

Effect of Calcination at Mg-Al Hydrotalcite Synthesis using co-Precipitation Method

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Received 30 May 2016; Revised 22 December 2016; Accepted 29 December 2016

ABSTRACT

The use of hydrotalcite in catalysis has wide attention in academic research and industrial parties. Based on its utilization, hydrotalcite can be active catalyst or support. This research is focused on the investigation of characteristic like spesific surface area of Mg-Al hydrotalcite which is prepared with different temperature of calcination. Synthesis of Mg-Al hydrotalcites with Mg/Al molar ratio 3:1 were prepared by co-precipitation method. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as precursors of Mg-Al hydrotalcite. Na_2CO_3 was used as precipitant agent and NaOH was used as buffer solution. The solution was mixed and aging for 5 hours at 650°C. The dried precipitate was calcined at 250°C, 350°C, 450°C, 550°C and 650°C. The characterization of functional group was determined by Fourier Transform Infra Red (FT-IR). The identical peaks diffractogram were analyzed by X-Ray Diffraction (XRD). The spesific surface area was determined by adsorption-desorption of nitrogen. The largest surface area that obtained from the calcination temperature of 650°C is 156.252 m²/g.

Keywords: Mg-Al Hydrotalcite, co-Precipitation, calcination

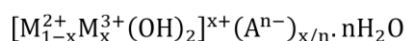
INTRODUCTION

Layered double hydroxides were first discovered in 19th century. The first mineral material which contains a double hydroxide layer was called hydrotalcite. Hydrotalcite found in Sweden at 1842 however, the formula not published until 1915 by Manasse, professor of mineralogy of the University of Florence Italy. The first general formula hydrotalcite is $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ [1,2].

Initial hydrotalcite is a hydroxycarbonate that an alloy of magnesium and aluminum which found in nature. At the same time with the discovery of hydrotalcite, a mixture of hydroxycarbonate that consist of magnesium and iron have been found, which is called pyroaurite [2]. Hydrotalcite is mineral, anionic clays, containing anionic species in the interlamellar space. Hydrotalcite is attractive mineral because it can be synthesized easily and useful in various applications. Hydrotalcite can be used to catalyst, addition for polymers, anion exchange, antacids, water purification, adsorbent, wastewater treatment, etc [2,3,4]. Based on its utilization, that material can be active catalyst or support. As an active catalyst or support hydrotalcite have a unique and highly tunable structure with both acidic and basic properties that depend on its composition. The basicity of Mg-Al hydrotalcite increases with increasing Mg/Al ratio. Potential reason for hydrotalcite applications is the ability to make a

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p-ISSN : 2302 – 4690 | e-ISSN : 2541 – 0733

metallic oxide at an atomic level instead of at the molecular level. Several mixed metal oxide is formed from hydrotalcite through decomposition temperature [3,4]. These compounds have the general formula as follows:



Whereas : M^{2+} show divalent metallic cations, such as Mg, Fe, Zn, Ni, Mn or Co. M^{3+} show trivalent metal cations such as Fe, Co, Mn, Ni, La, Cr and Al. A^{n-} is the counter anion which resides in the interlayer space to balance the residual positive charge of the hydroxide layers which results from isomorphous substitution of M^{2+} by M^{3+} , for example CO_3^{2-} [5,6]. Different amount of Al content are known to modify the basic properties, with hydrotalcite structures reported to form for compositions for a range of $0.25 < x < 0.44$, while $X = M^{3+} / (M^{2+} + M^{3+})$. Outside of these limits the high density of Mg^{2+} or Al^{3+} octahedral will lead to the formation of $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ respectively [2]. The basic sites in the alkali earth oxides component can originate from O^{2-} (strong basicity), O^- species near hydroxyl groups (medium strength) and OH groups (weak). The addition of Al^{3+} alters the acid base site distribution through the introduction of $\text{Al}^{3+}\text{O}^{2-}$ sites which are moderate Lewis acidity and only medium basicity [7].

The crystal structure of an LDH is often described by reference to structure of brucite ($\text{Mg}(\text{OH})_2$). In brucite, magnesium cations are located at the center of octahedral, which have hydroxyl anions on their vertices. A schematic representation of the structure of an LDH is shown in **Figure 1**.

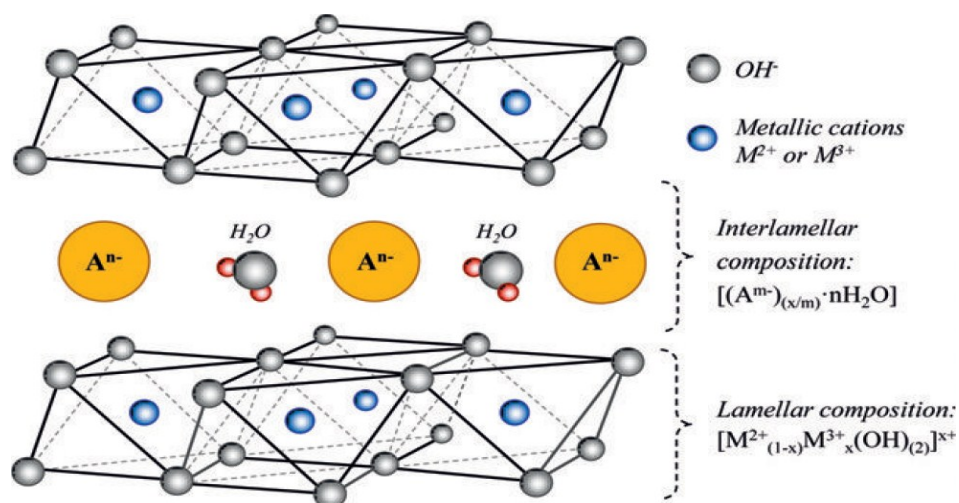


Figure 1. General structure of hydrotalcite [4]

These octahedral share their edges forming flat and neutral layers, which are held together by hydrogen bonds. In this type of structure, when divalent cations are isomorphically substituted by trivalent ones, the layers generate a positive residual charge. Electroneutrality of the system requires the presence of anions and water molecules between the lamellar, which leads to stacking of the double hydroxide layers with a slightly ordered interlayer domain. In the LDH case, the lamellar are not only held together by hydrogen bonds, in the case for brucite, but by electrostatic attraction between the positively charged layers and the interlayer anions [4,8].

This work is focused on the investigation of specific surface area of Mg-Al hydrotalcite which prepared with different temperatures of calcination. Mg-Al Hydrotalcite was synthesized by coprecipitation under low supersaturation which had aging time for 5 hours.

Synthesis of Mg-Al hydrotalcites with Mg/Al molar ratio 3:1 was chosen because of increasing basicity. Application of Mg-Al hydrotalcite is support catalyst which had basicity and large specific surface area that suitable for transesterification reaction. In previous research[18], Mg-Al hydrotalcite with Mg/Al molar ratio 1:1 as a supported catalyst had increasing acidity so that suitable for hydrocracking reaction.

EXPERIMENT

Chemicals

In term of Mg-Al hydrotalcite preparation, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck, 99%) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck, 99%) were used as precursor, while NaOH (Merck, 99%) and Na_2CO_3 (Merck, 99,9%) were used as precipitating agent.

Procedure and Instrumentation

Mg-Al hydrotalcite was prepared by the co-precipitation method at constant pH [5,9,10]. Synthesis of Mg-Al hydrotalcite with Mg/Al molar ratio 3:1 was adopted and modified from Gomes et al. [5] and Climent et al. [11]. 0.06 mol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.02 mol $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 100 ml aquadest. After preparation of precursor, it was drop wise added to solution of CO_3 in three neck flask. The solution of CO_3 was prepared by dissolving Na_2CO_3 in 100 ml aquadest in such way that the mol ratio $\text{CO}_3^{2-}/(\text{Al}+\text{Mg})$ is equal to 0.66. 1.8 M NaOH was drop wise to the solution for maintaining pH solution 10. The solution were mixed at a 1ml/min rate of drop wise with vigorous stirring and carried out at 65°C. After that, the solution was aging for 5 hours under same temperature and stirring condition. The precipitate was washed with 50°C distilled water until pH 7 and was filtered by vacuum pump. Then, the precipitate was dried in the oven at 110°C for overnight. The dried precipitate was crushed and sieved to get uniform sized particle. The Mg-Al hydrotalcite was calcined in the tubular furnace at various temperature (250, 350, 450, 550, 650)°C for 6 hours.

The characterization of the Mg-Al hydrotalcite was determined by XRD (X-ray diffraction) and BET (Brunauer-Emmet-Teller). XRD was used to determine the crystalline structure of the catalyst. The surface area was investigated by BET method and was identified chemical bond and functional groups of Mg-Al hydrotalcite by FT-IR analysis.

RESULT AND DISCUSSION

Catalyst Characterization

Brunauer Emmett Teller (BET) characterization explains the adsorption phenomenon of gas molecules on solid surfaces. Quantity of adsorbed gas molecules is highly depending on the surface area by the solid substance. In this study, effect of calcination on the surface area of the Mg-Al hydrotalcite has been investigated. **Table 1** shows the results of specific surface area by BET method.

Table 1 also shows effect of calcination temperature to specific surface area Mg-Al hydrotalcite. It shows that with an increasing of calcination temperature, the specific surface area rise too. Moreover, it is interesting to note that for temperature calcination at 550°C the specific surface area significantly increases, which compared to calcination at a temperature of 650°C. The largest surface area that is obtained from the calcination temperature of 650°C is 156 m²/g. Carbonat and hydroxyl leached through holes in the crystal surface which then appear as small, fairly regularly spaced craters [12].

Table 1. Effect of calcination to spesific surface area of Mg-Al hydrotalcite

Catalyst	Temperature Calcination (°C)	Spesific Surface Area (m ² /gram)
Mg-Al Hydrotalcite	250	88.173
	350	93.476
	450	95.885
	550	98.894
	650	156.252

Thermal decomposition of Mg-Al hydrotalcite is occured by gradual steps: interlamellar water molecules are lost irreversibly upon heating until approximately 200°C. From 200 °C to 400°C, decomposition of hydroxide ions and carbonate ions intercalated with water and CO₂, respectively, result on the formation of [Mg_{1-x}Al_xO(OH)_x]. Further heating, from 400°C up to 600°C, results in the decomposition of the remaining hydroxide ions and also in the formation of double oxides [Mg_{1-x}Al_xO_{1+x/2}]. Increasing significant spesific surface area is obtain at 650°C, caused by decomposition of entire ion hydroxides and production of pore holes (craters) [5,15].

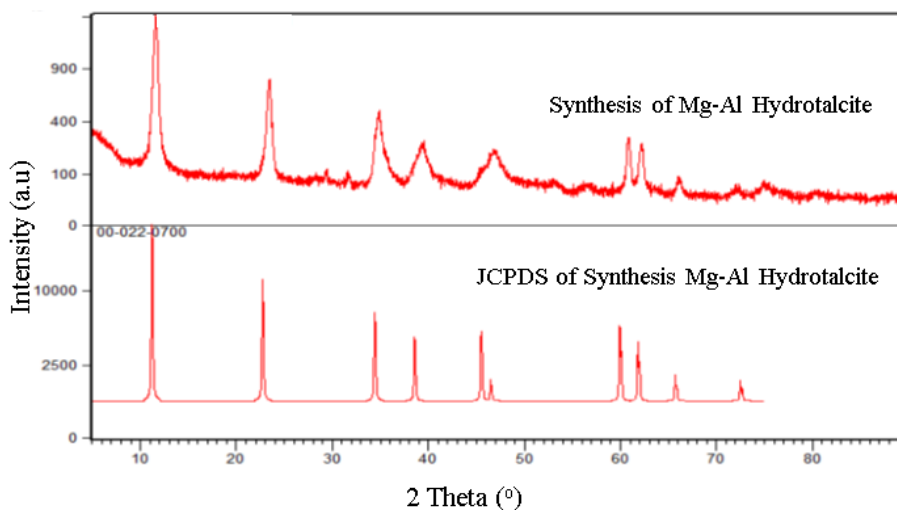


Figure 2. X-Ray diffractogram of Mg-Al hydrotalcite synthesis and JCPDS 00-022-0700

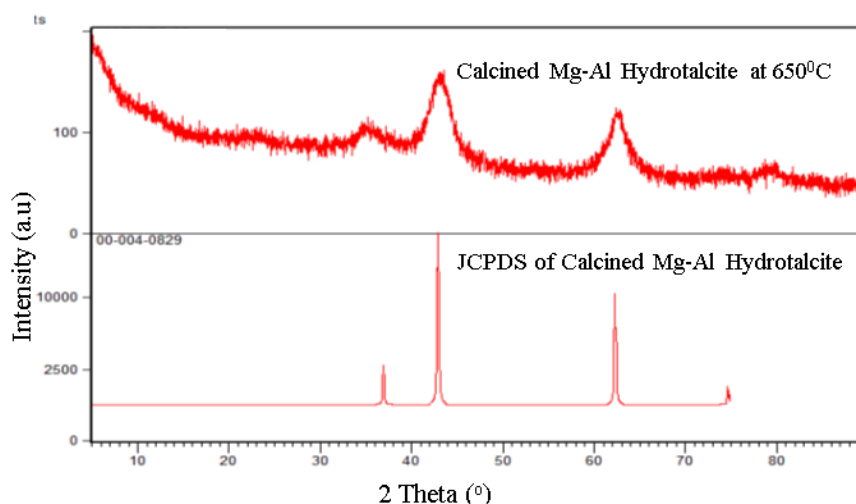


Figure 3. X-Ray diffractogram of calcined Mg-Al hydrotalcite at 650°C and JCPDS 00-004-0829

Mg-Al hydrotalcite synthesized was characterized using X-Ray Diffraction analysis. Analysis of X-Ray Diffraction (XRD) was carried out to determine the structure and crystallinity of the material. Resulting of Mg-Al hydrotalcite analysis was confirmed by The Joint Committee on Powder Diffraction Standards (JCPDS) 00-022-0700, as shown in **Figure 2**, which has diffractogram peaks at 11.277°, 22.783°, 34.467°, 38.610°, 46.284°, 59.983°, 61.891°. **Figure 3** shows diffractogram of the calcined Mg-Al hydrotalcite and JCPDS 00-004-0829. It has diffraction peaks appearing at 2 theta 36.947°, 42.909° and 62.306°. Using X'Pert HighScore Plus which obtained resemblance material of Mg-Al hydrotalcite and calcined Mg-Al hydrotalcite with JCPDS are 35% and 42% respectively.

Figure 4 shows the X Ray Diffraction spectra that obtained for Mg-Al hydrotalcite and calcined Mg-Al hydrotalcite. Diffractogram of Mg-Al hydrotalcite appears at 11.6°, 23.54°, 34.95°, 39.4°, 47.0°, 60.83°, 62.83°. While d-spacing value of Mg-Al hydrotalcite was 7.599 Å at 11.6°. As reported by Klopogge [9], the characteristics of CO₃²⁻ anions between layers of hydrotalcite has d-spacing (basal spacing) at 7.80 Å.

Figure 4 also shows diffractogram of calcined Mg-Al hydrotalcite at 650°C that appears at 36.91°, 43.36° and 62.62°. The peak at 62.62° is assigned to the reflections of MgO that can be used to calculate crystallite size of MgO (D) using sherrer's formula [10,14].

$$D = \frac{K \lambda}{\beta \cos \theta}$$

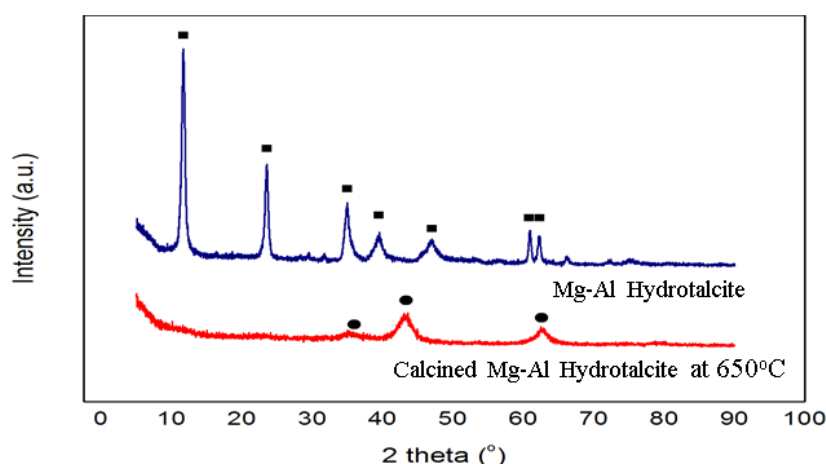


Figure 4. Diffractogram Mg-Al hydrotalcite and calcined Mg-Al hydrotalcite at 650°C

Where D was indicated the coherence length of the crystallite size of MgO-like phase (nm), K is the shape factor (value of $K = 0.9$ was used), λ is X-Ray wavelength of the used Cu $K\alpha$ radiation (0.154056 nm), β is full width at half maximum (FWHM) value in rad and θ is the diffraction angle (rad) [13]. The crystallite size of MgO-like phase is 8.14 nm. The peak is also indicates a change of structure hydrotalcite after decomposition thermal and confirms that the aluminum ion (Al^{3+}) is dispersed in MgO lattice without forming a separate phase [12,17].

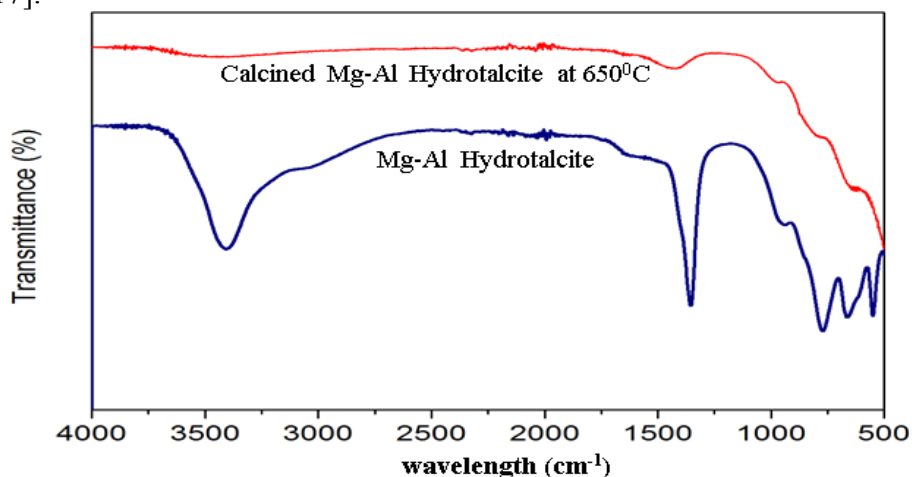


Figure 5. Spectrum of Mg-Al hydrotalcite and calcined Mg-Al hydrotalcite at 650°C

Compound structure analysis in this study was investigated by FT-IR spectrophotometry as shown in **Figure 5**. A broad absorption peak was indicated in the range of 400-4000 cm^{-1} . **Figure 5** shows the functional groups of carbonate ion (CO_3^{2-}), OH, Mg-O, Al-O, and Al-O-Al. The presence of vibrations in the area 3407.62 cm^{-1} which indicate the presence of OH stretching vibration of the hydroxyl group in Mg-Al hydrotalcite. The peak at 1355 cm^{-1} is due to the presence of ion CO_3^{2-} .

The band at a wavelength 772 cm^{-1} ; 666.98 cm^{-1} ; 550.36 cm^{-1} was indicated the band of Al-O, Mg-O, Al-O-Al respectively. This is according to Gomes et al [5] and Basahel et al [16] that absorption of hydroxyl band (O-H) by OH stretching vibration at 3200-3600 cm^{-1} . This band disappears when the catalyst was calcined at 650°C, due to the loss of water. The band appearing at wavelength at 1270 to 1500 cm^{-1} correspond to CO_3^{2-} . The intensity of this band is diminishes in the calcinated Mg-Al hydrotalcite, as a result of carbonated species

losses. The band of Al-O and Al-O-Al appears about 800 cm^{-1} , and 560 cm^{-1} . While the band of Mg-O appears at $600\text{--}717\text{ cm}^{-1}$ [9,16].

CONCLUSION

The largest surface area of Mg-Al hydrotalcite obtained from the calcination temperature of 650°C is $156\text{ m}^2/\text{g}$. Carbonat and hydroxyl leached through holes in the crystal surface which then appear as small, fairly regularly spaced craters. In the synthesis of Mg-Al hydrotalcite, identical peaks diffractogram to the JCPDS 00-022-0700 and characteristic functional groups hydrotalcite compound was occurred. The characteristic functional group of Mg-Al hydrotalcite is CO_3^{2-} , OH, Mg-O, Al-O and Al-O-Al of FTIR analysis. The calcined Mg-Al hydrotalcite also shows identical peaks diffractogram to the JCPDS 00-04-0829. This suggests that synthesis of Mg-Al hydrotalcite was successfully done although needs 5 hours aging. This study clearly establish the potensial synthesis of Mg-Al hydrotalcites.

ACKNOWLEDGMENT

The authors gratefully acknowledge funding from Indonesia Endowment Fund for Education (LPDP). Thanks to the crews of chemical reaction engineering laboratory, Department of Chemical Engineering, Faculty of Industrial Technology, Sepuluh Nopember Institute of Technology, Indonesia.

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