

Layered Metal Hydroxides Containing Calcium and Their Structural Analysis

Tae-Hyun Kim,^{II} Heo, Seung-Min Paek,[†] Chung-Berm Park,[‡] Ae-Jin Choi,[‡]
Sung-Han Lee, Jin-Ho Choy,^{§,*} and Jae-Min Oh^{*}

Department of Chemistry and Medical Chemistry, College of Science and Technology, Yonsei University, Wonju,
Gangwondo 220-710, Korea. *E-mail: jaemin.oh@yonsei.ac.kr

[†]Department of Chemistry, Kyungpook National University, Taegu 702-701, Korea

[‡]National Institute of Horticultural & Herbal Science (NIHHS) of RDA, Eumseonggun, Chungcheongbukdo 369-873, Korea

[§]Center for Intelligent Nano Bio Materials (CINBM), Department of Bio Inspired Science and Department of Chemistry
and Nano Science, Ewha Womans University, Seoul 120-750, Korea. *E-mail: jhchoy@ewha.ac.kr

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Layered metal hydroxides (LMHs) containing calcium were synthesized by coprecipitation in solution having two different trivalent metal ions, iron and aluminum. Two mixed metal solutions ($\text{Ca}^{2+}/\text{Al}^{3+}$ and $\text{Ca}^{2+}/\text{Fe}^{3+} = 2/1$) were added to sodium hydroxide solution and the final pH was adjusted to ~11.5 and ~13 for CaAl-and CaFe-LMHs. Powder X-ray diffraction (XRD) for the two LMH samples showed well developed $(00l)$ diffractions indicating 2-dimensional crystal structure of the synthesized LMHs. Rietveld refinement of the X-ray diffraction pattern, the local structure analysis through X-ray absorption spectroscopy, and thermal analysis also confirmed that the synthesized precipitates show typical structure of LMHs. The chemical formulae, $\text{Ca}_{2.04}\text{Al}_1(\text{OH})_6(\text{NO}_3)_5 \cdot 2.5\text{H}_2\text{O}$ and $\text{Ca}_{2.01}\text{Fe}_1(\text{OH})_6(\text{NO}_3)_4 \cdot 4.75\text{H}_2\text{O}$ were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Particle morphology and thermal behavior for the synthesized LMHs were examined by field emission scanning electron microscopy and thermogravimetric-differential scanning calorimetry.

Key Words : Layered metal hydroxide, Hydrocalumite, Rietveld refinement, X-ray diffraction, X-ray absorption spectroscopy

Introduction

Layered metal hydroxides (LMHs), consisting of positively charged metal hydroxide nanolayers and interlayer anions have been the subject of interest because they exhibit various advantages for drug delivery carriers. The interlayer anions can be easily exchanged by various anionic species including drug molecules and nucleic acid strands having size variation from small molecules (molecular dimension of ~0.3 nm) to large ones (molecular dimension of ~4 nm).¹⁻⁴ The incorporated anions can be safely preserved from external harsh conditions by the inert metal hydroxide layers.^{2,5,6} LMHs are known to have low toxicity because of their solubility in weakly acidic biological fluid into ions to be excreted.⁷⁻⁹ Since possible toxicity and hazardous effects of nanoparticles on environment and human beings are controversial,¹⁰ one should consider biocompatible constituents in designing drug delivery carrier with LMHs. Metal ions in human body are known to be abundant in the following order; calcium (~1.4 wt %), magnesium (~0.003 wt %), iron (~0.0004 wt %) and etc.¹¹ Furthermore, calcium and iron ions are well known to play an important role in skeletal structure, cell signaling or oxygen/electron transport.¹² Therefore, synthesis and analysis of LMHs having calcium and iron is very important in developing biocompatible nanocarriers for drug delivery.

LMHs can be classified into three categories according to

the structure and metal-ligand coordination type. One is a layered double hydroxide (LDH) which can be represented by a general formula of $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot \text{mH}_2\text{O}$ (M^{2+} : divalent metal, M^{3+} : trivalent metal, A: interlayer guest anion, $0 < x < 1$, m and n are integers). The divalent metal hydroxide octahedrons are aligned along 2-dimensional lattice by sharing edges and the isomorphic substitution of divalent metal with trivalent one resulted in positive layer charge.¹³ Another type is hydroxy double salt (HDS) of chemical formula $[(\text{M}_{1-x}\text{M}'_{1+x})(\text{OH})_3]^{+}(\text{A}^{n-})_{1/n} \cdot \text{mH}_2\text{O}$ (M and M': divalent metals, A: interlayer guest anion, $0 < x < 1$, m and n are integers). In this structure, edge-shared array of metal hydroxide octahedrons make periodic vacant sites, of which upper and down positions are occupied by metal hydroxide tetrahedrons to produce positively charged hydroxide layer.³ The other one is hydrocalumite (HC) structure having chemical formula $[\text{Ca}_2\text{M}(\text{OH})_6]^{+}[(\text{A}^{n-})_{1/n}] \cdot \text{mH}_2\text{O}$ (M: trivalent metal, A: interlayer guest anion). Upon characteristics of structural feature, the HC has distinctive structure resulted from relatively large size of Ca^{2+} (~99 pm) in the structure; hepta-coordinated calcium hydroxide decahedrons and hexa-coordinated trivalent metal hydroxide octahedrons are arranged in 2-dimensional lattice by sharing edges (Fig. 1). There are several studies on the structure and physicochemical properties of HC type LMHs with Ca/Al composition (CaAl-LMH) in cement industry or mineral sciences.^{14,15} However, few studies have been carried on the

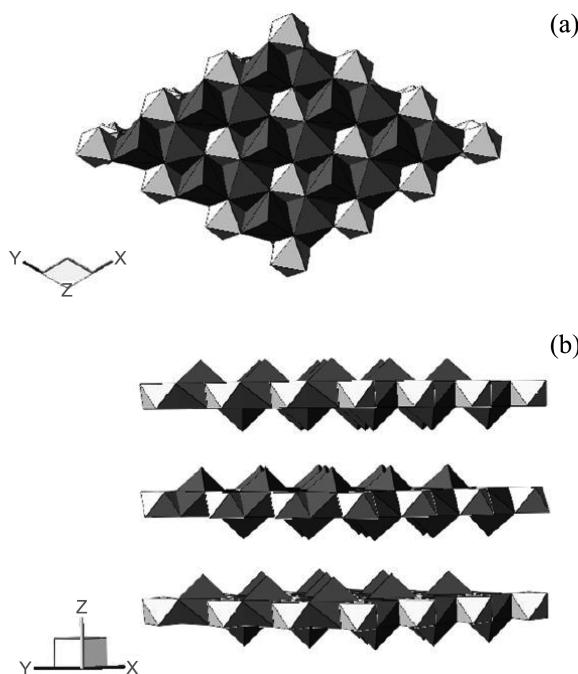


Figure 1. Crystal structure of calcium containing layered metal hydroxide, hydrocalumite. (a) top view (b) side view. Hepta-coordinated calcium hydroxides and the hexacoordinated M(III) hydroxides are represented as grey dodecahedrons and octahedrons, respectively. The seventh coordinations of calcium are positioned up and down of the layer.

LMHs with Ca/Fe composition (CaFe-LMH) for possible drug delivery carrier.

In this study, CaAl-LMHs are synthesized and characterized referred to the previously report on hydrocalumite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{NO}_3)_2\cdot 10\text{H}_2\text{O}$)¹⁶ and the optimal synthetic condition for CaFe-LMHs are investigated based on pH dependent precipitation of metal ions in aqueous media. Compared with CaAl-LMH, furthermore, we carried out the structural characterization on CaFe-LMH.

Experimental

Synthesis. In order to find an optimal coprecipitation pH of Ca^{2+} and trivalent metal ions (Al^{3+} or Fe^{3+}), we obtained the acid-base titration curve (Fig. 2) of mixed metal solution to strong base. Mixed metal solution of $\text{Ca}^{2+}/\text{M}^{3+}$ (Ca^{2+} : 0.126 M, M^{3+} (Al^{3+} or Fe^{3+}): 0.063 M) was titrated by 0.75 M of NaOH solution and pH changes were recorded as every 2 mL of alkaline solution was added. The titration showed that pH ranges of 11-12 and 12-13 for $\text{Ca}^{2+}/\text{Al}^{3+}$ and $\text{Ca}^{2+}/\text{Fe}^{3+}$ are the optimum condition to synthesize each LMH.

For CaAl- and CaFe-LMH samples, mixed metal nitrate solutions (0.315 M of $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ and 0.158 M of $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ for CaAl-LMH and 0.315 M of $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ and 0.158 M of $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ for CaFe-LMH) were prepared and titrated with NaOH solution until the final pH reached a region of coprecipitation. The reaction vessels were aged for 24 h with vigorous stirring under N_2 atmosphere. The resulting precipitates were filtered and washed

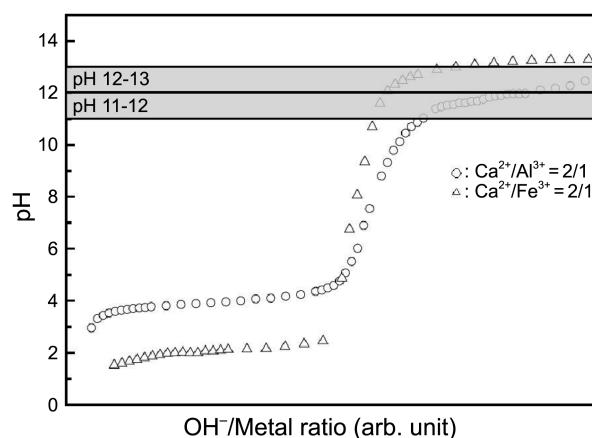


Figure 2. pH changes for mixed metal solutions containing $\text{Ca}^{2+}/\text{Al}^{3+}$ (empty circle) or $\text{Ca}^{2+}/\text{Fe}^{3+}$ (empty triangle) upon NaOH titration. The second plateau at pH 11-12 and 12-13 was selected as the coprecipitation condition for CaAl-LMHs and CaFe-LMHs.

with decarbonated water and dried in vacuum at 40 °C.

Structural Characterization. Powder X-ray diffraction patterns were obtained with Bruker AXS D2 phaser with increments of degree and time step of 0.02° and 3 sec/step. Program total pattern analysis solution (TOPAS), Bruker AXS, was used for Rietveld refinement. X-ray absorption spectroscopy (XAS) was gained at 7C XAFSII beam line at Pohang Acceleration Laboratory (PAL), Korea, and obtained data were analyzed by XAFSVIEW package for the examination of the local structure and coordination environment for Ca and Fe. XAS spectra were collected at the Ca K-edge of 4038 eV and Fe K-edge of 7100 eV. Especially, Ca K-edge was obtained under rich He atmosphere in sample chamber. The chemical composition and thermal behavior of CaAl- and CaFe-LMHs were evaluated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES: Perkin Elmer Optima-4300 DV), thermogravimetric analysis (TG: TA Instruments SDT-Q600) and differential scanning calorimetry (DSC: TA Instruments SDT-Q600). The thermal analysis was carried out from 25 to 1000 °C with a heating rate, 5 °C/min. The particle size and morphology of both LMHs were investigated by field emission scanning electron microscopy (FE-SEM) of Hitachi SU-70 at Korea basic science institute (KBSI) Kangneung branch.

Result and Discussion

We investigated the optimal pH for the coprecipitation of Ca/Al or Ca/Fe through NaOH titration to mixed metal solutions. Upon the NaOH titration, there are two plateaus at around pH 12 and 13 for both Ca/Al and Ca/Fe mixed metal solution, showing the precipitation of trivalent and divalent metal hydroxides (Fig. 2). The pH ranges of 11-12 and 12-13 were employed as the optimal condition for CaAl- and CaFe-LMH synthesis.

According to the powder X-ray diffraction patterns shown in Figure 3, both LMHs exhibit well developed (00l) diffractions patterns indicating the evolution of 2-dimensional

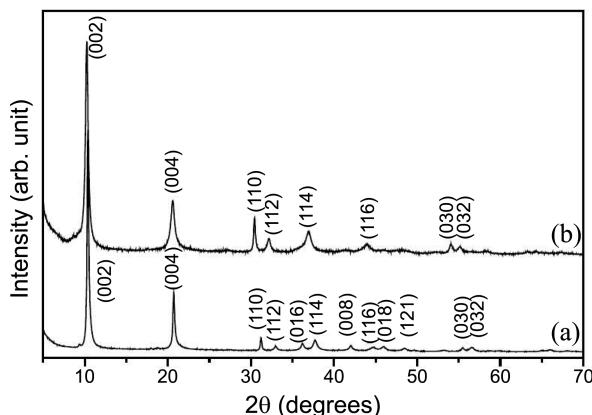


Figure 3. Powder X-ray diffraction patterns for (a) CaAl-LMHs and (b) CaFe-LMHs.

layered structures. According to the Bragg's equation, (002) peaks of CaAl- and CaFe-LMH at ~ 10.2 in 2θ , indicate the d-spacing of ~ 8.60 and 8.61 Å for CaAl- and CaFe-LMH, respectively. Considering the dimension of interlayer nitrate ion along z-axis (~ 1.89 Å) and the thickness of HC layer (~ 6.71 Å),¹⁶ we could confirm that both LMHs contain NO_3^- ions in the interlayer space.

All of the (hkl) peaks for the synthesized CaAl-LMH are well assigned to those of hydrocalumite $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{NO}_3)_2\cdot 10\text{H}_2\text{O}$ (ICSD ID: 54372) structure as reported.¹⁶ The (hkl) peaks of CaFe-LMH are similar to those of HC with a little peak shift. To verify the structure of CaFe-LMH precisely, Rietveld refinement from the X-ray diffraction patterns of both CaAl- and CaFe-LMHs was performed. We carried out structural refinement in the 2θ range $14\text{--}70^\circ$ with space group of P -3 C 1 (space group number = 165) based on the previous report demonstrating the single crystal analysis result on hydrocalumite.¹⁶ The observed (solid lines), calculated (open circles) and the difference profiles (solid line just above x-axis) are shown in Figure 4. Although it seems that there are some differences between observed and calculated values in CaFe-LMHs, the refinement results are accountable for R-factor (R_{exp} and R_{wp}) values (Table 1) referred to the previous report.¹⁷ Therefore, it is noted that the synthesized CaAl-LMH has the same structure of

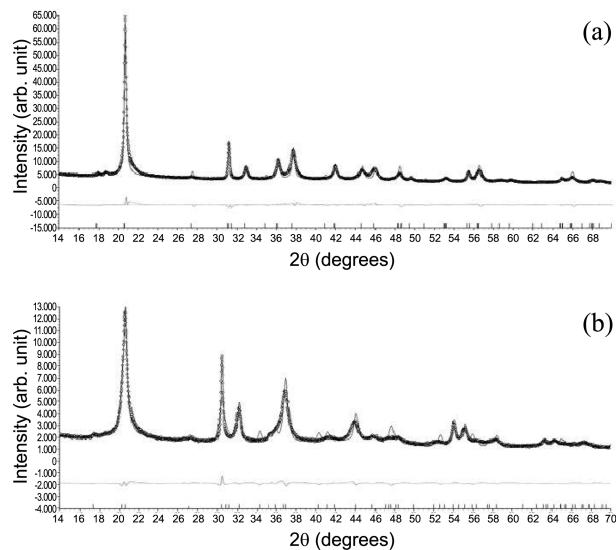


Figure 4. Rietveld refinement results for (a) CaAl-LMHs and (b) CaFe-LMHs. Observed powder X-ray diffraction patterns (solid line), calculated (empty circle), difference profile (line below diffraction patterns) and Bragg reflections (ticks) are represented.

previously reported HC¹⁸ and that the synthesized CaFe-LMH can be interpreted having HC structure. The lattice parameters obtained from the refinement were $a = 5.7557$, $c = 17.2181$ Å for CaAl- and $a = 5.8729$, $c = 17.2271$ Å for CaFe-LMH. Compared to CaAl-LMH, it is worthy to note that the CaFe-LMH has slightly larger lattice parameters, which could be resulted from the difference in an ionic radius between Al^{3+} (53.5 pm) and Fe^{3+} (64.5 pm).

We further investigated the local structure and coordination state around metal ions in synthesized CaAl- and CaFe-LMHs using X-ray absorption spectroscopic (XAS) analyses. Since XAS is a powerful tool to examine the coordination number and inter-atomic distances around a specific metal ion, we tried to verify that the Ca^{2+} ions in both LMHs are hepta-coordinated with oxygens and that the Fe^{3+} ions are coordinated with six oxygens in first shell and then surrounded by six Ca^{2+} ions in the second shell. The X-ray absorption near edge structures (XANES) on Ca K-edge of two LMHs are shown in Figure 5. Both spectra

Table 1. Rietveld refinement results for CaAl-LMH and CaFe-LMH

CaAl-LMH				CaFe-LMH					
Space group	P -3 c 1			Space group	P -3 c 1				
Lattice parameter	$a: 5.7557$ (Å) $c: 17.2181$ (Å)			Lattice parameter	$a: 5.8729$ (Å) $c: 17.2271$ (Å)				
$R_{\text{exp}}: 1.52$	$R_{\text{wp}}: 13.18$			$R_{\text{exp}}: 1.98$	$R_{\text{wp}}: 11.34$				
Fractional coordinate				Fractional coordinate					
x	y	z	Occ	x	y	z	Occ		
Al	0.00000	0.00000	0.00000	1	Fe	0.00000	0.00000	0.00000	1
Ca	0.33333	0.66667	0.02982	1	Ca	0.33333	0.66667	0.02362	1
O	0.28497	0.07345	0.05066	1	O	0.31468	0.07442	0.05581	1
N	0.34319	0.67406	0.09366	0.1667	N	0.35595	0.76863	0.21264	0.1667

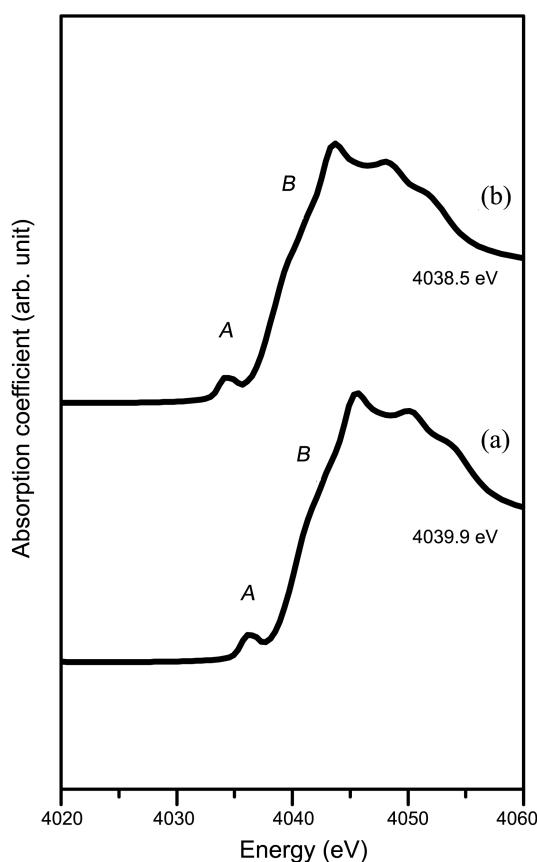


Figure 5. X-ray absorption near edge spectra (XANES) at calcium K-edge for (a) CaAl-LMHs and (b) CaFe-LMHs.

showed pre-edge peak (**A**) attributed to the $1s \rightarrow 3d$ transition and main edge with shoulder (**B**) due to the $1s \rightarrow 4p$ transition.^{19,20} The main edge positions for CaAl- and CaFe-LMHs were determined to be quite similar at 4039.9 and 4038.5 eV, respectively. From the previous report by Newport *et al.*,²¹ there is a correlation between edge position and coordination number (C.N.) for Ca-containing compounds in the C.N. region from 6 to 9. For comparative study, we measured the XANES spectra for $\text{Ca}(\text{OH})_2$ and CaF_2 , where Ca^{2+} ions are hexa- and octa-coordinated, respectively, showing main edge positions at 4037.6 and 4040.8 eV. Considering that the main edge positions of both LMHs lie between those of six-coordinated $\text{Ca}(\text{OH})_2$ and octa-coordinated CaF_2 , the Ca^{2+} ions in our LMHs have C.N. of ~7 which is a characteristic of HC structure.

In order to comprehend the local chemical environment around Fe^{3+} ions in CaFe-LMH, we analyzed extended X-ray absorption fine structure (EXAFS) spectrum at Fe K-edge (Fig. 6). We also carried out structural refinement utilizing program FEFFIT. The fitting conditions are following; k_{\min} : 2.20, k_{\max} : 14.80, r for 1st shell: 1.10-1.96, r for 2nd shell: 1.10-3.37. The first peak around 1.6 Å (not phase shift corrected) is attributed to the coordinated oxygen and the second one around 3.0 Å to the Ca^{2+} ions in the neighboring $\text{Ca}(\text{OH})_7$ decahedron. The ΔE and σ^2 values of refinement results are found to locate in the reasonable error

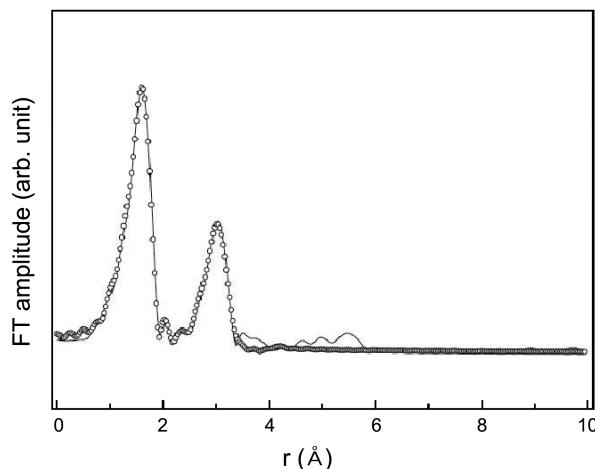


Figure 6. Fourier Transform (solid line) and fitting result (empty circle) for k^3 -weighted Fe K-edge extended X-ray absorptoin fine structure (EXAFS) of CaFe-LMHs.

Table 2. Results of nonlinear least-squares curve-fitting analysis for the Fe K-edge EXAFS spectrum of CaFe-LMH

Compound	Bond	CN	Bond distance (Å)	ΔE (eV)	σ^2 (\AA^2)
CaFe-NO_3	(Fe-O)	6	2.02	3.9	0.002
LMH	(Fe-Ca)	6	3.48	0.25	0.004

range (Table 2), suggesting that the refinement results are reliable. The Fe-O bond length and coordination number are determined to be 2.03 Å and 6, respectively. The distance between Fe and the nearest Ca is proven to 3.48 Å. These results indicate that the Fe^{3+} ions are well located in the octahedral center and the octahedrons are surrounded by six $\text{Ca}(\text{OH})_7$ decahedrons, as expected from the HC structure.

The chemical compositions of the synthesized LMHs were examined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and thermal analysis. The obtained Ca/Al and Ca/Fe ratio were 2.04 and 2.01, which are almost same value with the originally used ratio of $\text{Ca}^{2+}/\text{M}^{3+} \sim 2.00$. From the thermal analysis, we determined the water contents for the synthesized LMH samples. As described in Figure 7, there are four steps in the thermal decomposition of LMHs. The first step characterized by the endothermic DSC peak around 100 °C, is attributed to the loss of surface water molecules, and the second step at around 250 °C represents the loss of interlayer water molecules. The water contents calculated by the two weight loss steps are 25.85 and 22.20 wt % for CaAl- and CaFe-LMHs, respectively. From ICP-AES and the TG analysis, the chemical formulae are determined to $\text{Ca}_{2.04}\text{Al}_1(\text{OH})_6(\text{NO}_3)_5 \cdot 2.5\text{H}_2\text{O}$ and $\text{Ca}_{2.01}\text{Fe}_1(\text{OH})_6(\text{NO}_3)_4 \cdot 4.75\text{H}_2\text{O}$, which are the reasonable chemical composition for HC-like structure.

The thermal stability of the two LMHs was verified by TG-DSC analyses. The third step, which is associated with the loss of nitrate and dehydroxylation, appears in 300-600 °C region with endothermic signal at 550 °C for CaAl-LMH whereas CaFe-LMH show the same step in 250-500 °C with

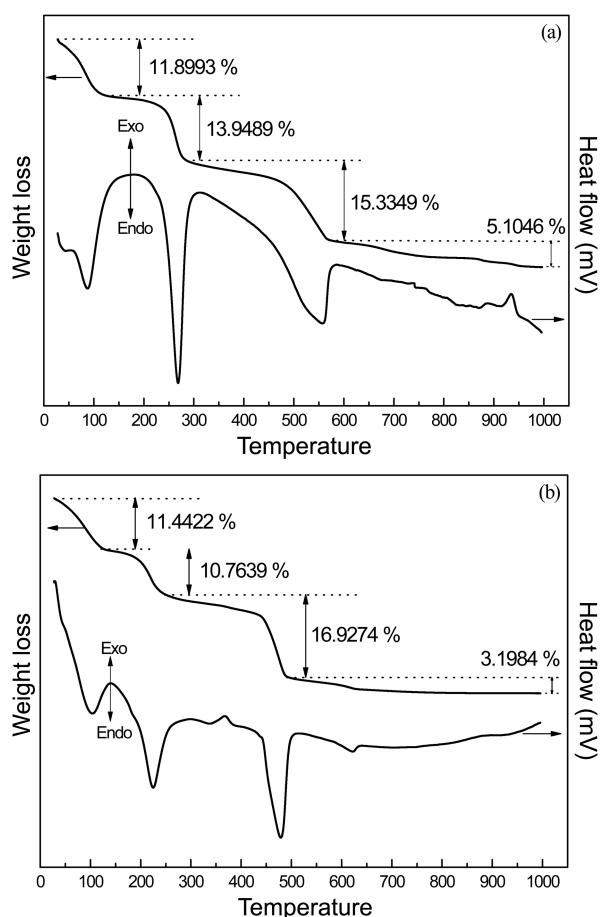


Figure 7. Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) results of (a) CaAl-LMHs and (b) CaFe-LMHs.

endothermic peak at 480 °C. From these results, it is found that the CaAl-LMH is better in thermal stability than that of CaFe-LMH. While CaAl-LMH is naturally occurring materials, the CaFe-LMHs are artificially synthesized by the isomorphic substitution of Al^{3+} (53.5 pm) with Fe^{3+} (64.5 pm). Compared to CaAl-LMHs, the slight lattice expansion originated from the different ion size might be the possible explanation for the less stability of CaFe-LMHs.

Particle size and morphology of both LMHs were investigated with FE-SEM (Fig. 8). All the particles showed plate-like morphology with larger lateral dimension than the longitudinal one, which is the typical feature of layered materials. It seems that the CaAl-LMHs are generally larger than CaFe-LMHs having more crystallized hexagonal-like plates (Fig. 8 white circles). From the X-ray diffraction patterns (Fig. 3), we could evaluate the crystallinity of both LMHs in lateral ($hk0$) directions. The full-width-half-maximum of ($hk0$) was determined to be higher in CaAl- than in CaFe-LMHs showing the better crystallinity of CaAl-LMHs. In the point of particle size, the diameter of primary LMHs particles was determined to lie between 50 and 800 nm although there observed some agglomeration between particles. In order to develop the Ca-containing LMHs as drug delivery carrier, the particle size in lateral dimension should be controlled 100 to 200 nm²² and the size controlling will be reported in the successive study.

Conclusion

We have demonstrated the synthesis and structural characterization of layered metal hydroxides containing calcium.

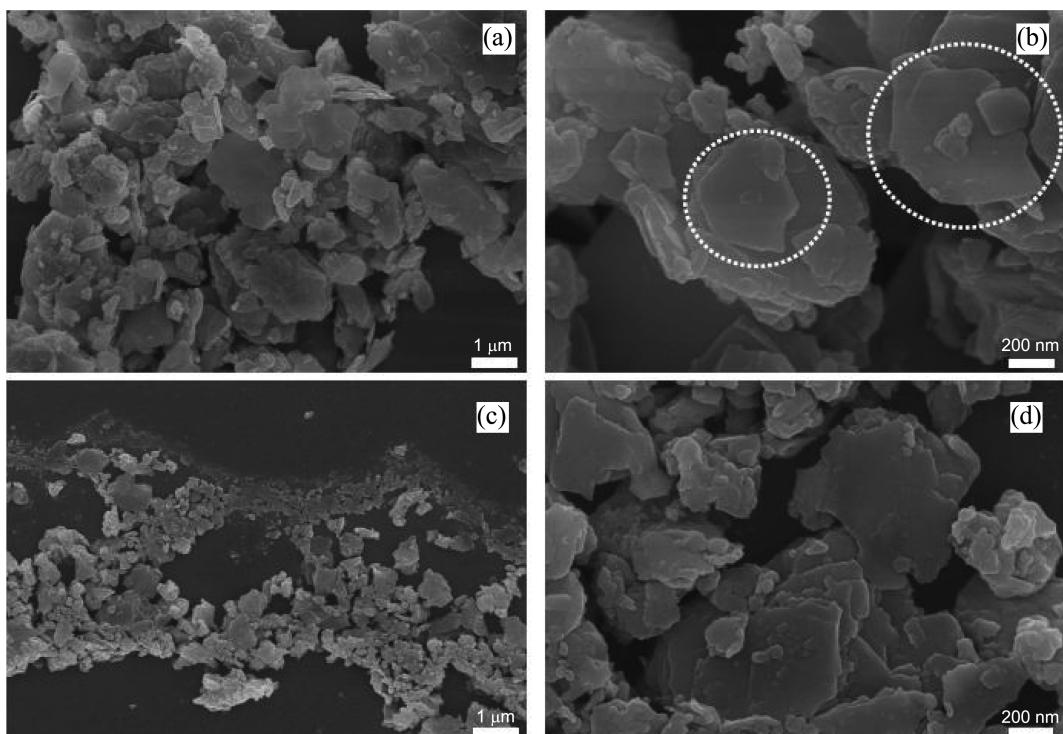


Figure 8. Field emission scanning electron microscopy image of (a) and (b) CaAl-LMHs, (c) and (d) CaFe-LMHs. White circles in (b) indicate crystallized hexagonal-like plates in CaAl-LMHs.

The CaAl- and CaFe-LMHs were synthesized by the co-precipitation methods with the preliminarily determined optimal pH range. Using both the X-ray diffraction analysis with Rietveld refinement and X-ray absorption spectroscopic study, our results show that the both CaAl- and CaFe-LMHs have hydrocalumite-like structure, where Ca is hepta-coordinated and trivalent metal is hexa-coordinated. It is also confirmed that both LMHs have submicron particle size with typical morphology of layered materials. Through thermal analyses, it was suggested that the thermal stability of LMHs could be altered by the isomorphic substitution of metal ions.

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