solutions were mixed inside the Durant bottle and stirred for 30 minutes. The mixed solution would form Metal-Organic Frameworks (MOF) by solvothermal reaction at 120°C for 24 h. Then, the ZIF-8 and filtrate were separated by decantation method. The ZIF-8 powders have been washed by using 15 mL of methanol. Then, it was separated by Bunchner funnel, and the ZIF-8 heated up at 70°C.

ZIF-8/Al$_2$O$_3$ was synthesized by a similar method with ZIF-8’s synthesis, but the process for the preparation of B solution has a different way. For the synthesis of ZIF-8/Al$_2$O$_3$, the preparation of B solution was followed by the addition of Al$_2$O$_3$ with a variation of 19, 38, and 76% w/w. The ZIF-8 and ZIF-8/Al$_2$O$_3$ were characterized by X-Ray Diffractometer Rigaku Miniflex II, Fourier Transform 8400 Shimadzu, Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) Vega3 Tesca, and N$_2$ physisorption.

### 3 RESULTS AND DISCUSSION

#### 3.1 Structural study of ZIF-8 and ZIF-8/Al$_2$O$_3$ used XRD

The structural characterization was carried out by XRD to determine crystal structure as well as their crystallinity. The observation was started from 2θ = 5-100° using x-ray source of Cu-Kα (λ = 1.5406 Å). Then, the XRD result was shown in Figure 1, and it was compared to a previous study reported by Nguyen et al. \[12\]. Based on Figure 1, XRD pattern of ZIF-8 shows a typical peak at 2θ = 7.26, 10.41, 12.66, 16.41, and 17.95°. The highest intensity appears at 2θ = 7.26°, which indicates that ZIF-8 has high crystallinity. The suitability of the results with reference shows that ZIF-8 was successfully synthesized, and there was no impurity contained therein. The ZIF-8/Al$_2$O$_3$’s XRD pattern synthesized has a match with ZIF-8, which is shown by a typical peak appearance at 2θ, which is almost the same as ZIF-8. Strong intensity is at 2θ = 7°. Al$_2$O$_3$ has been successfully impregnated on ZIF-8, which is indicated by a typical peak at 2θ = 60-68°. This peak has a low intensity because. Al$_2$O$_3$
is amorphous. This fact is also supported by the ZIF-8/Al₂O₃ diffractogram, where the more amount of Al₂O₃ decreases the crystallinity, which indicates a change in particle size. The lower the crystallinity, the smaller the particle size [13]

3.2 | Functional Group Analysis by FTIR

FTIR characterization was carried out to find out information about functional groups of ZIF-8 and ZIF-8/Al₂O₃. The synthesized ZIF-8 showed an absorption peak at 420 cm⁻¹ which showed stretching vibrations of Zn-N, 758.04 cm⁻¹ (bending vibration of C-H), 995.3 cm⁻¹ and 1145.75 cm⁻¹ (bending vibration of C-N), 1581.68 cm⁻¹ (bending vibration of C=N), 1680.05 cm⁻¹ (stretching vibration of C=O), 2929.96 cm⁻¹ (stretching vibration of C-H sp³), and 3134.43 cm⁻¹ (stretching vibration of C-H sp²). This absorption peak is in accordance with the research conducted by Hu et al. [14]. ZIF-8/Al₂O₃ material has the same absorption as ZIF-8, but there are additional Al₂O₃ absorption peaks at 825 cm⁻¹ (Al-O-Al vibration), 1642 cm⁻¹ (bending vibration of O-H) and 3458 cm⁻¹ (stretching vibration of O-H). This result indicates that Al₂O₃ has been successfully impregnated on ZIF-8. In samples A and B, the peak OH vibration absorption is clearly visible because the amount of Al₂O₃ added to ZIF-8 is also greater than that of sample C in Figure 2.

3.3 | Morphological observation of ZIF-8 and ZIF-8/Al₂O₃

ZIF-8 and ZIF-8/Al₂O₃ materials have been characterized using SEM-EDX to determine the morphology and the distribution of the elements. ZIF-8 material has a cubic shape and good regularity [12], while at ZIF-8/Al₂O₃ with a variation of 76%, it appears to have a spherical shape and not sharp can be seen in Figure 3. This appearance is due to Al₂O₃ is amorphous so that it will affect the shape of ZIF-8 when impregnated. The distribution of the composition of ZIF-8 and ZIF-8/Al₂O₃(76%) can be seen in Figure 4. Figure 4 shows that the elements Zn, C, O, and N have spread on the surface of ZIF-8, and the elements Zn, C, O, N, and Al has been successfully impregnated on the surface of ZIF-8/Al₂O₃(76)
3.4 Surface area and pore's properties of ZIF-8 and ZIF-8/Al₂O₃

The surface analysis using N₂ physisorption aims to determine the surface area and pore size of material ZIF-8, ZIF-8/Al₂O₃(38), ZIF-8/Al₂O₃(76) on table 1. The results of the characterization show that the synthesized material had micropore and mesoporous pore types. The result is because at low pressure, the material has adsorbed many adsorbates. During high pressure, a hysteresis pattern occurs where the amount of adsorption is not the same as desorption. Material with a ratio of ZIF-8/Al₂O₃(38)
FIGURE 4 Morphological of (a) ZIF-8 and (b) ZIF-8/\textit{Al}_2\textit{O}_3. 

TABLE 1 The specific surface area and pore size of ZIF-8 and ZIF-8/\textit{Al}_2\textit{O}_3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S BET (m²/g)</th>
<th>V micro (cc/g)</th>
<th>V meso (cc/g)</th>
<th>V total (cc/g)</th>
<th>Average Radius Pore (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-8</td>
<td>835.2</td>
<td>0.4289</td>
<td>0.0049</td>
<td>0.4504</td>
<td>1.078</td>
</tr>
<tr>
<td>ZIF-8/\textit{Al}_2\textit{O}_3 (38)</td>
<td>695.8</td>
<td>0.3555</td>
<td>0.0596</td>
<td>0.4188</td>
<td>1.204</td>
</tr>
<tr>
<td>ZIF-8/\textit{Al}_2\textit{O}_3 (76)</td>
<td>396.2</td>
<td>0.1976</td>
<td>0.1235</td>
<td>0.3046</td>
<td>1.538</td>
</tr>
</tbody>
</table>

FIGURE 5 Isotherm adsorption-desorption of ZIF-8, ZIF-8/\textit{Al}_2\textit{O}_3 (38), and ZIF-8/\textit{Al}_2\textit{O}_3 (76), relative pressure (P/P°) vs. volume of nitrogen adsorbed in STP (cc/g).

has a higher surface area compared to ZIF-8/\textit{Al}_2\textit{O}_3 (76), so that it has the potential to be applied as an adsorbent. The increasing \textit{Al}_2\textit{O}_3, which impregnated on ZIF-8, leads to a decrease in micropores volume and increase mesoporous volume. The role of \textit{Al}_2\textit{O}_3 in ZIF-8 material is the active side, which will bind the adsorbate and give effect to the presence of mesoporous pores in Figure 5.
4 | CONCLUSION

Based on the results of the research mentioned, it can be concluded that ZIF-8 has a regular, sharp cubic and spherical characteristics that are caused by $\text{Al}_2\text{O}_3$ being amorphous, which affected the shape of ZIF-8 when impregnated. In the XRD pattern of ZIF-8, the synthesis results showed a typical peak at $2\theta = 7.26, 10.41, 12.66, 16.41$, and $17.95^\circ$. In the $N_2$ adsorption-desorption test, it was found that the synthesized material had micropores and mesoporous of pore types which due to the low-pressure material had adsorbed many adsorbates and during high pressures a hysteresis pattern occurred where the amount of adsorption was not the same as desorption, where the material was ZIF-8/$\text{Al}_2\text{O}_3$(38) has a higher surface area compared to ZIF-8/$\text{Al}_2\text{O}_3$(76). It can be concluded that ZIF-8/$\text{Al}_2\text{O}_3$(38) can be applied as an adsorbent or catalyst support.

5 | ACKNOWLEDGEMENT

The authors thank the Ministry of Research and Higher Education of Indonesia for financial support for this research under "Program Kreativitas Mahasiswa (PKM) 2019" grants. We also thank Material Chemistry and Energy’s Laboratory ITS for providing research facilities.

References
