Rapid preparation of nano hexagonal-shaped hydrocalumite via one-pot mechanochemistry method

Abbas Fahami ^{a*}, Gary W. Beall ^{b,c}, Saeid Enayatpour ^d, Fariborz Tavangarian ^e,

Mohammad Fahami ^{f*}

Abstract

Hexagonal-shaped hydrocalumite (Ca-Al layered double hydroxides) was successfully synthesized by one-step mechanochemistry method within only 30 min. The product was characterized by X-ray diffraction, Fourier Transform Infrared spectroscopy, field emission scanning electron microscopy, energy dispersive spectroscopy, elemental mapping analysis, transmission electron microscopy, X-ray fluorescence, and thermogravimetric analysis. The results showed that the formation of a well-defined hydrocalumite and the microstructural evolution were strongly dependent on the milling time. From XRD profiles, a well-crystallized hydrocalumite with higher peaks intensity was formed after 60 min of milling, while the sharpness and intensity of LDH-derived XRD peaks decreased as milling time increased. Microscopic analysis showed that the product had hexagonal layered structure with lateral dimension of 100 to 200 nm. In addition, the thermal decomposition of the product is reported in details. This study offers a low-cost approach to synthesis of hydrocalumite owing to simplicity and extremely short processing time.

Keywords: Hydrocalumite; Mechanochemistry; Structural features; Electron microscopy.

1. Introduction

Hydrocalumite (HC) are anionic clays with the chemical formula of $\text{Ca}_{1-x}\text{Al}_x(\text{OH})_2 \text{A}^{n-}_x$, where A^{n-} represents the charge balancing anions such as CO_3^{2-} , Cl^- , SO_4^{2-} , OH^- , $\text{Al}(\text{OH})_4^-$ or NO_3^- (Sampieri et al., 2011). HC also belong to the family of layered double hydroxides (LDH) and differ from Hydrotalcites in that their main layer has well-ordered Ca/Al distribution in the hydroxide layers due to the large cationic radius of Ca^{2+} in comparison to Mg^{2+} , while the water and anions are placed in the interlayer spaces (Zheng et al., 2015). Some anions are preferentially intercalated to LDH over others, thus it may be used for targeted anion removal in terms of environmental protection (Toth et al., 2014). The carbonate ion owing to its high affinity is the most preferably intercalated anion and it is easily trapped in LDH (Sanderson et al., 2013). The presence of the carbonate in the interlayer region significantly affects the chemical reactivity of the LDH so that Yoon et al. (2014) reported calcined layered double hydroxide as an effective absorbent for chloride ions in the cement matrix. Linares et al. (2016) also demonstrated that carbonated hydrocalumite can be used as a promising antacids using a synthetic gastric juice compared with commercial ones. In general, HC has other industrial and environmental applications like mopping up of oil from oil–water mixtures (Dutta, and Pramanik, 2013), the removal of environmental hazards in acid mine drainage (Li et al., 2008), and a mechanism for the disposal of radioactive wastes (Das et al., 2003).

In past decade, many different chemical methods have been applied for fabrication of anionic clays. These methods include co-precipitation at different pH for the removal of heavy metal (Kovanda et al., 2003), hydrolysis (Hibino and Ohya, 2009), sol-gel (Paredes et al., 2006), Microwave-assisted structure reconstruction which help the

crystalline growth of Hydrotalcite (Benito et al., 2008), hydrothermal (Labajos et al., 1992), sonication (Climent et al., 2004), which have drawbacks in environmental pollution and energy consumption. Among various processes, mechanical alloying (MA) as a solvent-free process has been attracted special attention as an alternative method to prepare commercially nanostructured materials with proper structural characteristics due to its simplicity and versatility (Fahami, et al. 2011), however the information regarding preparation of clay materials through this process is still limited. It has been reported some new kinds of LDH such as Li-Al (French et al., 2010), and Ca-Sn (Ferencz et al., 2014) LDH by this method. Recently, Ferencz et al. (2015) reported their synthesis of Ca–Al–CO₃–LDH, using calcium hydroxide and aluminum hydroxide as raw materials, by a two-step MA process with some impurities (15.6 wt.% Katoite) in the final product. Note that Ca–Al–LDH was initially formed as a metastable compound in cement and converted to cubic Katoite (Ca₃Al₂(OH)₁₂) as a stable calcium aluminate hydrate during concrete curing (Wang et al., 2015). Qu et al. (2016) was also reported two steps mechanochemically induced Ca–Al–CO₃–LDH. Their initial results demonstrated that the milling of hydroxides only gave Katoite but no LDH phase. Thus, they added calcium chloride and calcium carbonate to their mixture and found that the addition of a third phase to Ca and Al hydroxides allowed the easy formation of stable Ca–Al–LDH phases.

Although few studies have examined the synthesis of various HC and the way in which they interact with various anions, the synthesis and characterization of Ca-Al-LDH via one-step mechanochemistry method has not been studied so far. So the present research was aimed to prepare and characterize Ca-Al-LDH through XRD, FT-IR, FESEM, elemental mapping analysis, EDS, XRF, TEM, and DTGA techniques.

2. Materials and methods

Calcium chloride (99 %, Sigma-Aldrich), Aluminum chloride (99 %, ACROS), and Sodium hydroxide pellets (97%, ACROS), were purchased and used without further purification. To prepare Ca-Al-LDH, the desired amounts of CaCl₂, AlCl₃, and NaOH were milled at different milling times (30, 60, 180, and 300 min) in a high energy ball mill (8000M Mixer/Mill) utilizing hardened chromium steel vials (vol. 65 ml) under air atmosphere. The weight ratio of ball-to-powder (BPR) was 10:1. The powders were washed three times with deionized water (20 ml) on a paper filter, and then were dried under oven at 60°C for 1h. The samples milled at different milling time were labeled as S1, S2, S3, and S4, respectively. The final composition was adjusted according to the following reaction (R1):

Composition of the reaction products between chemicals was determined using Bruker D8 Advance ECO using Cu-K_α radiation ($\lambda \approx 1.54\text{\AA}$). The samples were scanned from 5 to 70 degrees 2θ at a step size of 0.03 degrees. The XRD profiles were compared to standards compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS),

which involved card #31-0245 for Hydrocalumite. Fourier transform infrared spectroscopy (FT-IR, Bruker Tensor 27, USA) was used to determine the functional groups of products. All spectra were recorded at ambient temperature in the range 4000–600 cm^{-1} . Morphological evaluation of Ca-Al-LDH was carried out using FE-SEM (FEI Helios Nanolab 400 SEM) and TEM (JEOL JEM 1200 EXII). EDS analysis attached to the FESEM was used to determine the elemental composition. Thermal analysis was executed with a TGA (TA Q50 Thermogravimetric Analyzer) during heating in an argon atmosphere at a rate of 10°C/min from room temperature to 800 °C.

3. Results and discussions

3.1. XRD analysis

Fig 1 shows the XRD profiles of samples as a function of milling time (30, 60, 180, and 300). Based on Fig. 1, the main product of 30 min milling was in excellent agreement with the standard HC. With increasing of milling time up to 60 min, a well-crystallized Ca-Al-LDH with higher peaks intensity of HC was formed. Ca-Al-LDH displayed peaks corresponding to (002), (004), (112), (020), and ($\bar{3}$ 16) crystal planes. This trend continued for the 180 min milled specimen with slight decrease in peaks intensity of HC. Further increase in the milling time up to 300 min led to further decrease of the dominant peaks particularly for (002) plane. As is evident from Fig. 2, with increasing milling time, the LDH-derived XRD peaks decreased in both sharpness as well as intensity, and shift towards larger d spacings (i.e. lower 2θ). This effects could be explained on the basis of mechanically induced amorphization, which was accompanied by a significant change in lattice imperfections. Based on Fig 3, the basal spacing between layers of Ca-Al-LDH was strongly influenced by milling time so that it declined from 7.991 ± 0.001 (S1) to 7.833 ± 0.002 (S2) and then rose to 7.975 ± 0.001 and 8.04 ± 0.001 for S3 and S4, respectively. The presence of trigonal planar carbonate ion in interlamellar space instead of chloride ion may also contributes to this expansion (Fahami and Beall, 2016). This shows that the finding of optimum milling time to obtain carbonate free HC is essential.

In terms of local order of the cations, it was generally argued that M^{3+} cations should not occupy adjacent sites according to Pauling's rules. The results of this statement are that (I) the minimum possible $\text{M}^{2+}/\text{M}^{3+}$ molar ratio was 2 and (II) when the $\text{M}^{2+}/\text{M}^{3+}$ ratio was exactly 2, a long-range order exists with a superlattice involving an ordered array with each M^{3+} cation having six M^{2+} nearest neighbours and each M^{2+} cation having three M^{2+} and M^{3+} nearest neighbours (Forano et al., 2013). For this reason, the XRD pattern of the Ca/Al ratio of 2 was milled for 60 min and then compared with the XRD profile of Ca/Al ratio of 4 (Fig. 4). Based on Fig. 4, the main products of both samples were chloride form HC (Ca-Al-Cl-LDH), however a small fraction of calcite (JCPDS #086–2334) was identified in the Ca/Al ratio of 2, which probably due to some degree of contamination during the washing process. Our result was good agreement with the

outcomes of recent study (Pérez-Barrado et al., 2015). From the magnified region of 2θ between 10 to 27 ($^{\circ}$), the main peaks of the Ca/Al ratio of 2 were shifted slightly toward higher d space, which can be consequence of the presence of carbonate ions in interlamellar space owing to higher affinity of this ion. The basal distance for the reflection (002) (7.9 Å) of the Ca/Al ratio of 2 specimen agreed with the presence of chloride anions in the interlayer space (Pérez-Barrado et al., 2015). However, better crystallinity was observed for the Ca/Al ratio of 4 sample ($\text{FWHM}_{(002)} = 0.14^{\circ}$ for the Ca/Al ratio of 4 sample and $\text{FWHM}_{(002)} = 0.24^{\circ}$ for the Ca/Al ratio of 2 sample).

3.2. FTIR analysis

Fig. 5 displays the FT-IR spectra of samples as a function of milling time. The spectrum of 30 min milled sample exhibited two bands corresponding to the stretching vibrations of AlO–H at 3640 cm^{-1} , and a Hydroxyl band (ν_2) at 3492 cm^{-1} present in the inorganic main layers. From 3350 to 3650 cm^{-1} , the OH stretching vibrations of water can be observed as a broad band. Two weak bands at around 2918 and 2843 cm^{-1} (the shoulder of graph) were possibly owing to the hydrogen bonded (OH) stretching of intercalated water molecule (Fahami and Beall, 2016). A weak water band at 1636 cm^{-1} came from deformation vibration of water molecule (Xu et al, 2007). The absorption bands at around 1422 (ν_3), and 873 (ν_2), shows the stretching vibration of CO_3^{2-} , which is owing to the absorption of CO_2 from the air (Fahami et al., 2016). The band below 800 cm^{-1} were attributed to M–O vibrations (M = Ca or Al). The bands at 786 and 710 cm^{-1} correspond to the characteristic vibrations of hydrotalcite (Islam and Patel, 2011). The results demonstrate that the milling time affected intensity and the broadening bands which supporting outcomes obtained from XRD profiles.

3.3. Structural features

Table 1 presents the lattice constants and unit cell volume of milled nanopowders based on monoclinic structure of Ca–Al-LDH. The lattice parameters (a , b and c) can be calculated from the following relation (I) according to three Miller's planes of (002), (020) and ($\bar{3}16$):

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right) \quad (\text{I})$$

where h , k , and l are the Miller indices. The unit cell volume of milled samples was also computed using the following equation (II) (Brando and Kaplan, 2008):

$$V = (abc) \sin \beta \quad (\text{II})$$

Note, the data obtained from equation (I) should be compared to the unit cell parameters reported for the standard HC. From the standard data of HC (JCPDF#31-0245), a -axis, b -axis, and c -axis values were 9.853 Å , 5.715 Å , and 16.898 Å , respectively. The comparison study of those data reveals that the a -axis b -axis, and c -axis values were different as

milling time increased (30-300 min). Unit cell volumes of the milled powders increased slowly from 885.58 to 901.79 ($\text{\AA}^3$) as milling time rose (30-60 min) and then declined to 847.33 $\text{\AA}^3$ for 300 min milled sample. From the data, it is clear that the disparities in values of unit cell volume resulted mainly from increases in the c -axis values, rather than a -axis, and b -axis values. These findings prove that the structural characteristics of the mechanosynthesized Ca-Al-LDH were affected considerably by the milling time.

3.4. Morphological characterization

The FESEM and TEM images of 60 min milled sample Ca-Al-LDH are shown in Fig. 6. From Fig. 6a, the product had a hexagonal platelet structure composed of some fine particles. Pursuant their relatively large specific surface area of particles, the product had high tendency to agglomeration. This phenomenon commonly occurs in a three-step processes namely; *Rittinger*, *aggregation*, and *agglomeration* stage (Balaz, 2008). It is most likely that the mechanochemical reactions and structural changes mainly occur at the last stage owing to chemical bonding of fine particles (Fahami and Beall, 2016). During milling, the system included one ductile constituent (NaOH) and two brittle components (CaCl_2 and AlCl_3). Sodium chloride was formed owing to the hygroscopic nature of Halite, and followed by the formation of a ductile-brittle system. With continuous milling, both ductile and brittle particles got further refined. Ultimately, product with the layered structure was developed when equilibrium between fracturing brittle particles by trapping and ductile constituents by work hardening was established. Based on TEM image in Fig. 6b, a well-shaped layered structure with the lateral dimension of 100-200 nm can be observed. The morphology obtained by this method is similar to the other procedures that prepared through co-precipitation and hydrothermal methods (Sánchez-Cantú et al., 2015).

3.5. EDS and XRF analysis

Fig. 6c and d exhibit EDS and XRF spectra of 60 min milled sample. From the obtained data, the main components of the sample were oxygen, calcium, aluminum, and chlorine. Since sodium chloride was the only by-product of milled sample, and was washed from the sample, no other chemically stable contaminants were detected. Besides, Fe contamination resulting from the excessive wearing of the steel vials and balls was absent indicating the purity of the mechanosynthesized powders. The total amount of calcium and aluminum present in Ca-Al-LDH from both techniques were detected similarly, which are comparable with the accepted values. The mole ratio of calcium to aluminum was also achieved 3.98 by EDS and 4.01 by XRF, which were very close to actual mole ratio (4.00). The results illustrate that the composition and structure of chlorine incorporated Hydrocalumite were also very stable. Since the presence of amorphous phase in the final product were not detected through XRD, EDS, and XRF techniques, so the extent of the

amorphous phase is not negligible in the final product, and it can be a good candidate for future study of hydrocalumite preparation. Fig. 7 shows elemental mapping analysis of 60 min milled sample (Ca-Al-LDH). An appropriate spatial distribution of elements (Ca, Al, O, and Cl) was detected in elemental mapping images, indicating the formation of a homogenous microstructure after 60 min of milling.

Thermogravimetric analysis

8 shows the thermogravimetric analysis (TGA) of 60 min milled sample (Ca-Al-LDH) disclosing the degradation mechanism decomposition process covers three stages, which were ascribed to processes like elimination of physisorbed water, the structural around dissociation some of hydrated reactants, which was formed during milling or washing process. The second from 159°C to approximately 370°C, corresponding to a mass loss of 12.3% associated to the interlamellar water loss. The final and largest ethydroxylation of the HC lamellae, which is bonded mostly with Ca^{2+} $[\text{Ca}-(\text{OH})-\text{Ca}]$ and $[\text{Al}-(\text{OH})-\text{Ca}]$. It is worthy to note that the conventional LDH having carbonate anions had a decomposition temperature of 310°C (Theiss et al., 2012) been successfully intercalated in LDH. From 751°C, there is a constant residual mass associated to the formation of the calcium

4. Conclusions

Rapid synthesis of mechanically induced hydrocalumite was investigated. Results showed that the structural characteristics of product affected strongly by milling time so that the interlayer space of samples was increased as milling time rose. Based XRD and FTIR spectra, a pure phase composition of Ca-Al-LDH was formed after 30 min milling hexagonal

spectra, no other chemically stable impurities were detected. From TGA data, three mass loss characteristics events of the thermal decomposition of Ca-Al-LDH were observed demonstrating the successful chloride intercalation in LDH structure in various industries.

Acknowledgement

This research was supported by the National Science Foundation (PREM center for interfaces, DMR-1205670), and the Robert A. Welch Foundation (AI-0045).

References

- Baláž, P., 2008. [High-energy milling \(103-132\)](#). Springer Berlin Heidelberg.
- Benito, P., Guinea, I., Labajos, F. M., & Rives, V., 2008. [Microwave-assisted reconstruction of Ni, Al hydrotalcite-like compounds](#). *J. Solid State Chem.* 181, 987-996.
- Brandon, D., & Kaplan, W. D., 2008. [Scanning Probe Microscopy and Related Techniques](#). *Microstructural Characterization of Materials*, 2nd Edition, 391-421.
- Climent, M. J., Corma, A., Iborra, S., Epping, K., & Velty, A., 2004. [Increasing the basicity and catalytic activity of hydrotalcites by different synthesis procedures](#). *J. Catal.* 225, 316-326.
- Das, D. P., Das, J., & Parida, K., 2003. [Physicochemical characterization and adsorption behavior of calcined Zn/Al hydrotalcite-like compound \(HTlc\) towards removal of fluoride from aqueous solution](#). *J. Colloid Interf. Sci.* 261, 213-220.
- Dutta, K., & Pramanik, A., 2013. [Synthesis of a novel cone-shaped CaAl-layered double hydroxide \(LDH\): its potential use as a reversible oil sorbent](#). *Chem. Commun.* 49, 6427-6429.
- Fahami, A., Al-Hazmi, F. S., Al-Ghamdi, A. A., Mahmoud, W. E., & Beall, G. W., 2016. [Structural characterization of chlorine intercalated Mg-Al layered double hydroxides: A comparative study between mechanochemistry and hydrothermal methods](#). *J. Alloy. Compd.* 683, 100-107.
- Fahami, A., & Beall, G. W., 2016. [Mechanosynthesis and characterization of Hydrotalcite like Mg–Al–SO₄–LDH](#). *Mater. Lett.* 165, 192-195.
- Fahami, A., & Beall, G. W., 2016. [Structural and morphological characterization of Mg_{0.8}Al_{0.2}\(OH\)₂Cl_{0.2} hydrotalcite produced by mechanochemistry method](#). *J. Solid State Chem.* 233, 422-427.
- Fahami, A., Ebrahimi-Kahrizsangi, R., & Nasiri-Tabrizi, B., 2011. [Mechanochemical synthesis of hydroxyapatite/titanium nanocomposite](#). *Solid State Sci.* 13, 135-141.
- French, D., Schifano, P., Cortés-Concepción, J., & Hargrove-Leak, S., 2010. [Li–Al layered double hydroxides as catalysts for the synthesis of flavanone](#). *Catal. Commun.* 12, 92-94.
- Ferencz, Z., Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I., 2015. [Optimisation of the synthesis parameters of mechanochemically prepared CaAl-layered double hydroxide](#). *Appl. Clay Sci.* 112, 94–99.

- Ferencz, Z., Szabados, M., Ádok-Sipiczki, M., Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I., 2014. Mechanochemically assisted synthesis of pristine Ca(II)Sn(IV)-layered double hydroxides and their amino acid intercalated nanocomposite. *J. Mater. Sci.* 49, 8478–8486.
- Forano, C., Costantino, U., Prévot, V., Gueho, C.T., 2013. Chapter 14.1 – Layered Double Hydroxides (LDH), F. Bergaya, G. Lagaly (Eds.), *Handbook of Clay Science* (second ed.), Dev. Clay Sci., 5A, 745–782.
- Hibino, T., & Ohya, H., 2009. Synthesis of crystalline layered double hydroxides: Precipitation by using urea hydrolysis and subsequent hydrothermal reactions in aqueous solutions. *Appl. Clay Sci.* 45, 123-132.
- Islam, M., & Patel, R., 2011. Physicochemical characterization and adsorption behavior of Ca/Al chloride hydrotalcite-like compound towards removal of nitrate. *J. hazardous materi.* 190, 659-668.
- Kovanda, F., Grygar, T., & Dorničák, V., 2003. Thermal behaviour of Ni–Mn layered double hydroxide and characterization of formed oxides. *Solid State Sciences*, 5, 1019-1026.
- 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.
- Li, Y., Gao, B., Wu, T., Chen, W., Li, X., & Wang, B., 2008. Adsorption kinetics for removal of thiocyanate from aqueous solution by calcined hydrotalcite. *Colloid. Surface. A*, 325, 38-43.
- Linares, C. F., Moscosso, J., Alzurutt, V., Ocanto, F., Bretto, P., & González, G., 2016. Carbonated hydrocalumite synthesized by the microwave method as a possible antacid. *Mater. Sci. Eng. C*, 61, 875-878.
- Paredes, S. P., Fetter, G., Bosch, P., & Bulbulian, S., 2006. Sol-gel synthesis of hydrotalcite—like compounds. *J. Mater. Sci.*, 41, 3377-3382.
- Perez-Barrado, E., Salagre, P., Marsal, L.F., Aguiló, M., Cesteros, Y., Díaz, F., Pallares, J., Cucinotta, F., Marchese, L. and Pujol, M.C., 2015. Ultrasound-assisted reconstruction and delamination studies on CaAl layered double hydroxides. *Appl. Clay. Sci.*, 118, 116-123.
- Qu, J., Zhong, L., Li, Z., Chen, M., Zhang, Q., & Liu, X., 2016. Effect of anion addition on the syntheses of Ca–Al layered double hydroxide via a two-step mechanochemical process. *Appl. Clay Sci.* 124, 267-270.
- Sampieri, A., Fetter, G., Villafuerte-Castrejon, M. E., Tejeda-Cruz, A., Bosch, P., 2011. Nanoporous composites prepared by a combination of SBA-15 with Mg-Al mixed oxides. Water vapor sorption properties, *Beilstein J. Nanotechnol.* 2, 99–103.
- Sánchez-Cantú, M., Camargo-Martínez, S., Pérez-Díaz, L. M., Hernández-Torres, M. E., Rubio-Rosas, E., & Valente, J. S., 2015. Innovative method for hydrocalumite-like compounds' preparation and their evaluation in the transesterification reaction. *Appl. Clay Sci.* 114, 509-516.

- Sanderson, B. A., Sowersby, D. S., Crosby, S., Goss, M., Lewis, L. K., & Beall, G. W., 2013. Charge density and particle size effects on oligonucleotide and plasmid DNA binding to nanosized hydrotalcite. *Biointerphases*, 8, 8.
- Theiss, F. L., Palmer, S. J., Ayoko, G. A., & Frost, R. L., 2012. Sulfate intercalated layered double hydroxides prepared by the reformation effect. *J. thermal anal. calorim.* 107, 1123-1128.
- Tóth, V., Sipiczki, M., Pallagi, A., Kukovecz, Á., Kónya, Z., Sipos, P., & Pálinkó, I., 2014. Synthesis and properties of CaAl-layered double hydroxides of hydrocalumite-type. *Chemical Pap.* 68, 633-637.
- Wang, T., Zhang, P., Wu, D., Sun, M., Deng, Y., Frost, R. L., 2015. Effective removal of zinc (ii) from aqueous solutions by tricalcium aluminate (C3A). *J. Colloid Interface Sci.* 443, 65–71.
- Xu, Z. P., Walker, T. L., Liu, K. L., Cooper, H. M., Lu, G. M., & Bartlett, P. F., 2007. Layered double hydroxide nanoparticles as cellular delivery vectors of supercoiled plasmid DNA. *Int. J. Nanomed.* 2, 163.
- Yoon, S., Moon, J., Bae, S., Duan, X., Giannelis, E. P., & Monteiro, P. M., 2014. Chloride adsorption by calcined layered double hydroxides in hardened Portland cement paste. *Mater. Chem. Phys.* 145, 376-386.
- Zheng, L., Xia, S., Lu, X., & Hou, Z., 2015. Transesterification of glycerol with dimethyl carbonate over calcined Ca-Al hydrocalumite. *Chinese J. Catal.* 36, 1759-1765.

List of Figures Caption

Fig. 1 XRD patterns of specimens (Ca-Al-LDH) milled at different milling time (S1=30, S2=60, S3=180, and S4=300).

Fig. 2 The magnified 3D XRD profiles ($2\theta = 5-35$) of milled samples (S1, S2, S3, and S4).

Fig. 3 The interlayer spacing of specimens (Ca-Al-LDH) milled at different milling time (S1, S2, S3, and S4).

Fig. 4 XRD profiles of 60 min milled samples for different Ca/Al ratio.

Fig. 5 FT-IR spectra of milled specimens (S1, S2, S3, and S4).

Fig. 6 Morphological features and chemical composition of 60 min milled sample (Ca-Al-LDH): (a) FE-SEM, (b) TEM images, and (c, d) EDS and XRF spectra.

Fig. 7 The elemental mapping analysis of 60 min milled sample (Ca-Al-LDH).

Fig. 8 TGA of 60 min milled sample (Ca-Al-LDH) as a function of temperature.

Table Caption

Table1. Lattice parameters, and unit cell volume of Ca-Al-LDH.

Table 1. Lattice parameters, and unit cell volume of Ca-Al-Cl-LDH.

Sample	Milling Time (min)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å³)
S1	30	9.819	5.774	17.011	885.58
S2	60	10.00	5.756	17.060	901.79
S3	180	9.701	5.676	17.370	878.27
S4	300	9.116	5.780	17.512	847.33
STD	–	9.853	5.715	16.898	873.77

(d)

	EDS		XRF	
<i>Elements</i>	<i>Mass</i>	<i>Units</i>	<i>Mass</i>	<i>Units</i>
Al	6.95	<i>Wt.%</i>	6.89	<i>Wt.%</i>
Ca	41.1	<i>Wt.%</i>	40.9	<i>Wt.%</i>
Cl	9.16	<i>Wt.%</i>	9.21	<i>Wt.%</i>
O	42.79	<i>Wt.%</i>	–	<i>Wt.%</i>
Ca/Al	5.91	–	5.93	–