Constructing hydrotalcite Mg-Al-CO$_3$ by utilizing CO$_3^{2-}$ from natural resource

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Abstract. This research aims to construct hydrotalcite Mg-Al-CO$_3$ by tuning the pH synthesis and molar ratio. The tuning was carried out by applying different synthesis pH. In addition, utilization of snail shell waste is expected to replace CO$_3^{2-}$ ion that needed for anion component in hydrotalcite production. For this study precipitation and hydrothermal methods were applied for synthesis. The precipitation had been carried out in three steps, namely isolation of ion CO$_3^{2-}$ from snail shell, preparation of Na$_2$CO$_3$ solution using snail shell powder as ion CO$_3^{2-}$ source and synthesizing hydrotalcite, where hydrothermal method was carried out at 150 $^\circ$C. Confirmation of hydrotalcite obtained was done using SEM and FTIR.

1. Introduction

Belongs to class of anionic clays, hydrotalcite owns interesting properties, such as high surface area, basic properties, thermally stable, abundant ion exchange surface sites, small crystal size and memory effect [1-3]. Hydrotalcite as a functional interlayer material is composed from metal cations as layer with interlayer spaces consist of anion and water molecules as building blocks [1, 4-6]. With general formula of [M$^{2+}$x(A$^+$/x)x-nH$_2$O, the M$^{2+}$ and M$^{3+}$ as divalent and trivalent, respectively are changeable. There are a lot of studies on synthesizing hydrotalcite-like materials by substituting Mg$^{2+}$ and Al$^{3+}$ as main metal of the framework [2, 3, 7, 8]. This changeable condition also applicable for anion, where CO$_3^{2-}$ are typical ion existing in the interlayer of hydrotalcite [9, 10]. This is suggesting that by varying cations, their ratios and interlamellar anions hydrotalcite can be formed [11].

Designing and constructing hydrotalcite have been conducted in several methods, including precipitation and coprecipitation [12], sol-gel [13], urea hydrolysis [14], and thermal decomposition [15]. Most of studies were carried out by applying other metal ion for replacing M$^{2+}$, M$^{3+}$ and A$^+$ in the network using chemical source which is expensive. Therefore, some studies have been conducted on the potential starting materials for preparing hydrotalcite, like dolomite, aluminum slag, fly ash [16]. This fly ash, for example, was confirmed its chemical constituents consisted of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ with small amount of CaO. About 97.5% of calcium carbonate (CaCO$_3$) composed the snail shell [17-19] making snail shell is promising material for functional material, namely hydroxyapatite [20], perovskite [21] and catalyst [22].

In this study, we are reporting the construction of hydrotalcite Mg-Al-CO$_3$ where CO$_3^{2-}$ was obtained from snail shell waste. The effect of molar ratio of Mg-Al-CO$_3$ and pH were investigated.
2. Experimental

2.1 Chemicals and materials
Snail shell was obtained from local farmer. Mg(NO$_3$)$_2$.6H$_2$O, Al(NO$_3$)$_3$.9H$_2$O, NaOCl, HCl, Na$_2$SO$_4$ were purchased from PT. Merck Chemicals and Life Sciences, Indonesia. All chemicals were used with no further purification.

2.2 Methods

2.2.1 Preparation of CO$_3^2$ from snail shell
The snail shell was washed and soaked in NaOCl 0.01% for 2 h and washed again. Followed with soaking snail shell in HCl 0.6% for 30 min then washed again for several times. Cleaned snail shell was dried for 1 h at 110 °C prior for grinding and sieving for uniform size. The snail shell powder then calcined at 400 °C for 90 min. Calcined carbonate powder was obtained.

2.2.2 Formation of Na$_2$CO$_3$
Calcined carbonate powder was dissolved in distilled water. Sodium sulphate was added to the solution and kept for 30 min. The solution filtered and filtrate then was tested for sodium carbonate formation using phenolphthalein test.

2.2.3 Synthesis of Mg-Al-CO$_3$ hydrotalcite
The hydrotalcite was synthesized by precipitation and hydrothermal methods. The molar ratio of three solutions were varied with composition = 3:1:1 and 3:1:3 have been prepared as follow. Solution A was prepared by dissolving Mg and Al nitrate salts with different molar concentration, namely [Mg(NO$_3$)$_2$] = 0.048 M, [Al(NO$_3$)$_3$] = 0.050 M for 3:1:1 (hereafter known as A$_1$) and [Mg(NO$_3$)$_2$] = 0.016 M, [Al(NO$_3$)$_3$] = 0.05 M for 3:1:3 (known as A$_2$). Solution A$_1$ and A$_2$ then slowly added to solution B, which is sodium carbonate (Na$_2$CO$_3$) with concentration 0.016 M. The mixture, solution C$_1$ and C$_2$ was obtained. The pH of the solution C$_1$ and C$_2$ was maintained at 12 and 14 using NaOH, solution D$_1$ and D$_2$ was obtained. Solution D was kept for 24 h under constant stirring. Then placed into Teflon lined stainless steel autoclave for hydrothermal analysis for 48 h at 150 °C. The precipitate obtained by filtration was dried at 110 °C resulting hydrotalcite with different molar ratio and pH, namely H$_1$-12, H$_2$-14, H$_2$-12 and H$_2$-14.

2.2.4 Characterization
The surface functional groups of catalyst were detected by a Fourier transformed infrared (FTIR) spectrometer (Shimadzu IR-Prestige21). The samples (0.1 wt%) were mixed with KBr and analyzed in the 4000 – 400 cm$^{-1}$ wavenumber range, with resolution of 2 cm$^{-1}$, by averaging 45 scans. Scanning electron microscopy (SEM) was obtained with a Hitachi SU 3500 microscope using an accelerating voltage of 5 kV.

3. Results and discussion

3.1 Infra-red Spectroscopy
Confirmation on functional groups of hydrotalcite samples were carried out by infrared spectroscopy. Figure 1 exhibits all spectra of H$_1$-12, H$_2$-14, H$_2$-12 and H$_2$-14. All samples show similar IR spectra where a broad band was observed at 3500 cm$^{-1}$ assigned for –OH stretching vibration of brucite-like layer, the lattice H$_2$O and the interlayered water, as reported by others [3, 6, 10]. In addition, peak for deformation of –OH group was also observed at 1669 cm$^{-1}$. Other study reported that intensity of –OH deformation was varied depending on interlayer anions [23]. In this study, the anions for all samples were same, namely CO$_3^{2-}$ and NO$_3^-$, therefore the intensity for all spectra at this wavenumber was same.

Another broad but weak intensity peaks at about 3026 cm$^{-1}$ was detected and was attributed to H–bonding between water molecule and anions in the interlayer [1, 24]. In this case, carbonate ion-water interaction. Meanwhile, at wavenumber 1379 cm$^{-1}$, sharp and strong band indicating presence of NO$_3^-$ ion [23, 25-27], free carbonate ion and disordered nature of the interlayer [1]. Bending mode of
carbonate was observed at wavenumber 1123 cm\(^{-1}\) [28]. Bands at fingerprint area, 702 and 563 cm\(^{-1}\), were suggesting interaction between Al and Mg with lattice oxygen (M – O) [29] and asymmetric vibration of carbonate ion [1, 30].

![Infrared spectra](image)

**Figure 1.** The infrared spectra of (a) H\(_1\)-12, (b) H\(_1\)-14, (c) H\(_2\)-12, and (d) H\(_2\)-14, where H\(_1\): molar ratio of Mg:Al:CO\(_3\) = 3:1:1, H\(_2\): molar ratio of Mg:Al:CO\(_3\) = 3:1:3 and pH = 12 and 14.

### 3.2 Scanning Electron Microscopy

The morphology of the hydrotalcite synthesized in this study is shown in figure 2. There is no difference on the crystal morphology as the effect of molar ratio and pH. All hydrotalcite has well-crystallized mix of hexagonal and plate-like shape. These results are in the accordance with some studies although the method of synthesis was different, namely urea method [4], co-precipitation and hydrothermal [5, 27]. However, the size of crystal as seen in figure 2 has irregular size which opposite to the results of study of Hibino et.al. and Wang et.al which has identical crystal particles. In addition, the crystal was agglomerated and interconnected with each other and formed nano particles aggregates. This is also similar with the previous study [5] where hydrotalcite synthesize at pH ≥ 11 formed mesoporous Mg\(_3\)Al\(_1\)-CO\(_3\) from accumulation of uniform nano particles aggregates. This is because according to isoelectric point (IEP), the more basic the solution, the growth of Mg\(_3\)Al\(_1\)-CO\(_3\) was repressed as result of negative charge of the hydrotalcite surface [5].
Figure 2. The image of SEM result of (a) H₁-12, (b) H₁-14, (c) H₂-12, and (d) H₂-14, where H₁: molar ratio of Mg:Al:CO$_3$ = 3:1:1, H₂: molar ratio of Mg:Al:CO$_3$ = 3:1:3 and pH = 12 and 14.

4. Conclusion
The constructing of hydrotalcite with promote the carbonate ion (CO$_3^{2-}$) from natural resource had been done. CO$_3^{2-}$ from snail shell is successfully incorporated by precipitation and hydrothermal methods with variation of molar ratio and pH of solution. The results were confirmed by FTIR and SEM analysis. From FTIR results, peaks assigned for CO$_3^{2-}$ were observed at 1379 and 3026 cm$^{-1}$. As for SEM analysis, the morphology of hydrotalcite with different pH showed no different that mesoporous Mg$_3$Al$_1$-CO$_3$ particles was formed.

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