Effect of reaction time and (Ca+Mg)/Al molar ratios on crystallinity of Ca-Mg-Al layered double Hydroxide

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Abstract. Ca-Mg-Al Layered Double Hydroxides (Ca-Mg-Al-LDH) compounds were successfully synthesized from brine water and AlCl₃.6H₂O as the starting materials by coprecipitation method. The product result was characterized by X-ray powder diffraction (XRD) and Fourier transform infrared (FT-IR). The effects of the reaction time and the molar ratios of the raw material on the crystallinity of Ca-Mg-Al-LDH were examined. Results show that increasing reaction time (30; 60 and 90 min.) could improve the crystallinity and monodispersity of layered double hydroxide compounds particles. The well-defined Ca-Mg-Al-LDH could be prepared with (Ca+Mg)/Al molar ratios 0.5.

Keywords: Ca-Mg-Al layered double hydroxide, brine water, reaction time, (Ca+Mg)/Al molar ratios, crystallinity

1. Introduction

Recently, considerable interest has been focused on the synthesis of layered double hydroxides (LDH) or hydrotalcite (HT) is known as one of the minerals of prospective and promising, mainly because it can be synthesized easily and are useful in various applications [1-5]. A number of binary, ternary or quaternary LDH compounds could be synthesized via isomorphic substitution of Al or Mg with divalent or trivalent transition metal cations with a similar radius, and it was reported in literature that hydrotalcite-like materials with catalytic properties had been synthesized by introducing various kinds of transition metals or other active metal ions into the brucite-like layer of Mg and Al hydrotalcite. The commonly used methods of preparation of layered double hydroxide compounds at present includes: co-precipitation method, a sol-gel method, hydrothermal method, roasting and recovery method as well as ion exchange method [6].

At present, Mg-Al hydrotalcite has successfully synthesized from brine water as in [7-8]. Meanwhile, Ca-Mg-Al hydrotalcite-like compounds could be prepared by co-precipitation method [9]. With the success as Gao et al. [9] who has the preparation of Ca-Mg-Al-hydrotalcite by combining calcium, magnesium and aluminum ions, brine water utilization (without Ca removal) should be considering for further synthesis. As one of the most important LDH, Ca-Mg-Al-LDH is a promising material for potential applications in many fields, such as catalyst [9]; fire retardant; and adsorbent [10]. In the present work, we
employed co-precipitation method to synthesize Ca-Mg-Al-LDH compounds by adjusting (Ca+Mg)/Al molar ratios and variation of reaction temperature.

2. Experiment

2.1. Synthesis procedure
All of the chemicals used in this experiment were analytical grade and were as received without further purification. Brine water sample were taken from Tanjung Jati B CFPP, Jepara, Indonesia. Quantitative analysis of Mg and Ca in brine water using Atomic Absorption Spectrophotometer (AAS) Shimadzu AA 630-12. In the variation of (Ca+Mg)/Al molar ratios, the AlCl$_3$.6H$_2$O was added into the water brine solution until (Ca+Mg)/Al molar ratios are 0.5; 1.0 and 2.0 under stirring and then heated at 70 °C for 1 h with the pH of the solution were adjusted to 10. While, in the variation of temperature, the AlCl$_3$.6H$_2$O was added into the water brine solution under stirring until (Ca+Mg)/Al molar ratios are 2.0 with the pH of solution pH was adjusted to 10 with 0.1 M Na$_2$CO$_3$ solution and then heated to 70 °C for 30; 60 and 90 min. The product was centrifuged to recover the white solid at a speed of 2000 rpm for 20 min. The wet cake was washed to remove chloride ions with aquadest until free of ion Chloride (AgNO$_3$ test). The treated cake then was dried overnight in the oven. To investigate the effects of different temperature on the phase composition of the products, the samples was characterized by X-ray diffraction (XRD). Meanwhile, the Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze functional group.

3. Results and Discussion

3.1. XRD analysis
Figure 1 showed the XRD pattern of the prepared sample at various time at 30; 60 and 90 min.; (Ca+Mg)/Al molar ratios 2.0; pH 10 and temperature at 70 °C; while Figure 2 shows the XRD pattern of as-prepared samples at different (Ca+Mg)/Al molar ratios 0.5; 1.0 and 2.0 ; pH 10 at 70 °C for 1 h. As we could see from Figure 1 and Figure 2, all samples appeared strong diffraction peaks at low angles ($2\theta$ = 11°, 23°, and 35° corresponding to the (003), (006) and (009) reflections) [8]. While the samples appeared weak diffraction peaks at high angles ($2\theta$ = 39°, 47°, and 61° corresponding to the (105), (108), and (110) reflection. The XRD pattern of the Ca-Mg-Al hydrotalcite consists of both sharp and symmetrical peaks with some asymmetrical peaks at a high angle, indicating good crystallinity [11]. The diffraction peak near 61.0° corresponds to the (110) crystal plane and also the existence of diffraction peaks at angles between 61.0 to 62.0° indicates that the interlayer of hydrotalcite is carbonate anionic. It was confirmed by the results of the study as in [12]-[15]. Compared to the JCPDS standard pattern, the synthetic samples had hydrotalcite-like structure. All reflection peaks of different products can be easily indexed as $d_{003}$, $d_{006}$ and $d_{100}$ that are consistent with the literature value Mg/Al hydrotalcite (JCPDS Card No. 89-0460) and $d_{003}$, $d_{006}$ and $d_{132}$ Ca/Al hydrotalcite (JCPDS Card No. 87-0493). The basal spacing of all samples is listing in Table 1.
Figure 1. XRD patterns of the samples Ca-Mg-Al-LDH with different reaction time (A) 30; (B) 60 and (C) 90 min. at pH 10, (Ca+Mg)/Al molar ratios 2.0 and temperature 70 °C.

Table 1. The basal spacing of all samples.

| Basal spacing | Reaction time (min.) | (Ca+Mg)/Al molar ratio | Mg/Al hydrotalcite | Ca/Al hydrotalcite |
|---------------|----------------------|------------------------|--------------------|--------------------|
|               | 30                   | 60                     | 90                 | 0.5                | 1.0                | 2.0                |
| d_{003}       | 7.52 Å               | 7.59 Å                 | 7.63 Å             | 7.63 Å             | 7.59 Å             | 7.63 Å             |
| (2θ)          | (11.8°)              | (11.7°)                | (11.7°)            | (11.6°)            | (11.7°)            | (11.6°)            |
| d_{006}       | 3.89 Å               | 3.89 Å                 | 3.87 Å             | 3.87 Å             | 3.90 Å             | 3.87 Å             |
| (2θ)          | (23.0°)              | (23.3°)                | (23.4°)            | (23.4°)            | (23.2°)            | (23.4°)            |
| d_{009}       | 2.67 Å               | 2.68 Å                 | 2.70 Å             | 2.67 Å             | 2.68 Å             | 2.67 Å             |
| (2θ)          | (35.1°)              | (35.3°)                | (34.9°)            | (35.1°)            | (35.0°)            | (35.2°)            |
| d_{132}       | 2.48 Å               | 2.48 Å                 | 2.43 Å             | 2.48 Å             | 2.48 Å             | 2.48 Å             |
| (2θ)          | (38.5°)              | (38.4°)                | (38.3°)            | (38.5°)            | (38.5°)            | (38.5°)            |

The characteristic diffraction peaks in Figure 1 became stronger and narrower with the prolonging of reaction time, indicating that crystalline structure of the samples became more perfect. Also, Figure 2 showed that the diffraction peaks were broadened gradually and weakened with an increase of aluminum content, which implying that the structure regularity worsened and the crystallinity decreased. These may be attributing to the trivalent metal cation in a layered structure having a relatively large polarization, which resulted in difficulties in directional alignment. Both the reaction time 60 and 90 min. and (Ca+Mg)/Al molar ratio 0.5 and 2.0 agrees well with the empirical phase composition suggested by the XRD analysis that was confirming according to the references [12]-[13]. However the reaction time 30 °C and (Ca+Mg)/Al molar ratio 1.0, a little of the other hydrotalcite phase generated in the product. It is suspected to be Mg(OH)₂ and Al(OH)₃.
Figure 2. XRD patterns of the samples Ca-Mg-Al-LDH with different (Ca+Mg)/Al molar ratios (A) 0.5; (B) 1.0 and (C) 2.0 at pH 10, temperature 70 °C for 1-hour reaction.

Figure 3. XRD patterns of the samples Ca-Mg-Al-LDH with (Ca+Mg)/Al molar ratios (A) 0.5; (B) 1.0; (C) 2.0 at pH 10, temperature 70 °C for 1 hour reaction and different reaction time (D) 30; (E) 60; (F) 90 min. in comparison with (G) Mg/Al hydrotalcite and (H) Ca/Al hydrotalcite.
3.2. FTIR analysis

Figure 4 and Figure 5 illustrate the FT-IR spectra of Ca-Mg-Al hydrotalcite with carbonate anion interlayer and Table 2 show a comparison of the functional group the hydrotalcite products. As seen from Figure 4 and Table 2 shows the broad absorption bands around 3500-3000 cm\(^{-1}\) were derived from the –OH stretching vibration of the hydroxyl groups in layer structures, which shifted towards low wave number in comparison with –OH of the free state, implying the presence of the hydrogen bonds between interlayer water and layer –OH [14,16-19]. The absorption bands at near 1627-1643 cm\(^{-1}\) were originated by the bending mode of an interlayer water molecule with anion interlayer [7,16,17,19-21]

All FT-IR spectra of LDH display the bands at 1361-1364 and 1633-1650 cm\(^{-1}\) are due to the antisymmetric C-O and C=O stretching vibration mode of interlayer carbonate that also confirmed according to the references [7,14,16,21]. Furthermore, in the low wavenumber region between 400 cm\(^{-1}\) and 1000 cm\(^{-1}\) at around 677 cm\(^{-1}\) show the O=C-O carbonate bending vibration. Peak around 551 cm\(^{-1}\) which is associated with stretching vibration Al-O [6,16] and around 448 cm\(^{-1}\) as stretching vibration Mg-O. While the appearance of peaks around 449-466 cm\(^{-1}\) and 538-561 cm\(^{-1}\) that are suspected as stretching vibration Mg-O, Ca-O and Al-O of products. It is corresponding as in Zhou et al. [19] that mention peaks at around 428-433 cm\(^{-1}\) are stretching vibration M-O (where M=Mg, Ca and Al). Also, the appearance of the new peaks at 848-858 indicated Ca-O bonding that are consistent according to [19] and [22] who have varied Ca and Mg in synthesis hydrotalcite. The more Ca ions in the synthesis due to new peaks will appear around 800 cm\(^{-1}\). Therefore, from spectra analysis in Figure 4 was shown Mg-O, Ca-O, Al-O bonding, hydroxyl, C=O, and C-O indicated that the product is Ca-Mg-Al hydrotalcite with carbonate anion interlayer.

![Figure 4](image1.png)

**Figure 4.** The FT-IR spectra of hydrotalcite with variation reaction time (a) 30; (b) 60 and (c) 90 min.

![Figure 5](image2.png)

**Figure 5.** The FT-IR spectra of hydrotalcite with (Ca+Mg)/Al molar ratios (a) 0.5; (b) 1.0 and (c) 2.0.
Conclusions
In summary, Ca-Mg-Al-LDH has been synthesized using brine water and AlCl$_3$·6H$_2$O as the starting materials by coprecipitation method, and some factors on the synthesis were examined. The results show that the prolonging reaction time at a pH 10 and temperature 70 °C is improving the crystallinity and monodispersity of layered double hydroxide compounds. Moreover, well-defined Ca-Mg-Al-LDH could be synthesized under the (Ca+Mg)/Al molar ratios 0.5 and 2.0.

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| Functional group | Reference | Reaction time (min.) | (Ca+Mg)/Al molar ratio |
|------------------|-----------|----------------------|------------------------|
|                  |           | 30                   | 60                     | 90 | 0.5 | 1.0 | 2.0 |
| OH stretching    | a,b,c,d,e | 3468                 | 3442                   | 3442 | 3446 | 3469 | 3442 |
| OH/C=O bending   | a,b,c,d,e,f | 1631           | 1627                   | 1641 | 1782 | 1633 | 1627 |
| C-O stretching   | a,b,c,d,e,f | 1365           | 1367                   | 1359 | 1361 | 1361 | 1363 |
| O=C-O bending    | b,c,e,f   | 673                | 677                    | 667  | 677  | 667  | 667  |
| M-O stretching   | a,b,c,d,e,f | 445           | 451                    | 449  | 451  | 449  | 451  |

Reference: [8],[14],[16],[17],[20],[21]

4. Conclusions
In summary, Ca-Mg-Al-LDH has been synthesized using brine water and AlCl$_3$·6H$_2$O as the starting materials by coprecipitation method, and some factors on the synthesis were examined. The results show that the prolonging reaction time at a pH 10 and temperature 70 °C is improving the crystallinity and monodispersity of layered double hydroxide compounds. Moreover, well-defined Ca-Mg-Al-LDH could be synthesized under the (Ca+Mg)/Al molar ratios 0.5 and 2.0.
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