From the Research Laboratories
В изследователските лаборатории

THE EFFECT OF AGING TIME ON Mg/Al HYDROTALCITES STRUCTURES

[1]Eddy Heraldy, [2]Triyono, [2]Sri Juari Santosa, [2]Karna Wijaya, [3]Shogo Shimazu
[1]Sebelas Maret University (Indonesia)
[2]Gadjah Mada University (Indonesia)
[3]Chiba University (Japan)

Abstract. In this study, the Mg/Al hydrotalcites-like compounds with Mg/Al molar ratio of 2 was synthesized by coprecipitation method at pH ± 10.0, temperature 70°C for 1 hour. After cooling, it treated under aging treatment conditions at 30°C. The effect of various aging time on treated samples was studied for 1, 2, 3 and 4 days were chosen. The materials were characterized by powdered sample X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The XRD pattern obtained was typical of a hydrotalcite, where show the narrow and sharp symmetric (*003*) reflection and strong lines at low 2Θ angles. The spectra demonstration wide asymmetric peaks at higher angles, that are typical of clay crystals possessing a layered structure and are similar to the form of natural hydrotalcite. Furthermore, it is shown that aging at an increased time, better crystallinity and the treatment in water slightly than in the mother liquid caused in a crystalline matter.

Keywords: Mg-Al hydrotalcites-like compounds; synthesized; aging treatment; crystallinity; mother liquid

Introduction

Hydrotalcite (HT) is a type of hydroxycarbonate of magnesium and aluminum with the layered structure, fitting to the anionic clays group. The general formula of HT is $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{b+}[A^{n-}]_{b/n}\ .mH_2O$, where M^{2+} and M^{3+} are the divalent and trivalent cations in the octahedral positions in the hydroxide layers. The value of *x* has usually varied between 0.17 and 0.33, while A^{n-} is an interlayer anion with a negative charge, and *n*, *b* is the charge of the layer and *m* is the number of water molecules (Cavani et al., 1991; Kovanda et al., 2009; Liao et al., 2012). The varied in a range of this type of materials, causing the synthesis results can be applied in various fields. The variety of applications including adsorbents, ion exchangers, catalysts and catalyst precursors, stabilizers, anion scavengers, and biological aspects (Vaccari, 1998; Perez et al., 2006; Choy et al., 2007; Musumeci et al., 2010).

Hydrotalcite-like is normally synthesized by coprecipitation method when the metal cations M(II) and M(III) solution in adequate proportions react with an alkaline solution. Some factors are essential in the precipitation of hydrotalcite (HT) compounds, such as the nature of the anions, pH, and the nature of the cations, temperature, their ratio, aging, and the precipitation method. The product crystallinity is affected by temperature, pH and concentration and/or post-synthesis operations (e.g., aging of the precipitate). The significant development of the product crystallinity can be attained by hydrothermal treatment at temperatures. The hydrothermal crystallization is commonly carried out at to a temperatures of 200°C autogenously pressure within hours to days. Cavani et al. (1991) had reviewed some points of hydrothermal treatment concerning hydrotalcite-like compounds. As long as the hydrothermal treatment of Mg/Al hydrotalcite, a maximum crystal size was attained when longtime crystallization process at a temperature of 150-200°C (Miyata, 1980; Hickey et al., 2000; Oh et al., 2002; Kovanda et al., 2005; Sharma et al., 2007). In general, although, the anionic clay elements is greater than the cationic clays, which makes quite interesting in the capability for improved particle size, their physical and chemical properties. More studies have investigated the influence of different times on constant temperature (Labajos et al., 1992). Badreddine et al. (1998) had demonstrated that the carbonate anion concentration in the hydrotalcite interlayer region is influenced by aging and temperature treatment.

In the current work, we have studied the effect of aging treatment on physical-chemical properties at room temperature (30°C) condition. The purpose of the present work was to find understanding the character of hydrotalcite-type materials in the experimental conditions during different aging treatments.

Experimental

Preparation of samples

One thousand milliliters of 0.10 M Na_2CO_3 solution was added dropwise slowly into 500 mL of the $MgCl_2.6H_2O$, which has been mixed with $AlCl_3.6H_2O$ compound with Mg/Al molar ratio 2, under vigorous stirring while maintaining a pH of 10.5. Once the adding is complete, the mixture stirred, heated to 70°C, and further maintained for 1 h. During synthesis, pH is maintained at about 10.5. When the synthesis results have cooled at room temperature, then the synthesis results divided into two equal portions for different aging treatments. One portion, call N sample, was filtered, washed in distilled water until it is free of chloride ions. The sample then dried for one night and not aged. The remaining portion is prepared to undergo different aging treatments. Half of the remaining part, called the SNML sample, is centrifuged at 2800 rpm for 15 min to get a white slurry. After that, the white slurry is separated from the mother liquid. The white slurry that has been separated from the mother solution is fed into a 200 mL Erlenmeyer and then is added distilled water to the mark. While the other half of the samples called DML sample were not washed and remained in their mother liquid, transferred to a 200 mL Er-

lenmeyer. Then the two samples were each aged for 1, 2, 3 and 4 days at 30°C and continuously stirred. After aging, the sample slurry filtered, washed with distilled water until free of chloride ions. Subsequently, the sample dried for one night.

Experimental techniques

The XRD profile was obtained on a Mac Science MXP3 X-ray diffract meter with Cu Kα radiation, operated at 25 kV and 20 mA at room temperature from 5° to 70° 2Θ. The detection of the existing crystalline phase is determined by comparison with pre-existing JCPDS data diffraction files. It is well known that the crystallinity of the hydrotalcite is significantly influenced by the synthesis procedure and the time of aging. To minimize errors in results due to the synthesis procedures and other factors, the percentage of hydrotalcite crystallinity in different aging treatments and crystallization times was analyzed by comparing the sum of integral intensities of the (*003*) and (*006*) planes. Samples having maximum intensities of the *(003*) and (*006*) planes were considered as 100% crystalline samples (Sharma et al., 2007). Fourier-transform infrared (FTIR) spectra were recorded using the KBr (2 wt. % sample) pellets technique on Horiba FT-720 spectrometer in the of 400 – 4000 cm^{-1} range. The scanning electron microscopy images the hydrotalcite sample was taken on a microscope JEOL-6330F. The sample is coated with gold using a sputter coating to avoid any charge. The analysis was employed at an acceleration voltage of 15 kV.

Results and discussion

The XRD pattern of all hydrotalcite samples synthesized by aging treatment is shown in Fig.1.

The presence of carbonate anions in the hydrotalcite interlayer gallery is confirmed by characteristic basal spacing d_{003} of 7.8 Å. The XRD patterns obtained shows a good agreement with the results obtained by Kloprogge & Frost (1999a; 1999b), Kloprogge et al. (2002), Millange et al. (2000) and Nyambo et al. (2008). The crystalline components in the N, SNML and DML samples show very similarly to some slight differences. The identification of the crystalline components in the sample shows of one major component, hydrotalcite, accompanied by a trace amount of other compounds. The XRD pattern of the three samples undoubtedly demonstrates a layered structure. Peaks appear showing the reflection symmetry (*003*) and (*006*) are narrow, sharp and strong at low 2Θ (11 – 23°). The spectra also show broad asymmetric peaks at 34 – 66°, which are typical of clay minerals that have a layered structure and are similar to natural hydrotalcite pattern (Miyata, 1980). In addition, the characteristics of the hydroxide lattice sheets in the synthesized hydrotalcite arise from reflection d_{110} and d_{113} were around two thetas 61° and 64°. If the three samples were compared further, then the N samples prepared by normal synthesis procedures or not aging treatment, it appears to form the hydrotalcite phase, although the crystallinity is still poor. In the DML and SNML samples, the XRD pattern changed significantly when compared to N sample. Changes in XRD patterns on SNML

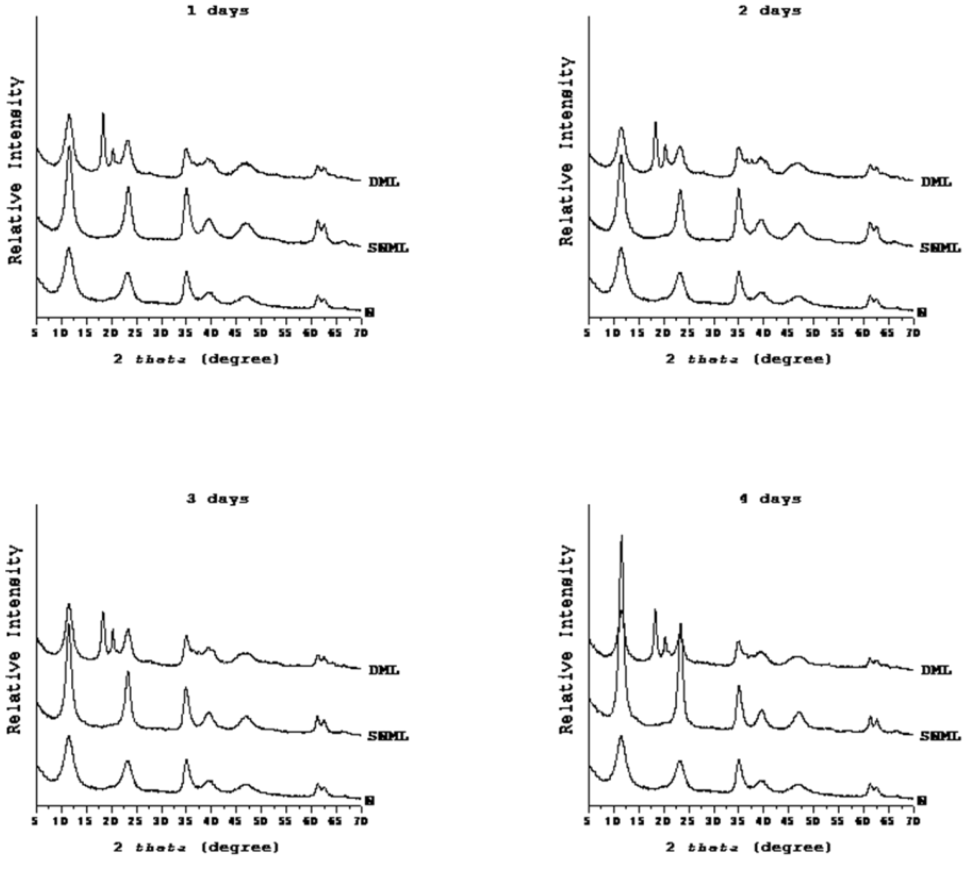

Figure 1. Diffractogram of the aging effect on Mg / Al HTlc synthesis at 30^0 C for 1, 2, 3 and 4 days, respectively

samples showed a crystalline hydrotalcite phase with better crystallinity crystalline) than the N sample. However, the DML sample showed an additional peak associated with impurities or new crystalline phase that predicted is $Mg(OH)_2$ or $Al(OH)_3$ compounds. With increasing time, impurities appear on the DML sample. It is proved that the mother liquid has an influence on the formation of hydrotalcite crystals. The presence of $Mg(OH)_2$ and/or $Al(OH)_3$ as impurities in the DML sample that has been aged for several days is suspected due to the mother liquid still containing a high concentration of OH^-. With high OH-concentrations in the mother liquid, more likely the formation of complex ions $[MgOH]^+$ and $[Al(OH)_4]^-$ in the mother liquid. Aging treatment in a given time, provide the opportunity for these complex ions to react perfectly to form hydrotalcite compounds even though there is an opportunity of Mg^{2+} or Al^{3+} ions forming $Mg(OH)_2$ and $Al(OH)_3$.

To prove the existence of impurities or a new crystalline phase in N, SNML and DML samples, the XRD pattern of the aging results is compared with the standard XRD pattern of $Al(OH)_3$ and $Mg(OH)_2$ compounds. The XRD diffractogram profile on the effect of the mother liquid in hydrotalcite synthesis compared with the standard XRD pattern of $Al(OH)_3$ and $Mg(OH)_2$ compounds is shown in Figs. 2 and 3.

The analysis results of Figs. 2 and 3 on all samples have been compared, it is proved that only the DML samples show the phases of $Al(OH)_3$ and $Mg(OH)_2$. This phase appears in the same two thetas $Al(OH)_3$, which is around 18-21° (Fig. 2) and on the same two thetas $Mg(OH)_2$, is around 19° (Fig. 3).

While two theta around 61-63º or reflections (*110*) and (*113*) for the three samples appear identical peaks showing the layered hydroxide structure or the sample having a layer similar to brucite.

Besides characterized by XRD, the hydrotalcite sample is also characterized by FT-IR. The characterization results with FTIR are presented in Fig. 4, where previously several scientists have recorded the infrared hydrotalcite spectrum (Cavani et al., 1991; Labajos et al., 1992; Fernández et al., 1997; Abelló et al., 2005).

The spectrum obtained for N and SNML samples showed a good match with only slight differences in the peak position compared to the data in the literature (Cavani et al., 1991).

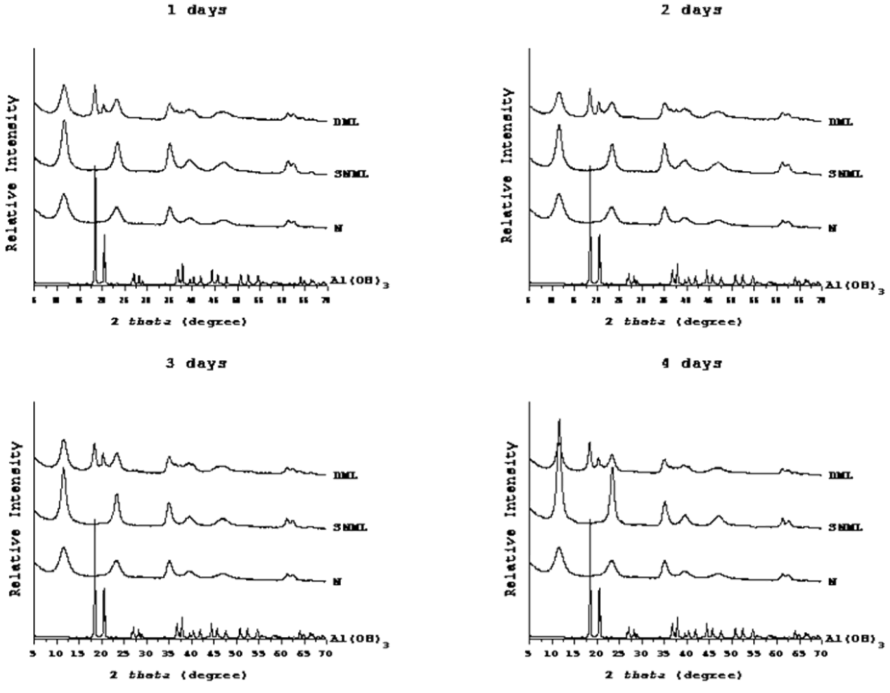

Figure 2. Diffractogram of the aging effect on Mg/Al HTlc synthesis at 30^{0}C for 1, 2, 3 and 4 days, respectively were compared with the XRD pattern of $Al(OH)_3$

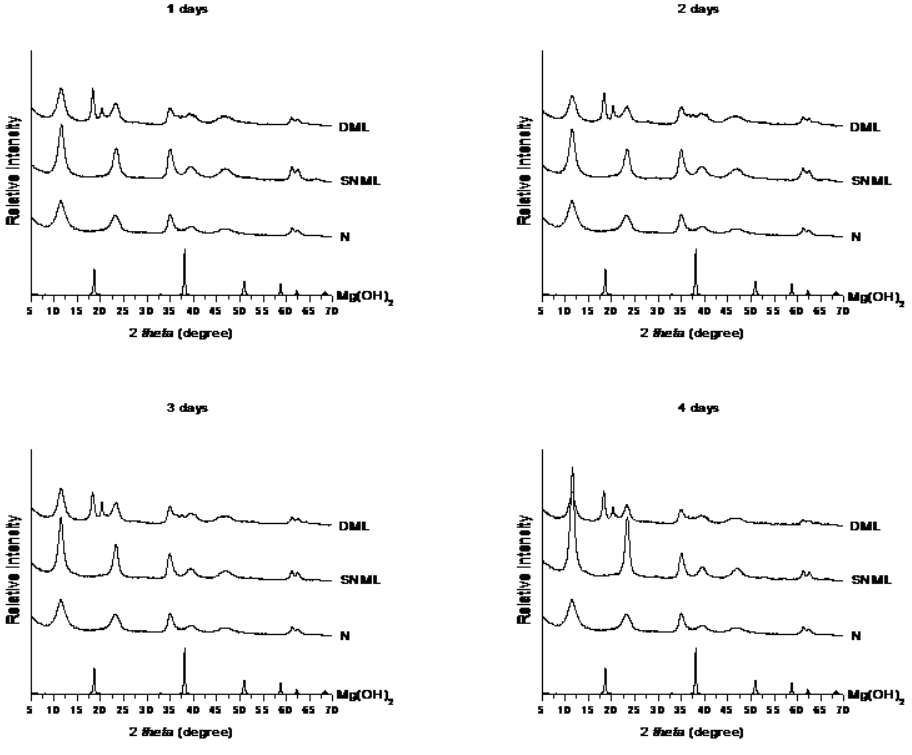

Figure 3. Diffractograms of the aging effect on Mg/Al HTlc synthesis at 30^0C for 1, 2, 3 and 4 days, respectively were compared with the XRD pattern of $Mg(OH)_2$

A very broad band centered around 3500cm^{-1} is assigned to the H-bonding stretching and bent vibrations of the hydroxyl group. This hydroxyl presents on brucite type layer (Mg/Al-OH) and water molecules interlayer. Shoulders that look around 3000cm^{-1} are hydrogen bonds between water molecules and carbonate anion interlayer. The intensity of this shoulder increases with increasing hydrotalcite crystallinity. It was indicated by the stronger interactions between layers and interlayer and a well-ordered interlayer region (Labajos et al., 1992). The presence of the shoulder at 1640cm^{-1} is a type of the H_2O band. Sharp and strong vibrational carbonates band (antisymmetric stretching) seen at 1370cm^{-1} may be attributed with a carbonates interlayer (chelating or bridging bidentate). However, for samples, with lower crystallinity degree, asymmetric carbonates vibrational band are detected. The band intensity at 1370cm^{-1} was also decreased in the low crystalline samples. Bands at 950cm^{-1} for Al-OH deformation and at 760 cm^{-1} for the Al-OH translation were also detected. A peak that appears around 650cm^{-1} is attributed with in-plane carbonate bending. As the molar ratio of Mg/Al hy-

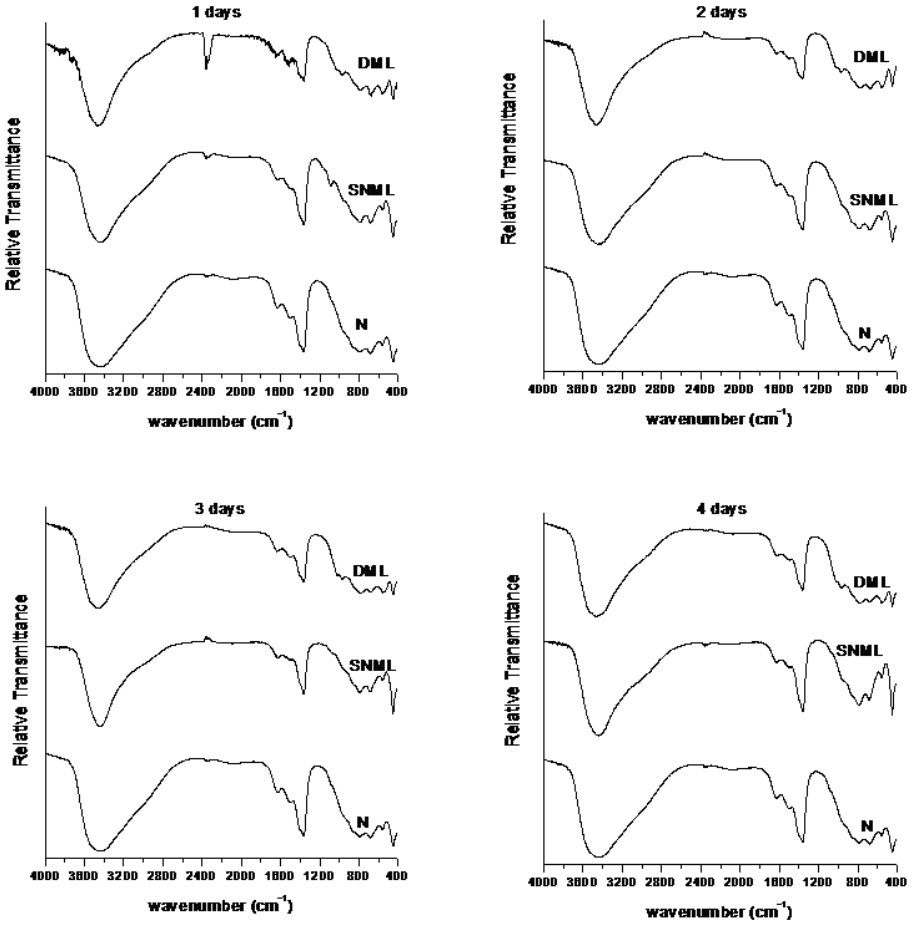

Figure 4. Spectrogram of the aging effect on Mg/Al HTlc synthesis at 30^0C for 1, 2, 3 and 4 days, respectively

drotalcite increases, the broadening peak at about 650cm^{-1} is detected. A band at 554cm^{-1} is attributed with the hydroxyl group translation mode due to influence Al^{3+} cations (Mg/Al-OH translation) (Abelló et al., 2005). Fig. 4 is FT-IR spectra of the samples with an aging treatment at a constant temperature 30º C for 1, 2, 3 and 4 days, respectively. It appears that the spectra are displayed showing the same pattern as before the aging treatment, except the DML spectrum residing in the wavenumber below 1000cm^{-1}. These changes are suspected due to the formation of new Al-O bond or Mg-O.

Scanning electron micrographs of N samples with DML samples and N samples with SNML samples are illustrated in Fig. 5 and 6, respectively.

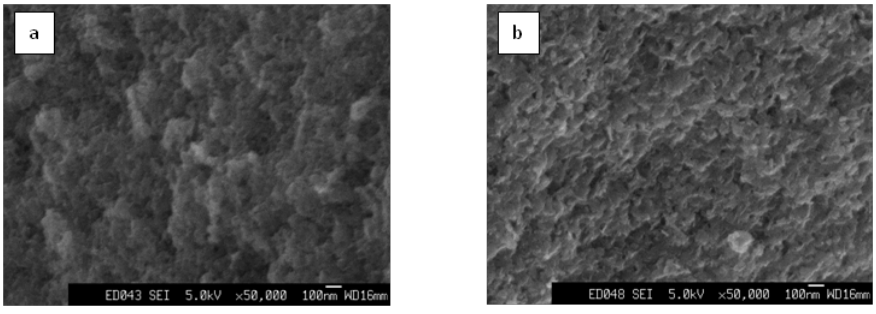

Figure 5. SEM images of Mg/Al HTlc in (a) N sample and (b) DML-aging sample at 30 º C for 4 day

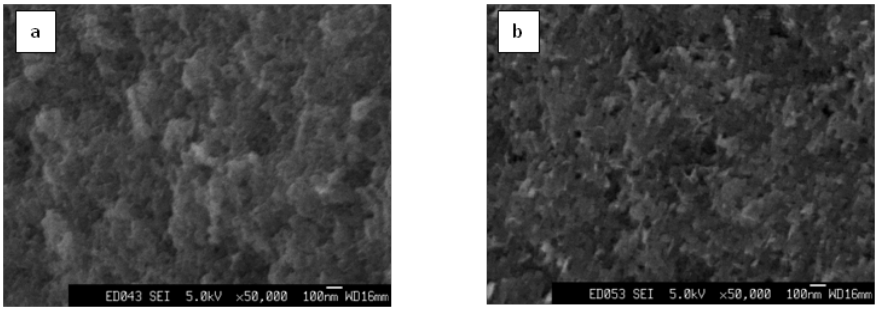

Figure 6. SEM images of Mg/Al HTlc in (a) N sample and (b) SNML-aging sample at 30 º C for 4 day

From electron micrographs, it appears that the general morphology of Mg/Al HTlc was changed during aging treatment. In the N sample, there appears a fine aggregate, which is considered as an amorphous phase conglomeration. As the aging time increases, aggregates grow and grow to form flat hexagonal crystals. Fig. 5 shows that in the DML sample there is still an amorphous phase, whereas in Fig. 6, the aggregate SNML sample grows to form crystals.

Conclusion

The effect of aging treatment on hydrotalcites leads to an increase in crystallinity. The crystallization of hydrotalcite is significantly affected by the time of aging treatment. In addition, the hydrotalcite aged in water is obtained a higher crystallinity than that aged in the mother liquid. The high pH and the presence of soluble ions may hinder the dissolution of small particles and consequently the growth of larger particles.

Acknowledgements. We would like to thank to Directorate General of Higher Education Ministry of National Education for research grants and Chiba University, Japan for providing research facilities.

REFERENCES

Abelló, S., Medina, F., Tichit, D., Pérez-Ramírez, J., Rodríguez, X., Sueiras, J.E., Salagre, P. & Cesteros, Y. (2005). Study of alkaline-doping agents on the performance of reconstructed Mg–Al hydrotalcites in aldol condensations. Appl. Catal. A-Gen., 281, 191 – 198.

Badreddine, M., Khaldi, M., Legrouri, A., Barroug, A., Chaouch, M., De Roy, A. & Besse, J.P. (1998). Chloride-hydrogenophosphate ion exchange into zinc-aluminum chloride layered double hydroxide. Mater. Chem. Phys., 52, 235 – 239.

Cavani, F., Trifiro, F. & Vaccari, A. (1991). Hydrotalcite-type anionic clays: preparation, properties and application. Catal. Today, 11, 173 – 301.

Choy, J.-H., Choi, S.-J., Oh, J.-M. & Park, T. (2007). Clay minerals and layered double hydroxides for novel biological applications. Appl. Clay Sci., 36, 122 – 132.

Fernández, J.M., Barriga, C., Ulibarri, M.A., Labajos, F.M. & Rives, V. (1997). New hydrotalcite-like compounds containing yttrium. Chem. Mater., 9, 312 – 318.

Hickey, L., Kloprogge, J.T. & Frost, R.L. (2000). The effects of various hydrothermal treatments on magnesium-alumunium hydrotalcites. J. Mater. Sci., 35, 4347 – 4353.

Kloprogge J.T. & Frost, R.L. (1999a). Fourier transform infrared and Raman spectroscopic study of the local structure of Mg-, Ni-, and Co-hydrotalcites. J. Solid State Chem., 146, 506 – 515.

Kloprogge, J.T. & Frost, R.L. (1999b). Infrared emission spectroscopy study of the thermal transformation of Mg, Ni and Co hydrotalcite catalysts. Appl. Catal. A-Gen., 1814, 61 – 71.

Kloprogge, J.T., Wharton, D., Hickey, L. & Frost, R.L. (2002). Infrared and Raman study of interlayer anions CO_3^{2-}, NO_3^-, SO_4^{2-} and ClO_4^- in Mg/Al-hydrotalcite. American Mineralogist, 87, 623 – 629.

Kovanda, F., Kolousek, D., Cılova, Z. & Hulınsky, V. (2005). Crystallization of synthetic hydrotalcite under hydrothermal conditions. Appl. Clay Sci., 28, 101– 109.

Kovanda, F., Rojka, T., Bezdicka, P., Jiratova, K., Obalova, L., Pacultova, K., Bastl, Z. & Grygar, T. (2009). Effect of hydrothermal treatment on properties of Ni–Al layered double hydroxides and related mixed oxides. J. Solid State Chem., 182, 27– 36.

Labajos, F.M., Rives, V. & Ulibarri, M.A. (1992). Effect of hydrothermal and thermal treatments on the physicochemical properties of Mg-Al hydrotalcite- like materials. J. Mater. Sci., 27, 1546 – 1552.

Liao, L., Zhao, N. & Xia, Z. (2012). Hydrothermal synthesis of Mg–Al layered double hydroxides (LDHs) from natural brucite and $Al(OH)_3$. Mater. Res. Bull., 47, 3897 – 3901.

Millange, F., Walton, R.I. & O'Hare, D. (2000). Time-resolved in situ X-ray diffraction study of the liquid-phase reconstruction of Mg-Al-carbonate hydrotalcite-like compounds. J. Mater. Chem., 10, 1713 – 1720.

Miyata, S. (1980). Physico-chemical properties of synthetic hydrotalcites in relation to composition. Clay. Clay Miner., 28, 50 – 56.

Musumeci, A.W., Mortimer, G.M., Butler, M.K., Xu, Z.P., Minchin, R.F. & Martin, D.J. (2010). Fluorescent layered double hydroxide nanoparticles for biological studies. Appl. Clay Sci., 48, 271 – 279.

Nyambo, C., Songtipya, P., Manias, E., Jimerez-Gasco, M.M. & Wilkie, C.A. (2008). Effect of MgAl-layered double hydroxide exchanged with linear alkyl carboxylates on fire-retardancy of PMMA and PS. J. Mater. Chem., 18, 4827 – 4838.

Oh, J.-M., Hwang, S.-H. & Choy, J.-H. (2002). The effect of synthetic conditions on tailoring the size of hydrotalcite particles. Solid State Ionics, 151, 285 – 291.

Perez, M.R., Pavlovic, I., Barriga, C., Cornejo, J., Hermosin, M.C. & Ulibarri, M.A. (2006). Uptake of Cu^{2+}, Cd^{2+} and Pb^{2+} on Zn–Al layered double hydroxide intercalated with EDTA. Appl. Clay Sci., 32, 245 – 251.

Sharma, S.K., Kushwaha, P.K., Srivastava, V.K., Bhatt, S.D. & Jasra, R.V. (2007). Effect of hydrothemal conditions on structural and textural properties of synthetic hydrotalcites of varying Mg/Al molar ratio. Ind. Eng. Chem. Res., 46, 4856 – 4865.

Vaccari, A. (1998). Preparation and catalytic properties of cationic and anionic clays. Catal. Today, 41, 53 – 71.

✉ **Dr. E. Heraldy (corresponding author)**
Department of Chemistry
Sebelas Maret University
36A, Jl. Ir. A. Sutami Kentingan
57126 Surakarta, Indonesia
E-mail: eheraldy@mipa.uns.ac.id