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ORIGINAL RESEARCH

SYNTHESIS AND CHARACTERIZATION OF ZEOLITIC IMIDAZOLATE FRAMEWORK-8 (ZIF-8)/Al_2O_3 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/Al_2O_3 were successfully synthesized by the solvothermal method with an Al variation of 19%, 38%, and 76%. The ZIF-8/Al_2O_3 were characterized by XRD, FTIR, SEM, and N_2 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/Al_2O_3 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/Al_2O_3 has an additional spike on 825 cm^{-1} due to the vibration of $Al-O-Al$.

KEYWORDS:

Synthesis, ZIF-8, Al_2O_3, 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 [1]. In this era, MOF used in many fields and applications such as adsorbent, catalyst, porous support, hydrogen storage material, etc. [2]. 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 [3].

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 [4]. 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_2O_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_2O_3 on the hydrogenation reaction of acetic acid. On the other hand, Zhou et al. [11] also used Al_2O_3 as support material for the synthesis of Au/Al_2O_3 for hydrogenation of acetylene. This research aims to synthesize the ZIF-8/Al_2O_3 composite and identity of structural, morphological, functional groups, and surface as well as pores of ZIF-8/Al_2O_3.

2 | MATERIAL AND METHOD

2.1 | Materials

All percusors and Al_2O_3 from Merck were used to synthesis ZIF-8/Al_2O_3. The precursors such as $Zn(NO_3)_2, 4H_2O$, 2-methyl-imidazole, DMF, Al_2O_3, and methanol.

2.2 | Synthesis of ZIF-8 and ZIF-8/Al_2O_3

ZIF-8 was synthesized by solvothermal method, i.e. 2.091 g of $Zn(NO_3)_2.4H_2O$ as a source of Zn^{2+} was 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_2O_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_2O_3, the preparation of B solution was followed by the addition of Al_2O_3 with a variation of 19, 38, and 76% w/w. The ZIF-8 and ZIF-8/Al_2O_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_2O_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_2O_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_2O_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_2O_3

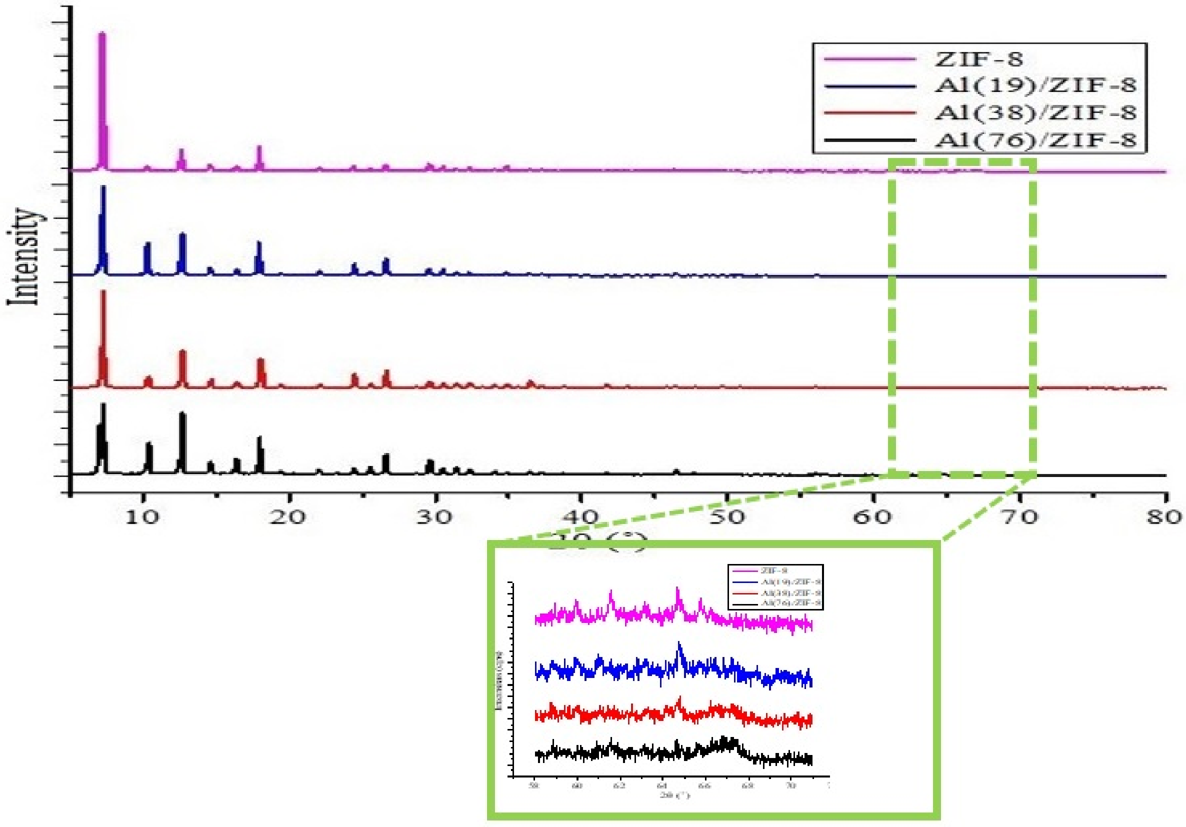

FIGURE 1 XRD pattern of ZIF-8/Al2O3 with variation of 0, 19, 38, and 76%w/w, 2ϑ vs intensities (cps).

is amorphous. This fact is also supported by the ZIF-8/ Al_2O_3 diffractogram, where the more amount of Al_2O_3 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/ Al_2O_3. 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=C), 2929.96 cm^{-1} (stretching vibration of C-H sp^3), and 3134.43 cm^{-1} (stretching vibration of C-H sp^2). This absorption peak is in accordance with the research conducted by Hu et al. [14]. ZIF-8/Al_2O_3 material has the same absorption as ZIF-8, but there are additional Al_2O_3 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 Al_2O_3 has been successfully impregnated on ZIF-8. In samples A and B, the peak OH vibration absorption is clearly visible because the amount of Al_2O_3 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/Al_2O_3

ZIF-8 and ZIF-8/Al_2O_3 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/Al_2O_3 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 Al_2O_3 is amorphous o that it will affect the shape of ZIF-8 when impregnated. The distribution of the composition of ZIF-8 and ZIF-8/Al_2O_3(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/Al_2O_3(76

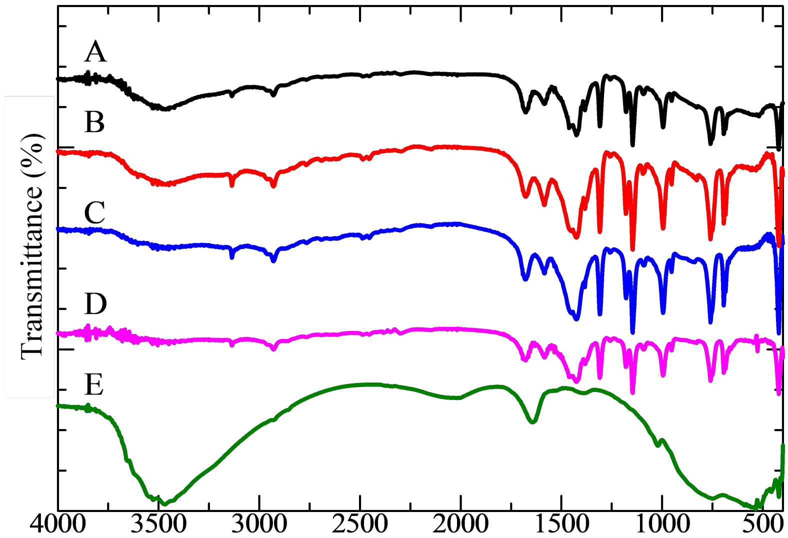

FIGURE 2 FTIR spectra of ZIF-8/Al2O3 with variation of (A) 76, (B) 38, (C) 19, (D) 0% w/w, and (E) γ-Al_2O_3, absorbance (cm^{-1}) vs transmittance (%).

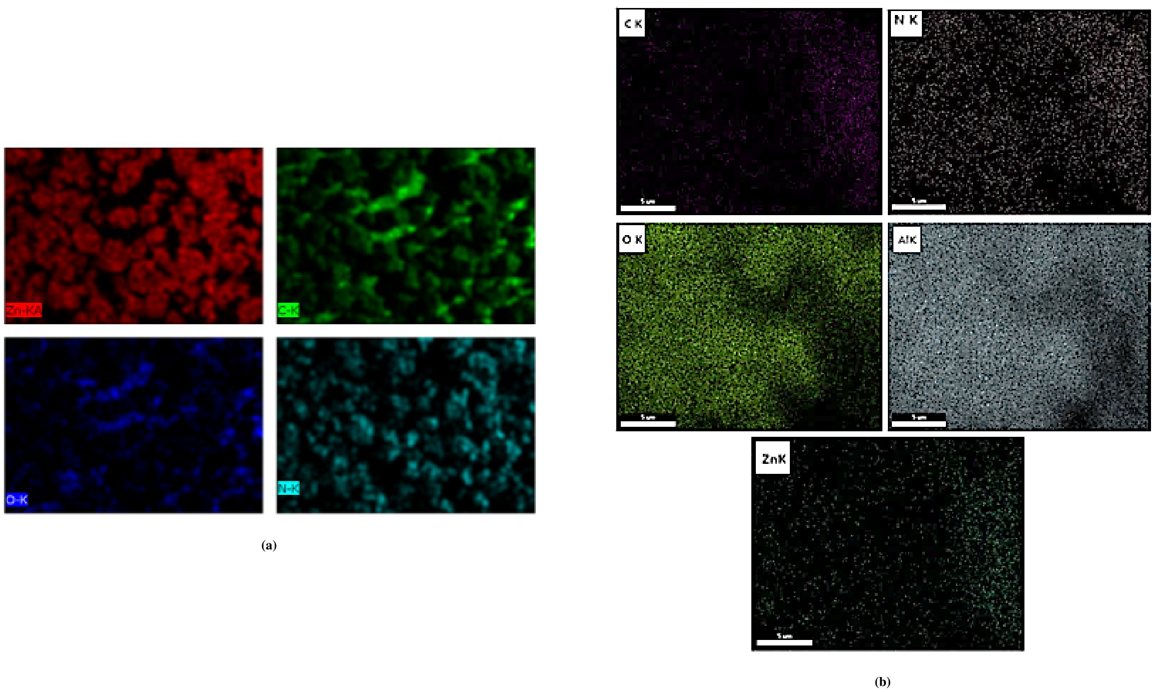

FIGURE 3 Elemental distribution of (A) ZIF-8 and (B) ZIF-8/Al_2O_3 (76% w/w).

3.4 | Surface area and pore's properties of ZIF-8 and ZIF-8/Al_2O_3

The surface analysis using N_2 physisorption aims to determine the surface area and pore size of material ZIF-8, ZIF-8/Al_2O_3(38), ZIF-8/Al_2O_3(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/Al_2O_3(38)

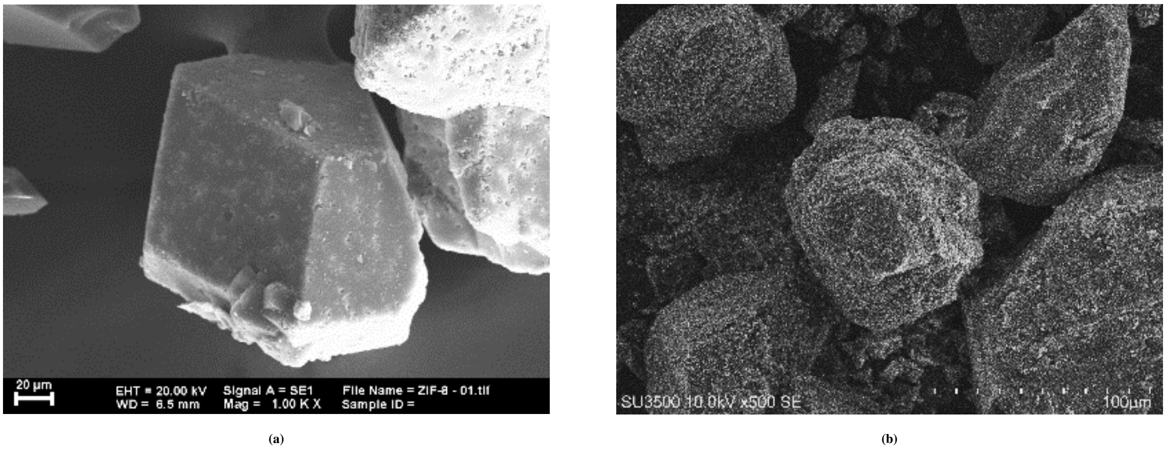

FIGURE 4 Morphological of (a) ZIF-8 and (b) ZIF-8/Al_2O_3.

TABLE 1 The specific surface area and pore size of ZIF-8 and ZIF-8/ Al_2O_3.

Sample)	S BET (m2/g)	Pore Volume (cc/g)			Average Radius Pore (nm)
		V micro	V meso	V total	
ZIF-8	835.2	0.4289	0.0049	0.4504	1.078
ZIF-8/Al2O3 (38)	695.8	0.3555	0.0596	0.4188	1.204
ZIF-8/Al2O3 (76)	396.2	0.1976	0.1235	0.3046	1.538

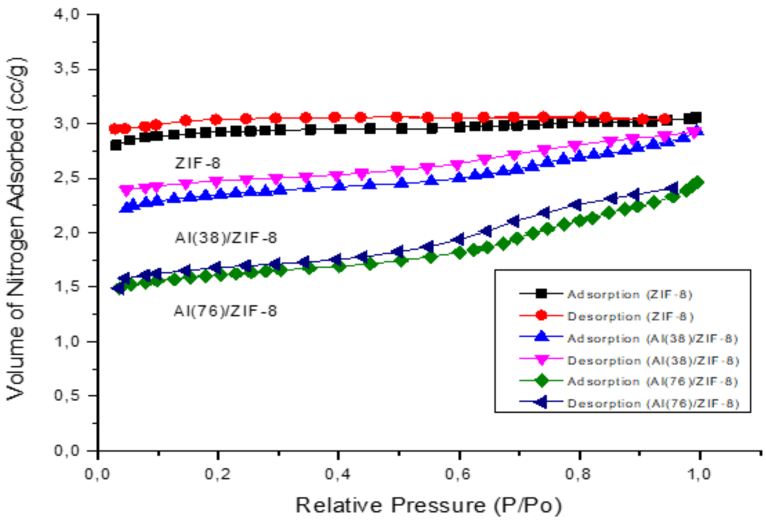

FIGURE 5 Isotherm adsorption-desorption of ZIF-8, ZIF-8/Al_2O_3 (38), and ZIF-8/Al_2O_3 (76), relative pressure (P/Po) vs. volume of nitrogen adsorbed in STP (cc/g).

has a higher surface area compared to ZIF-8/Al_2O_3(76), so that it has the potential to be applied as an adsorbent. The increasing Al_2O_3, which impregnated on ZIF-8, leads to a decrease in micropores volume and increase mesoporous volume. The role of Al_2O_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 Al_2O_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 $2\vartheta = 7.26, 10.41, 12.66, 16.41$, and $17.95°$. 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/Al_2O_3(38) has a higher surface area compared to ZIF-8/Al_2O_3(76). It can be concluded that ZIF-8/Al_2O_3(38) can be applied as an adsorbent or catalyst support.

5 | ACKNOWLDGEMENT

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