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以白云岩为原料制备 Mg-Al-CO_3 类水滑石/方解石复合粉体及机理

白　仟[1]，刘　全[2]，柴玉朴[3]，吴　迪[2]

(1. 巴斯夫(中国)有限公司，上海 200137；2. 中国地质大学(北京)，北京 100083；
3. 中铁建工集团山东有限公司，山东 青岛 266000)

摘　要：以白云岩为原料，通过酸溶和共沉淀工艺合成了 Mg—Al—CO_3 类水滑石/方解石复合粉体。利用白云岩的镁、钙和二氧化碳，无 CO_2 温室气体排放，属绿色合成工艺。确定了优化的工艺条件：酸溶温度为 60 ℃，$OH^-/(Mg^{2+}+Al^{3+})$摩尔比为 3.5:1.0，Mg^{2+}/Al^{3+}摩尔比为 3:1，结晶温度和时间分别为 120 ℃和 18 h。结果表明：复合粉体中 Mg—Al—CO_3 类水滑石和方解石的质量分数分别为 39.5%和 60.5%；方解石粒度在 0.6~1.8 μm，形态为规则粒状；类水滑石呈规则六边形片状，片径在 100~200 nm。对酸溶与共沉淀过程及其 Mg—Al—CO_3 类水滑石和方解石的结晶过程及其机理进行了讨论。

关键词：白云岩；类水滑石；方解石；复合粉体；绿色工艺
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Green Synthesis and Mechanism of Mg—Al—CO_3 Layered Double Hydroxides/Calcite Composite Powders from Dolomite

BAI Qian[1], *LIU Quan*[2], *CHAI Yupu*[3], *WU Di*[2]
(1. BASF(China) Co.,Lit, Shanghai 200137, China; 2. China University of Geosciences (Beijing), Beijing 100083, China;
3. China Railway Construction Engineering Group Shandong Co. LTD, Qingdao 266000, Shandong, China)

Abstract: Green synthesis of Mg–Al–CO_3 layered double hydroxides/calcite composite powders (LDH/Cal) *via* the acid dissolution and co-precipitation process was investigated in this paper. This method uses dolomite as a source of magnesium, calcium, and carbon dioxide with no CO_2 release in the process of preparation. LDH/Cal prepared under optimized conditions (acid dissolution temperature was 60 ℃, $OH^-/[Mg^{2+}+Al^{3+}]$ mole ratio was 3.5:1.0, Mg^{2+}/Al^{3+} mole ratio was 3:1, temperature and time of crystallization were 120 ℃ and 18 h, respectively) was characterized. LDH/Cal consists of LDH (39.5%) and calcite (60.5%). The calcite was regular and granular with a diameter of about 0.6 to 1.8 μm, and LDH contained well-defined plate-like particles with regular hexagonal shape, and sizes between 100 and 200 nm. The acid dissolution process of dolomite and the compound mechanism of LDH and calcite were discussed.

Keywords: dolomite; layered double hydroxides; calcite; composite powders; green synthesis

1　Introduction

In recent decades, layered double hydroxides (LDHs), also known as hydrotalcite-like compounds (HTlc), have attracted attention from both academia and industry due to their attractive properties (such as large surface area, high anion exchange capacity, good chemical and thermal stability, memory effect) with respect to potential applications, such as adsorbents, anion exchangers, medical antacids, targeted drug delivery, additives in polymers, anti-wear additives in lubricants, flame retardants, base catalysts, and metal oxides precursors[1–16].

The structure of an LDH is related to that of brucite, $Mg(OH)_2$, in which some of the Mg^{2+} cations in the

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第一作者：白　仟(1985—)，女，博士。
通信作者：刘　全(1967—)，男，学士，工程师。

Received date: 2020–10–15.　**Revised date:** 2020–11–07.
First author: BAI Qian (1985–), female, Ph.D.
E-mail: 315099820@qq.com
Corresponding author: LIU Quan (1967–), male, Bachelor, Engineer.
E-mail: liuquan@cugb.edu.cn

layered structure were replaced by Al^{3+}. CO_3^{2-} is intercalated between the layers to maintain electroneutrality. The Mg–Al–CO_3 LDHs the chemical formula $Mg_{0.75}Al_{0.25}(OH)_2(CO_3)_{0.125}\cdot 0.5H_2O$ is the most typical representative of the hydrotalcite family[17–18]. Although CO_3^{2-}-intercalated LDHs have broad application prospect as antacids, flame retardants, and wastewater treatment agents[1, 19], this LDH mineral and its natural sources are rare and would not be capable of meeting industrial application requirements. Generally, the synthesis of Mg–Al LDHs mostly use $Mg(NO_3)_2$ as the magnesium source in the laboratory, but it is relatively uneconomical to synthesize this compound on an industrial scale. Some researchers investigated $Mg(OH)_2$, MgO, and calcined dolomite as new magnesium sources for the production of Mg–Al–LDHs[19–23]. However, these preparation methods usually require very long reaction times or produce greenhouse gas emissions. Our research group has been successfully preparing Mg–Al–LDHs using magnesite as new Mg and CO_2 sources for a short time period, which is a process without carbon dioxide emissions[24]. Following our new method, we have also been successful in preparing Mg–Al–CO_3 LDHs/Cal composite powders (LDH/Cal) using dolomite as new Mg and CO_2 sources. The dissolution process of dolomite acid and the compound mechanism of Mg–Al–CO_3 HTlc and Calare discussed.

2 Experimental and characterization methods

2.1 Materials

The dolomite was obtained from Changping of Beijing, China. For the follow-up experiments, the dolomite was powdered in an agitating mill. The maximum particle diameter of dolomite powders was <74 μm. The X-ray diffraction (XRD) pattern (Fig. 1) shows that only a small amount of brucite exists in the raw material in addition to the dolomite. The chemical composition of the sample was MgO 21.72%, CaO 28.53%, LOI 45.51%, SiO_2 1.61%, Al_2O_3 1.54%, Fe_2O_3 0.31%, FeO 0.16%, MnO 0.012%, K_2O 0.057%, P_2O_5 0.02%, and TiO_2 0.031%. Deionized water (18 MV/cm) was used throughout this study. The starting reagents were analytical grade aluminum nitrate hydrate ($Al(NO_3)_3\cdot 9H_2O$), sodium hydroxide (NaOH), and nitric acid (HNO_3).

2.2 Synthesis of LDH/Cal

In order to obtain the optimized process for preparing LDH/Cal from dolomite, a preliminary study of dolomite acid solution and preparation of LDH/Cal was conducted. The experiment arrangement and detailed experimental conditions used for the synthesis of LDH/Cal are given in Fig. 2 and Table 1. Briefly, solution I was prepared by injecting dolomite powder, $Al(NO_3)_3\cdot 9H_2O$ and HNO_3 into a conical flask and reacted at a set temperature for 4 h. The carbon dioxide gas that is associated with the formation of solution I from the dolomite decomposition was passed into the NaOH solution to form solution II. Solutions I and II were then dropped into a sealed chamber at a flow rate of 8 to 10 mL/min and were hydrothermally treated at different temperatures ranging from 100 to 140 ℃ for 12 to 24 h. The resulting solids were washed with deionized water and dried at 80 ℃ for 24 h.

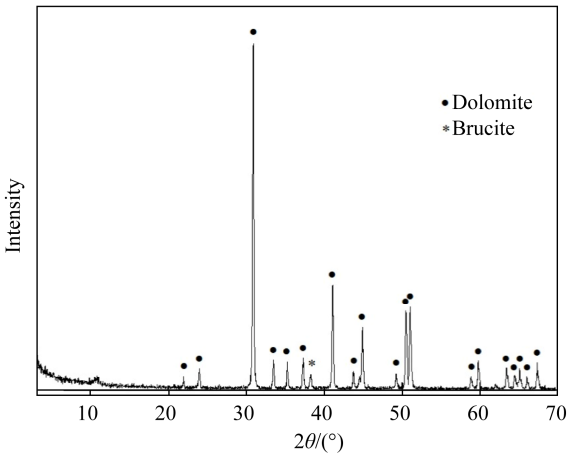


Fig. 1 X-ray diffraction patterns of dolomite

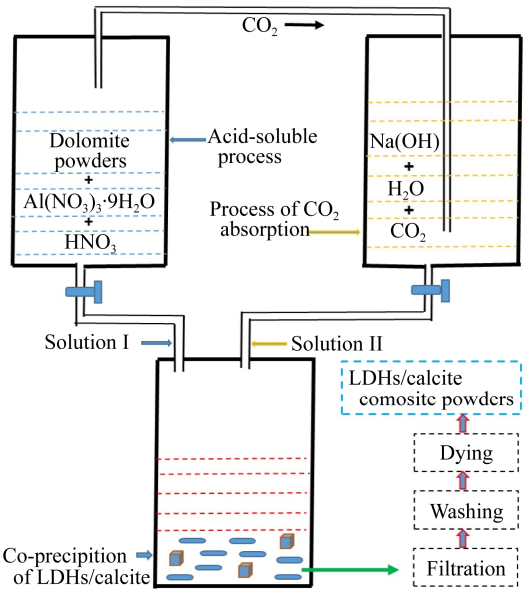


Fig. 2 Synthetic strategy of LDH/Cal

On the basis of the pre-study results of various synthetic parameters, acid dissolution of 60 ℃, OH^-/(Mg^{2+}+Al^{3+}) mol ratio of 3.5:1, Mg^{2+}/Al^{3+} mol ratio of 3:1, crystallization temperature of 120 ℃, and crystallization time of 18 h were chosen as the optimum synthetic parameters for preparing LDH/Cal. The LDH/Cal that was prepared under optimal conditions was used as the research compound in this paper.

Table 1　List of conditions for preparation of LDH/Cal from dolomite

Experiment process	Experiment conditions
Acid dissolution of dolomite	Acid dissolution temperature: 25, 60 ℃;Acid dissolution time: 4 h; Dolomite powder: 0.02 mol; $Al(NO_3)_3·9H_2O$: 0.01 mol; HNO_3 (1mol/L): 40 mL
Synthesis of LDH/Cal	$OH^-/(Mg^{2+}+Al^{3+})$: 2:1, 2.5:1.0, 3:1, 3.5:1.0; Concentration of salt (solution I) ($mol·L^{-1}$): 0.6, 0.9, 1.2; Mg^{2+}/Al^{3+}: 2:1, 3:1, 4:1; Crystallizing temperature: 100, 120, 140 ℃; Crystallizing time: 12, 18, 24 h

2.3　Characterization of LDH/Cal

The LDH/Cal samples were characterized by powder XRD using a Model D/MaX-RC diffractometer (Cu K_α radiation, λ=0.154 1 nm). Data were collected over a 2θ range of 3° to 70° (increment of 0.02°, scanning rate of 8 (°)/min). Model STA449F3 differential-thermal scale (DSC-TG) was used to determine the features of the phase transition under heat. The instrument is capable of heating up at 10 ℃/min from room temperature to 1 000 ℃ in N_2. A Model S4800 scanning electron microscope (SEM) with cold-emission was used for micro-morphological observations. Model Nieolet Nexus670 Fourier infra-red spectrometer (FT-IR) and KBr pressing disc were used for infrared spectroscopic analyses. The ratio between masses of powder sample and KBr was 2:100.

3　Results and discussion

3.1　Results of experimental and characterization

The crystalline phases of the products identified by XRD were layered double hydroxides (LDHs, JCPDS-14-191) and Cal (JCPDS-47-1743) as shown in Fig. 3. The results from the evaluation of the Rietveld-based quantitative analysis method indicated that the mass percentages of the LDHs and Cal were 39.5% and 60.5%, respectively[25].

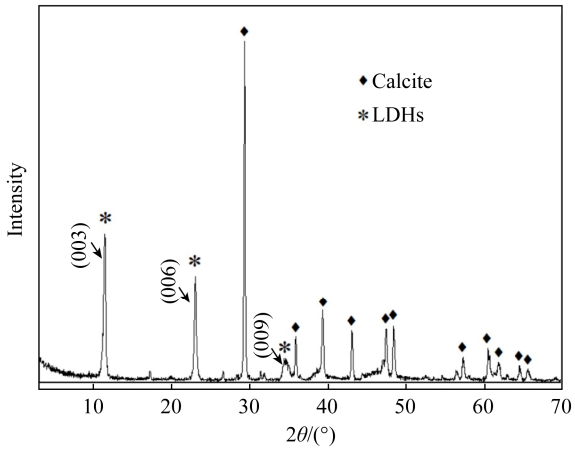


Fig. 3　XRD patterns of LDH/Cal

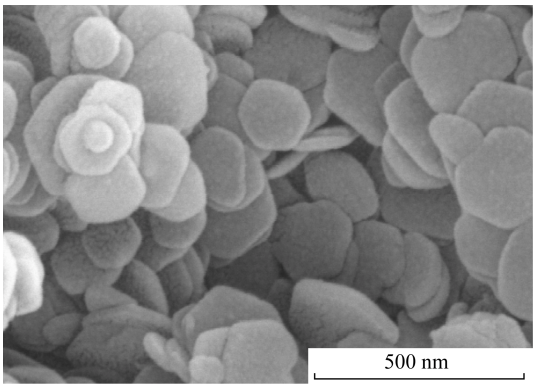
The (003), (006), and (009) crystal planes of the LDHs suggest the presence of hexagonal lattice with rhombohedral 3R symmetry as reported earlier[1]. The LDHs present a cell parameter a_0 of 0.305 and c_0 of 2.300 nm in addition to d-spacing of 0.772 nm and gallery height of 0.492 nm. The values agree well with previous results obtained from similar phases[26].

SEM images of LDH/Cal are shown in Fig. 4. The morphology of the Cal was regular and granular with diameter of about 0.6 to 1.8 μm. The morphology of the LDHs consisted of well-defined plate-like particles with regular hexagonal shape and sizes between 100 nm and 200 nm. Fig. 4(b)–4(d) also shows that the calcite surface adheres to some flaky LDHs.

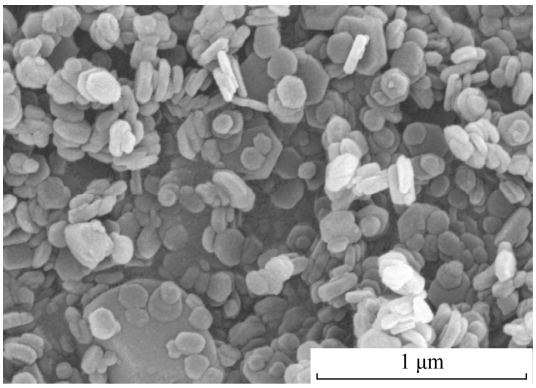
The FT-IR spectra of LDH/Cal prepared under optimized synthetic conditions is shown in Fig. 5. The strong, broad band observed at about 3 485 cm^{-1} was assigned to O—H stretching ($\nu_{O—H}$) due to the presence of a hydroxyl and both an adsorbed and interlayer water[27]. The shoulder observed 3 065 cm^{-1} was attributed to hydrogen bonds between water molecules and CO_3^{2-} in the interlayer[28]. The presence of vibrational bands at 1 426, 872 cm^{-1} and 711 cm^{-1} were attributed to the asymmetrical stretching vibration (ν_3) and the carbonate out-of-plane bending vibration (ν_4 and ν_2 mode) of calcium carbonate[29–30]. The band observed at about 1 369 cm^{-1} was attributed to the ν_3 asymmetric stretching of the CO_3^{2-} in LDH. The weak absorptions at 672 and 553 cm^{-1} could have been due to Mg(Al)—OH vibrations. It was noted that the characteristic vibration of NO_3^- at 1 380 cm^{-1} was absent in the LDHs[31], indicating that the NO_3^- anion did not enter the interlayer of LDHs.

The thermogravimetric differential scanning calorimetry curve of LDH/Cal (Fig. 6) shows three stages of weight loss in TG: the first occurred in the range of 25 to 225.7 ℃, (2) the second in the range of 225.7 ℃ to 407.2 ℃, and (3) the third in the range of 407.2 to 749.7 ℃. The first weight loss of around 7% is attributed to the loss of interlayer and weakly adsorbed water molecules. The second mass loss, around 10%, is associated with the removal of water molecules from the LDHs network and CO_3^{2-} from the interlayer anion resulting in the destruction of the layered structure. The third mass loss of around 26% is attributed to CO_2 leakage due to Cal decomposition. DSC support the TG results in exhibiting three endotherms corresponding to three weight losses in the same temperature ranges.

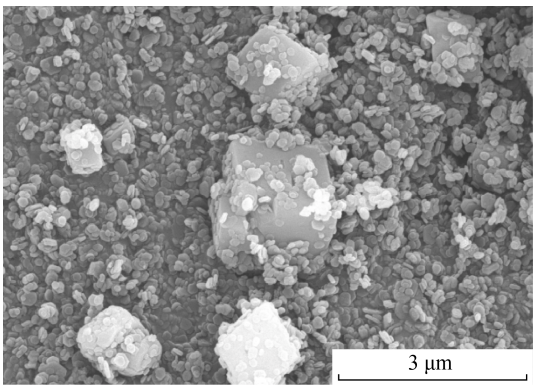
Based on the total weight loss of the first and second stages (17%) and the weight loss of the third stage (26%) combined with the theoretical components of Mg—Al—CO_3—LDHs (MgO 40.04%, Al_2O_3 16.88%, H_2O 35.79, CO_2 7.29%) and Cal (CaO 56.03%, CO_2 43.97%), the content of LDHs (40%) and Cal (60%) in LDH/Cal were calculated. This result was shown to be consistent with the content of LDHs (39.5%) and Cal (60.5%) as calculated by XRD.



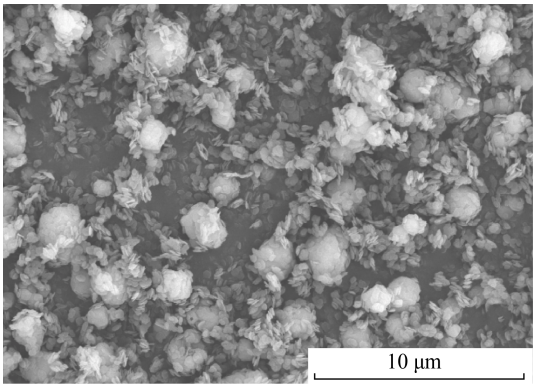
(a) High magnification



(b) High magnification



(c) Low magnification



(d) Low magnification

Fig. 4 SEM images of LDH/Cal with different magnification

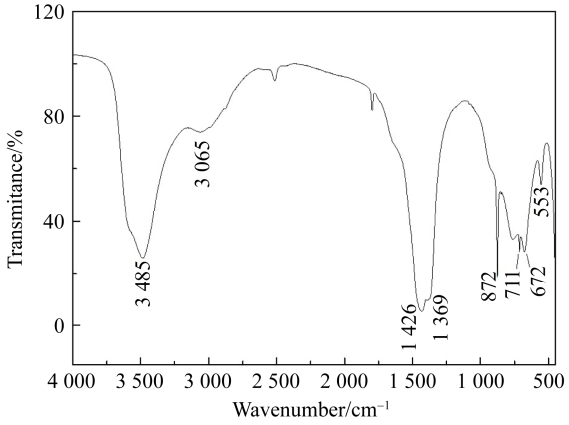


Fig. 5 Fourier-transform infrared spectra of LDH/Cal

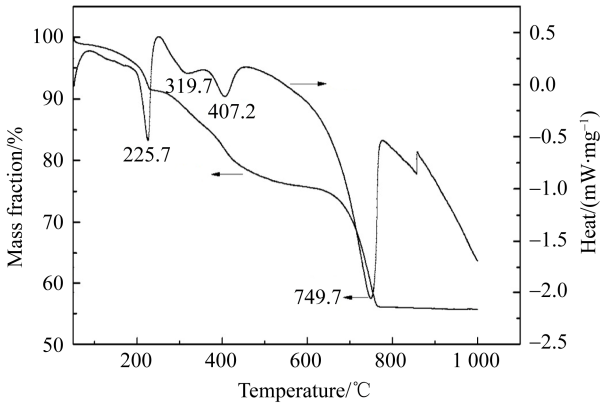


Fig. 6 Thermogravimetric differential scanning calorimetry curve of LDH/Cal

3.2 Mechanism and Discussion

1) Dolomite is a native carbonate mineral normally represented by a stoichiometric chemical composition of $CaMg(CO_3)_2$ (MgO 21.86%, CaO 30.41%, CO_2 47.73). Dolomite is a major rock-forming mineral and has abundant reserves on Earth. Dolomite could be used as an Mg and CO_3^{2-} source for preparation of Mg—Al—CO_3—LDHs and as calcium and CO_3^{2-} sources of Cal. The preparation process of LDH/Cal was expressed in equations (1) to (3):

$$CaMg[CO_3]_2(S)+2HNO_3(L)+Al(NO_3)_3\cdot 9H_2O(S)\rightarrow Mg(NO_3)_2(L)+Ca(NO_3)_2(L)+Al(NO_3)_3(L)+H_2O(L)+CO_2(G) \quad (1)$$

$$CO_2(G)+NaOH(L)\rightarrow Na_2CO_3(L)+H_2O(L) \quad (2)$$

$$Mg(NO_3)_2(L)+Ca(NO_3)_2(L)+Al(NO_3)_3(L)+Na_2CO_3(L)+H_2O(L)\rightarrow Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O(LDHs,(S))\downarrow+CaCO_3(calcite,(S))\downarrow+Na_2NO_3(L) \quad (3)$$

In Equation (1), dolomite and aluminum nitrate hydrate powders were dissolved by nitric acid (HNO_3) solution to yield magnesium and aluminum sources (solution I). According to Equation (2), the NaOH solution was used as the absorbent of CO_2 which was released from dolomite(solution II). Equation (3) is the co-precipitation process of HTlc and Cal after solutions I and II are mixed.

2) Cal($CaCO_3$) had the lowest reaction free energy

($\Delta G^{\theta}_{298.15}$) as shown in Table 2. It was first crystallized in the mixture of Solutions I and II by a combination of Ca^{2+} and CO_3^{2-}, which was confirmed by the fact that Cal has a larger particle size than LDHs and LDHs are closely adherent to the surface of calcite (Fig. 7).

Table 2　Standard molar Gibbs free energies ($\Delta G^{\theta}_{298.15}$) of several compounds related to this study at 298.15 K

Compound	$\Delta G^{\theta}_{298.15}$ (kJ/mol)
Mg-Al-CO_3 LDHs	–170.6
Mg-Al-NO_3 LDHs	–155.8
Calcite ($CaCO_3$)	–1 128.8
Magnesite ($MgCO_3$)	–1 012.1
Dolomite ($CaMg[CO_3]_2$)	–520.5
$Ca(NO_3)_2$	–743.2
$Mg(NO_3)_2$	–589.5
$Al(OH)_3$	–271.9
$Mg(OH)_2$	–88.6
$Ca(OH)_2$	–898.9

The results of molecular dynamics simulations indicate that the interaction energies of small inorganic anions, such as CO_3^{2-} (with an ionic radius of 0.164 nm) with the LDHs host structure were higher than for the interaction with larger organic anions, such as NO_3^- (with an ionic radius of 0.335 nm)[32]. Thermodynamic studies have also confirmed that carbonate anions (CO_3^{2-}) are thermodynamically favored in the LDHs interlamellar region due to their small $\Delta G^{\theta}_{298.15}$ values compared to nitrate (NO_3^-) as shown in Table 2[33]. In this study, Mg—Al—CO_3 LDHs instead of Mg—Al—NO_3 LDHs were formed under the conditions of coexistence of CO_3^{2-} carbonate and NO_3^-, which is consistent with results from the molecular dynamics simulations and thermodynamic studies. The crystallization process and crystal characteristics of calcite and Mg—Al—CO_3 LDHs are shown in Fig. 8.

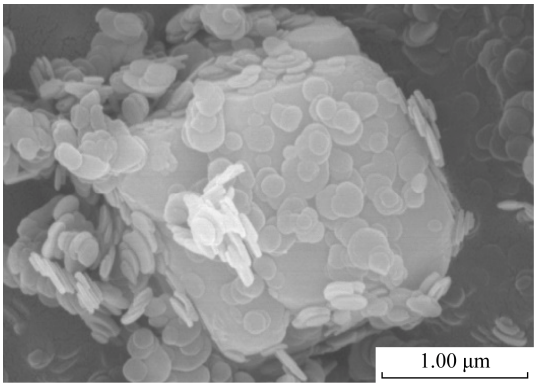


Fig. 7　SEM images of LDHs and Cal

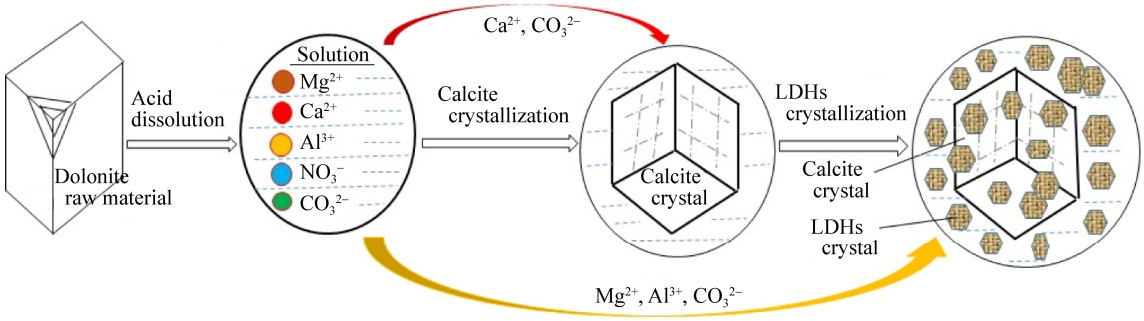


Fig. 8　Schematic diagram of the crystallization of LDHs/Cal composite powder

3) Cal is a filler used in many applications, such as plastics, rubbers, and paints. Polymers filled with Cal filler show improved mechanical properties, such as impact resistance, tensile strength, glass temperature, and decomposition temperature. The global demand for Cal is continuously increasing and is expected to reach 108.5 million tons by roughly 2016[34]. Research shows that LDHs-polymer composites containing small amounts of LDHs would be improved mechanical strength, reduced permeability toward gases and liquids, and self-extinguishing characteristics[35]. Numerous dolomite mines are present worldwide. The preparation of LDH/Cal from dolomite makes full use of the calcium, magnesium, and carbonate from dolomite with no greenhouse gas emission during the processing, which makes it a green process. It is expected that the LDH/Cal product should have broad market prospect and strong competitiveness.

4　Conclusions

Mg—Al—CO_3 layered double hydroxides/calcite composite powders (LDH/Cal) were successfully prepared using dolomite as magnesium, calcium and carbon dioxide source under acid dissolution and co-precipitation process. The optimized condition for preparation of LDH/Cal was the acid dissolution of 60 ℃, $OH^-/(Mg^{2+}+Al^{3+})$ mol ratio of 3.5:1.0, Mg^{2+}/Al^{3+} mol ratio of 3:1, crystallization temperature of 120 ℃, and crystallization time of 18 h. The results showed that the composite powders consist only of Mg—Al—CO_3—LDHs and Cal, and the mass percentages of the LDHs and calcite were 39.5% and

60.5%, respectively. The Cal was regular and granular with a diameter of about 0.6 to 1.8 μm. The LDHs consisted of well-defined plate-like particles with regular hexagonal shape and sizes between 100 nm and 200 nm. The preparation of LDH/Cal from dolomite makes full use of the calcium, magnesium, and carbonate from the dolomite and produces no greenhouse gas emissioh, which make it a green process.

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