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Study on synthesizing Mg/Al layered double hydroxides at different pHs

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Abstract: Mg/Al layered double hydroxide (LDH) was successfully synthesized at different pHs values. The Mg/AL LDH was well characterized by X-Ray diffraction and Fourier transform infrared analysis. The morphology of the LDH was observed using Scanning electron microscopy with energy dispersive X-ray spectroscopy. The influence of pH values on the morphology of the Mg/Al LDHs were studied. The result showed that the well-synthesized Mg/Al LDHs could be obtained when the pH value was about 10.0 at room temperature.

Keywords: Mg/Al Layered double hydroxide, XRD, FTIR, pH.

INTRODUCTION

The terms layered double hydroxides (LDHs) or hydrotalcite-like compounds (HTLc) are used to designate synthetic or natural lamellar hydroxides with two or more kinds of metallic cations in the main layers and hydrated interlayer domains containing anionic species [1]. This large family of compounds is also commonly referred to as hydrotalcites or anionic clays, the latter term indicating a complementarity with the more usual cationic clays whose interlamellar domains contain cationic species [2]. Mg/Al layered double hydroxide (Mg/Al LDH: $[Mg^{2+}_{1-x}\cdot Al^{3+}_{x}(OH)_2](A^{n-})_{x/n}\cdot mH_2O$) is widely recognized as a clay mineral exhibiting an anion exchange property [3-5]. LDHs are a layered structure with positively charged brucite-like sheets, where Mg and Al are octahedrally coordinated. The excess charge is balanced by anions in the interlayer, together with water molecules [6].

Recently, LDHs have attracted much attention because of their unique applications in many fields. For example, they can be used as catalysts, catalyst supports, ion exchangers, adsorbents, and pigments and also be used in sensor and magnetic technologies [6-8]. Scotter and Ken B, prepared Ni/Al, Mg/Al, Co/Al, Cu/Al LDHs and used them as the catalysts of the steam reforming of methanol to produce hydrogen [9]. Alejandre *et al*. used Cu/Ni/Al LDHs as precursors of catalysts for the wet air oxidation of phenol aqueous solutions. Most of these advanced functions depend strongly on the composition, size, and morphology [10].

Nowadays, an intensive economic growth of Mongolia is due to high price of copper mining product, gold production and other mineral resources [11]. Therefore, ground and surface water are polluted with metal oxy anions caused by mining activities. To date, no previous report has described a study of the removal of metal oxy anions from water using LDH in Mongolia. Therefore, the LDH and its derivatives are able to use as one of the best adsorption materials removing metal oxy anions from water.

The aim of this study was to synthesize primary Mg/Al LDH at different pHs and to investigate their physicochemical characterization. The synthesis and structure of the Mg/Al LDH was examined using X-Ray diffractometer (XRD), Fourier transform infrared (FT-IR) spectroscopy, Scanning electron microscopy with energy dispersive X-ray (SEM-EDX) spectroscopy.

EXPERIMENTAL

Materials: Stock solutions of Magnesium Chloride Hexahydrate $MgCl_2\cdot 6H_2O$, Aluminum Chloride Hexahydrate $AlCl_3\cdot 6H_2O$, sodium carbonate Na_2CO_3

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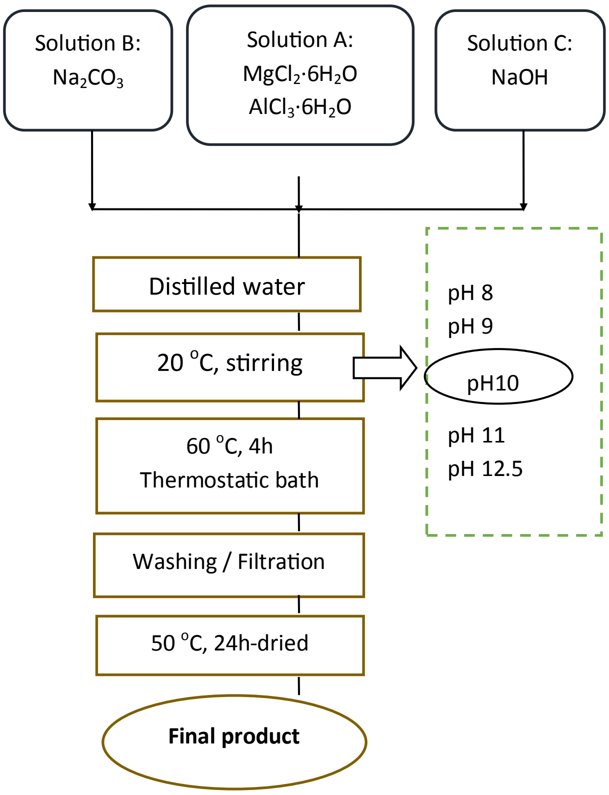
and sodium hydroxide NaOH were purchased from Daejung Chemical and Metals (Korea) and used to prepare Mg-Al layered double hydroxides.

Synthesis of Mg-Al LDH: Mg/Al LDH materials were synthesized by traditional co-precipitation method [12]. In a typical procedure, an amount of 24.1 g of $MgCl_2 \cdot 6H_2O$ (0.198 M) and 9.6 g of $AlCl_3 \cdot 6H_2O$ (0.0662 M) were dissolved in 600 ml distilled water (Solution 1). Solution 2 was prepared by dissolving 31.8 g of Na_2CO_3 (0.3 M) in 400 ml distilled water. Solution 1 and 2 was added into 1 L distilled water under constant stirring at a temperature of 20°C (at room temperature) and then the mixed solution was controlled at a constant pH 10 by adding 1M NaOH solution. The mixture was then aged at 60°C for 4 h. After that, the precipitates were filtered and thoroughly washed with distilled water. The wet residue was dried at 50°C for 24 h to obtain the Mg-Al LDH. Schematic diagram of layered double hydroxides showed in Scheme 1.

Scheme 1. Preparation method of Mg/Al LDH



Measurements: FT-IR spectra (4000-400cm^{-1}, KBr disc) were recorded on a Bruker Alpha spectrometer. X-ray diffraction patterns were recorded using CuK α radiation (n = 1.5418Å) on a Philips PW1800 diffractometer operating at 40 kV and 40 mA with 0.25° divergence slit, 0.5° anti-scattter slit, between 1.5 and 20° (2θ) at a step size of 0.0167°. A scanning electron microscope (SEM, S-3400 N, Hitachi, Tokyo, Japan) equipped with energy dispersive X-ray (EDX) was used. pH values were measured using pH 300 (Hanna Instruments, Italy) digital pH meter.

RESULTS AND DISCUSSION

Synthesized Mg/Al LDH was examined by chemical analysis with mass percentage of Mg, Al, and precipitation yields of LDHs prepared at different pHs which were confirmed with EDX analysis (Table 1). As seen from the table, the Mg:Al ratio of 3:1 suggests the incomplete precipitation of Mg^{2+} ions at pH of 8. The yield was dramatically increased while the pH level was increasing till 10. However, it was decreased gradually with pH level above 10.

Table 1. Determination of Mg and Al ion by titration in Mg/Al LDH

Mg/Al mole ratio	pH	Mg, %	Al, %	Yeild (g)
	8	19.54	7.59	4.82
	9	68.56	26.63	10.62
3:1	10	99.60	38.68	12.58
	11	95.23	36.98	12.50
	12.5	94.00	36.51	11.42

Characterization of LDH: Mg/Al layered double hydroxides with various pHs were successfully synthesized by co-precipitation method. As seen from the XRD patterns (Fig. 1), the hydrotalcite type phase was identified in all synthesized layered double hydroxides except LDH with pH value 8 [13]. More intensive and sharper reflections with (003) and (006) planes at low 2θ values (11-23°), and broad asymmetric reflections at higher 2θ values (34-66°) can be observed in the XRD patterns. The (009) reflection overlaps with the (102), resulting in a broad signal. Therefore, we can conclude that it is possible to obtain hydrotalcite-like layered structures with the Mg^{2+} and Al^{3+} cations in selected range of compositions. However, the intensities of some reflections for different LDH samples are slightly

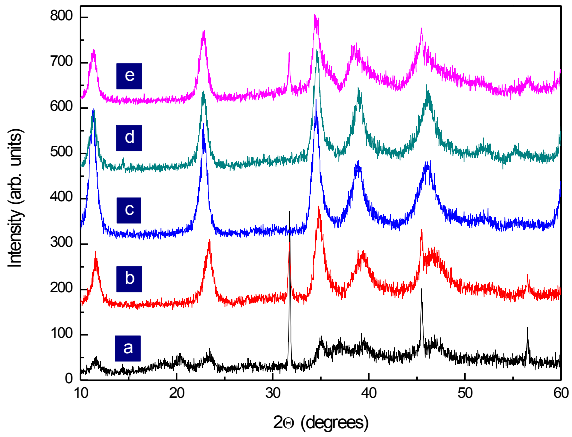


Fig. 1. XRD powder pattern of the products prepared at different pH values a: 8, b: 9, c: 10, d: 11, e: 12.5

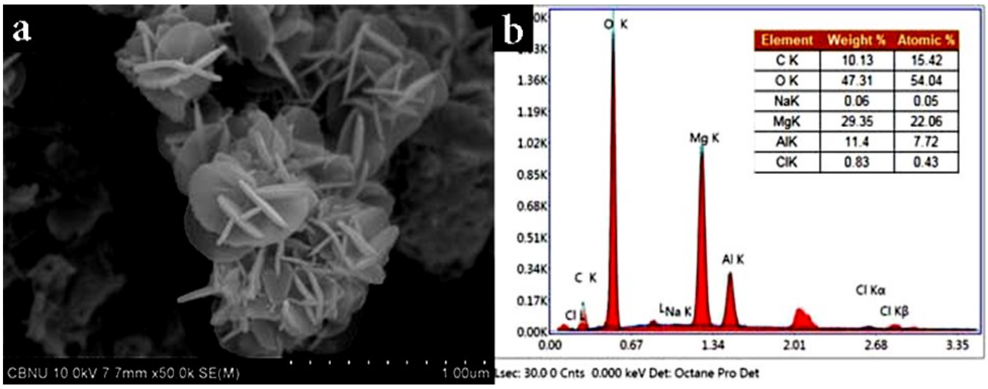


Fig. 2. SEM image of Mg/Al LDH and their EDX results.

different, possibly indicating different degrees of their crystallinity.

Figure 2 (a) and 2 (b) show the SEM image and SEM-EDX results. The ratio of metals is an important parameter for characterizing LDH compounds (7). It is shown in Figure 2 (a) where the synthesized material was observed as homogenously distributed nano particles and layered double structure. A distance between layered double structure was measured around 20-30 nm. The molar ratio of Mg to Al was 2.57, consistent with the initial ratio of Mg/Al.

Figure 2 (c-f) also show the FT-IR spectra of Mg/Al LDH with increasing pH which were in the range of 4000 to 500 cm^{-1} region. In the investigation on all LDH, the spectra reveal the presence of coordinated water molecules that indicated by broad bands at 3400-3500 cm^{-1} [12]. This peak was attributed to stretching vibrations of the OH groups of water molecules. The peak around 1640 cm^{-1} can be attributed to vibration of H_2O. The spectra in Figure 2 (b-e) are shown a broad band 3200-3000 cm^{-1} which is attributed to the bridging mode H_2O-CO_3^{2-}. However, this band is not clear at the Figure 2 (a). Very strong peaks CO_3^{2-} were appeared at 1373-1365 cm^{-1} in spectra of the LDHs with pH value above 8.

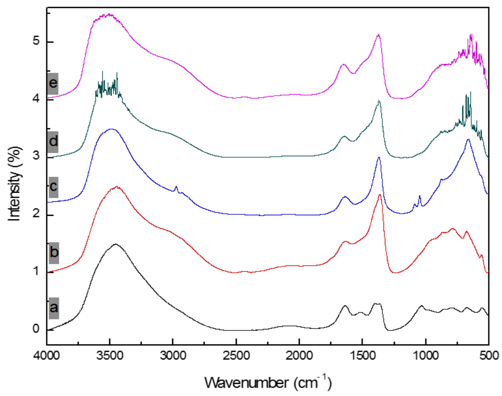


Fig. 3. IR spectra of Mg/Al LDHs prepared at different pH values (a: 8, b: 9, c: 10, d: 11, e: 12.5)

The symmetry of the carbonate anions is lowered D_{3h} to C_{2s} resulting in activation of the IR inactive mode at 1050 cm^{-1}. This peak is observed Figure 2(c). They are also ascribed to the metal-oxygen vibration (500–1000 cm^{-1}).

CONCLUSIONS

This study was dealt with the investigation synthesized the Mg/Al LDH and its physico-chemical properties. The confirmation of structures and morphology of the Mg/Al LDH with different pHs were performed by XRD, FTIR and SEM-EDX. The Mg/Al LDH was confirmed as hydrocalcite like compound using XRD. The morphology of the Mg/Al LDH was observed homogenously distributed nano particles. The molar ratio of Mg to Al was 2.57. The peaks corresponded to CO_3^{2-} groups and water molecules at 1360 cm^{-1}, and 3465 cm^{-1} were certified FTIR, respectively.

This investigation leads further possibilities to study rest of derivatives of LDHs and their physicochemical characterizations.

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