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Synthesis and characterization of two-dimensional (2D) nanosheet zinc aluminum layered double hydroxide (Zn/Al LDH) via an alkali-free route

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ABSTRACT

The effect of different molar ratios on the synthesis of zinc aluminium layered double hydroxide (Zn/Al LDH) via an alkali-free route was carried out in this research. This method was prepared by mixing zinc nitrate solution, aluminium nitrate solution, and ammonium carbonate solution at a constant pH of 8.5 with a spanning ratio of Zn to Al from 4:1, 3:1, and 2:1. The XRD patterns showed crystal nanostructure of Zn/Al LDHs was successfully formed. The lattice parameters (*a* and *c*) were slightly increased with the increasing of Zn/Al molar ratio. A larger hexagonal platelet is observed in the SEM image align with the high molar ratio of Zn/Al synthesized. The same trend has been observed in the FTIR spectra.

Keywords: *Zn/Al LDH, alkali-free route, different molar ratio, XRD, SEM, FTIR*

INTRODUCTION

Layered double hydroxide (LDH) or known as a hydrotalcite-like compound is a two-dimensional (2D) layered inorganic clay-based material that can be represented by the general formula $[M^{II}_{1-x} M^{III}_{x} (OH)_2] [(A^{m-})_{x/m}]. nH_2O$ [1],[2]. It has high catalytic activity and selectivity since it consists

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of two or more transition metal cations that are not clustered and distributed uniformly in the hydroxide layer. This uniqueness contributes to LDH feasibility to act as a precursor in the preparation of nanocatalyst [2]. Several methods have been discovered to synthesis the LDH, such as the sol-gel method, ion-exchange method, alkali co-precipitation method, and alkali-free methods[3]. The most persistent method used in the synthesis of LDH is an alkali co-precipitation method [3]. However, this method can harm the environment due to the emulsification and saponification process during the reaction, in the presence of an alkali substance, namely sodium hydroxide. It is notably known that sodium hydroxide would lead to leach because of sodium in the structure backbones [4]. To ensure the sustainability of the environment, an alkali-free method was introduced in this study.

An alkali-free method becomes more preferred in synthesis LDH because various metal group elements can be used[3]. Research on synthesis of Zn/Al LDH via this method, where zinc nitrate solution and aluminum nitrate solution are representing as a divalent cation (M^{II}) and a trivalent cation (M^{III}) respectively, are mixed with the addition of ammonium carbonate solution under constant pH [4],[5]. The mixing of both divalent and trivalent cations can cause the electrostatic interaction between the positive and negative interlayer because of the anion exchange capacity affected by the molar ratio [6]. The studies on the different molar ratios of Zn/Al LDH can lead to changes in its structure and properties.

The molar ratio of Zn:Al in the synthesis of LDH material can lead to a change in the unit cell parameter because of the structure formation, properties and bonding stability affected by the molar ratio used [7]. Several different molar ratios of Zn:Al were used in the synthesis of Zn/Al LDH via an alkali-free route and their properties were distinguished using analytical instruments.

EXPERIMENTAL

Zn/Al LDH materials were prepared via an alkali-free route where $Zn(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ were purchased from Sigma-Aldrich and R&M, respectively. Both solid metal nitrates were prepared at 100 mL, 1.5 M as the stock solution. Both stock solution is then used to prepare 100 mL of mixed metal nitrates solution. The volume needed for each metal nitrates stock solution to prepare the 100 mL of the mixed solution was based on the molar ratio of Zn: Al which are 2:1, 3:1, and 4:1. 2 M of ammonium carbonate solution which was added simultaneously while stirring at room temperature with a constant pH of 8.5. 25 % of ammonium hydroxide solution from Aldrich acts as a buffer was added dropwise to ensure the pH was constant at pH 8.5. The mixture was aging overnight at a temperature of 65 °C under stirring. The solid product was filtered and washed with deionized water until pH 7. Next, the white solid product was dried in an oven overnight at a temperature of 80 °C. The Zn/Al LDH sample was calcined under a flow rate of oxygen gas (O_2) of 20 ml/min at a temperature of 350 °C for 5 h.

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The properties of the Zn/Al LDH sample with different molar ratio had been distinguished by several characterization techniques. The structure of the Zn/Al LDH material and its crystalline structure was determined by the XRD analysis. It was performed by using Bruker D8 Advance with Cu Kα radiation where the sample was measured in the range of 2θ of 10° to 90° with setting parameters of 0.02° step size, 1 second step time, and 0.1 nm of wavelength. The functional group identification was carried out by using the PerkinElmer Spectrum One Fourier Transform Infrared Spectrophotometer (FTIR) by using the KBr disc technique. The spectrum was analyzed in the region of 4000 to 400 cm^{-1} with 4 cm^{-1} resolution. FTIR analysis was also used to identify foreign anions in the interlayer of the Zn/Al LDH structure, to get information about the type of bonds formed by the anions and their orientations. The morphology of the Zn/Al LDH sample was determined by the Scanning Electron Microscopy Analysis (SEM). The details about surface information provided by the Philips XL40 SEM when the sample is in a raster pattern traced by an electron beam at voltages of 5 kV.

RESULTS AND DISCUSSION

The Zn/Al LDH samples were successfully synthesized via an alkali-free route. The diffraction peaks of the as-synthesis of the different molar ratios of Zn/Al LDH samples were characterized by XRD as shown in Figure 1. The diffraction patterns of the hexagonal unit cell of Zn/Al LDH were observed at 2 thetas, which are 15°, 21°, 26°, 32°, 39°, 42°, 65°, and 71°, corresponding to the plane of (003), (006), (009), (102), (105), (108), (110) and (113), respectively [4],[5].

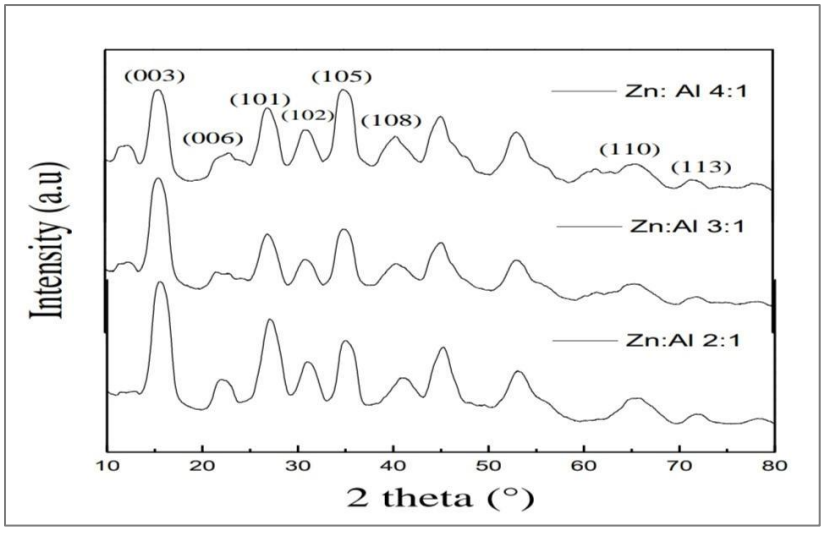

Figure 1: The X-RD intensity peaks for the three different molar ratios of Zn/Al LDH samples

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The structure of the as-synthesis of the Zn/Al LDH sample was moderately crystalline nanostructure. However, the broad intensity peaks were observed in the XRD result. As reported in the literature, a sharp and symmetric reflection intensity peak was observed [8]. Somehow, the broad intensity peak formed in this research was probably due to an impurity in samples, which is water. The increasing the molar ratio of Zn:Al for Zn/Al LDH caused the cell parameter (*a* and *c*) slightly increased because of the replacement of Al^{3+} with Zn^{2+}. The greater ionic radii of Zn^{2+} (0.74 nm) as compared to ionic radii of Al^{3+} (0.533 nm) can lead to an increase in d value due to the greater average radii of metallic cations [9]. To determine the value of lattice parameters (*a* and *c*), the Bragg equation as stated in equation 1 was used:

$$\lambda = \frac{2\, a\, sin\, \theta}{\sqrt{h^2 + k^2 + l^2}} \qquad (1)$$

where *a* is lattice constant, h, k, and l are miller indices, θ is the Bragg diffraction angle and λ is the X-ray wavelength [10].

Table 1 shows the calculated a and *c* values of the plane (110) with different molar ratios of Zn/Al LDH samples.

Table 1: The calculated a and c values of the plane (110) with different molar ratios of Zn/Al LDH samples

Sample	Zn:Al 2:1	Zn:Al 3:1	Zn:Al 4:1
$\mathbf{a_{(110)}}$ **(nm)**	0.3046	0.3067	0.3083
$\mathbf{c_{(110)}}$ **(nm)**	2.2675	2.2799	2.3028

The changes in values of lattice parameter (*a* and *c*) are depending on the difference of molar ratio used in the synthesis of Zn/Al LDH material. The higher the molar ratio used can attribute to an increase in the values of lattice parameter (*a* and *c*). Therefore, the crystal size was small as the higher molar ratio was used in the synthesis of Zn/Al LDH [11]. To support this finding, the samples' morphology was observed by characterizing them with SEM as showing in Figure 2.

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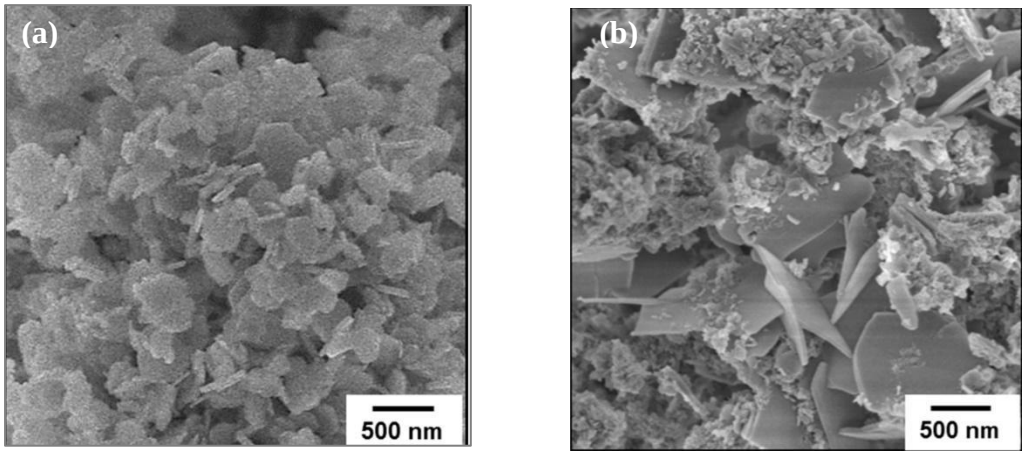

Figure 2: The morphology images of the different molar ratio of Zn/Al LDH at magnification of 30 kX at (a) low molar ratio and (b) high molar ratio

As shown in Figure 2a and 2b, small, stacked hexagonal nanoplatelets which identify as ZnO phase is showing in a typical Zn/Al LDH compound. The image in Figure 2a shows a small hexagonal platelet of Zn/Al LDH material, while the image in Figure 2b shows a large hexagonal platelet. The size of hexagonal platelet of Zn/Al LDH was large as increasing in the molar ratio of Zn^{2+}/ Al^{3+} because of more ZnO phase and $ZnAl_2O_4$ spinel were present [6]. The information about the type of bonds formed by the anions and their orientations of Zn/Al LDH material was obtained by FTIR analysis. The main absorption band in Zn/Al LDH material for the three different molar ratios samples was observed in the FTIR spectra. Spectra's result was shown in Figure 3 and listed in Table 2.

Based on Table 2, the five important adsorption bands of Zn/Al LDH material are O-H stretch band, H_2O-CO_3^{2-} band, CO_3^{2-} band, Al-O band, and Zn-O band. The presence of the O-H stretch band (3448, 3455, and 3461 cm^{-1}) in the three samples was due to the intercalation of hydroxyl ion from water in the layer of the brucite-like structure. The interaction between water molecules and the carbonate ion in the interlayer caused the peak in the region of 3200-3100 cm^{-1} to be present which attribute to the bridging mode H_2O-CO_3^{2-} [12]. The absorption band of bridging mode H_2O-CO_3^{2-} of synthesis Zn/Al LDH at a molar ratio of 3:1 was not present because it might have less intensity at that ratio.

The regions for Al-O and Zn-O bands were observed in 1200-200 cm^{-1}. This infrared vibration appeared in the compounds because of the ordering of cations in the octahedral brucite-like structure. The different molar ratio used in the synthesis of Zn/Al LDH affected the frequency of the FTIR spectrum. The frequency is slightly high with an increase in the molar ratio of Zn/Al because of the difference in the atomic mass between zinc (65.40 g/mol) and aluminium (26.98 g/mol), which caused the wavelength in the FTIR spectrum to become shorter [13].

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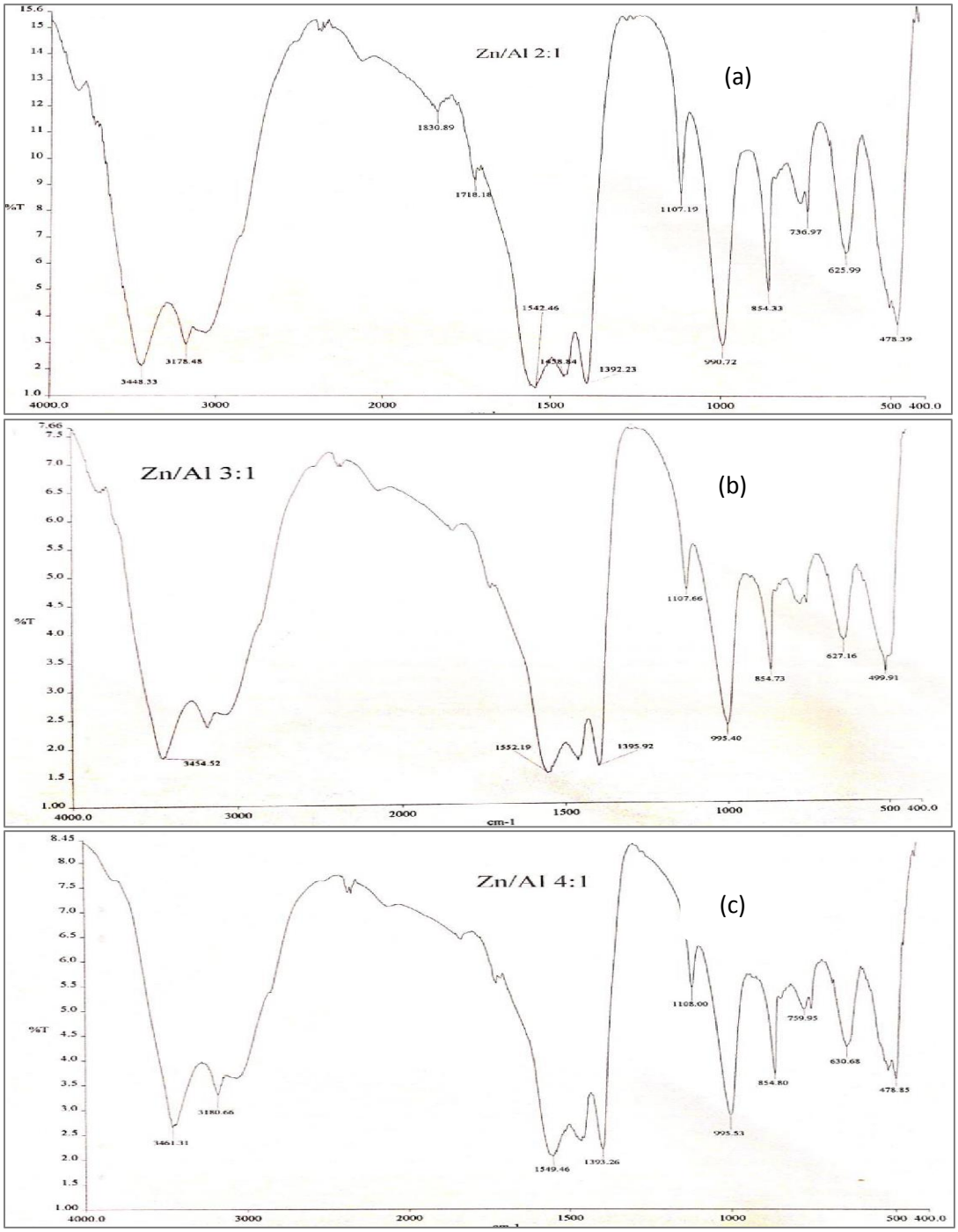

Figure 3: FTIR spectra of Zn/Al LDH at molar ratio of: (a) Zn:Al 2:1, (b) Zn:Al 3:1, (c) Zn:Al 4:1

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Table 2: The important IR absorption band presence in the Zn/Al LDH sample

LDH Compound	Wavenumber,cm^{-1}				
	υ(O-H stretch)	**υ(H_2O-CO_3^{2-})**	**υ(CO_3^{2-})**	**υ(Al-O)**	**υ(Zn-O)**
2:1 Zn/Al LDH	3448	3178	1392 854 626	1107	478
3:1 Zn/Al LDH	3455	_	1393 855 627	1108	499
4:1 Zn/Al LDH	3461	3181	1396 855 631	1108	479

CONCLUSION

Zn/Al LDH had been successfully synthesized with several different molar ratios of Zn:Al via an alkali-free route. The effect on different molar ratio used in the synthesis of Zn/Al LDH was examined through several characterization techniques. The XRD analysis results showed the Zn/Al LDH compound is moderately crystalline nanostructure. The lattice parameter (*a* and *c*) slightly increased when the molar ratio of Zn/Al increased. The morphology image showed by SEM is a large hexagonal platelet size when the Zn/Al LDH synthesized in high molar ratio due to more presence of ZnO phase and $ZnAl_2O_4$ spinel. The FTIR results displayed the five important absorption bands of Zn/Al LDH that confirm the compound's formation. The high molar ratio used in synthesized Zn/Al LDH caused the frequency of the spectrum to slightly increase. The method used in the research can ensure the sustainability of the environment and suitable for any metals group element.

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