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Synthesis of aragonite by carbonization from dolomite without any additives

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ABSTRACT

A simple carbonization method was developed to synthesize rod-like aragonite in $CaCl_2$-NH_4Cl solution prepared from dolomite. Scanning electron microscopy and X-ray diffraction were used to characterize the morphology and crystal structure of the aragonite produced. The influences of carbonization time and temperature and aging time on the morphology and polymorph of the precipitated $CaCO_3$ particles were investigated. The aragonite was obtained at room temperature by carbonization for 0.5 h without any additives and aging for 12 h. Aragonite rods with a length of 2.5–3 μm, a width of 0.3–0.4 μm, and an aspect ratio of 6–10 can be synthesized. The mechanism of the phase transformation from calcite to aragonite is also discussed.

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1. Introduction

Calcium carbonate ($CaCO_3$) is a chemical industrial product that is extensively used as a novel functional material in fields such as plastics, rubber, paint, printing ink, weaving, toothpaste, make-up, and foodstuffs. It has three polymorphs, calcite, aragonite, and vaterite, which have trigonal, orthorhombic, and hexagonal crystal system, respectively. The morphologies of $CaCO_3$ include chains, cubes, spheres, spindles, sheets (or plates), needles, and amorphous (Matsumoto et al., 2010; Schmidt et al., 2010). Different polymorphs of $CaCO_3$ can have different functions as additives. For example, dispersion can be increased if cubic $CaCO_3$ is added as an addition in paint; acicular or rod-like $CaCO_3$ has a reinforcing effect on rubber and plastics; and spherical $CaCO_3$ has a significant impact on the brightness and transparency of ink (Matsumoto et al., 2010). Therefore, controlling the structure and morphology of $CaCO_3$ is an important subject for research and development scientists.

Many approaches have been studied to control the phases and morphologies of $CaCO_3$ to meet the demands of practical applications (Hu and Deng, 2004; Hu et al., 2009; Konno et al., 2002; Skapin and Sondib, 2010; Wang et al., 2009). By controlling the initial concentration of $CaCl_2$-NH_4Cl solution, stirring speed, pH, type and amount of additives, and other reaction conditions, $CaCO_3$ with different polymorphs, morphologies, and grain sizes can be obtained. However, studies have mainly focused on the effects of organic additives on the crystallization of $CaCO_3$ in batch reactors by carbonization at high temperature (30–70 °C) (Galai et al., 2007; Huang et al., 2007; Nan et al., 2008; Yan et al., 2009).

In this paper, calcium is extracted simply from dolomite after preparation of magnesium oxide. Rod-like aragonite $CaCO_3$ is successfully prepared at room temperature by carbonization in the absence of any additives. The effects of carbonization time, aging time, and carbonization temperature on the aragonite crystal morphology are explored. The experimental conditions used to prepare rod-like $CaCO_3$ are discussed. In addition, the phase transition mechanism from calcite to aragonite is elucidated.

2. Experimental

2.1. Experimental procedure

The raw ore used in this work was collected from Luonan county of Shaanxi province, China. The mineral phase content of the raw ore was calculated to be 30.1% talc, 62.1% dolomite, 3.9% quartz, and 3.9% other minerals (Li et al., 2011).

The procedure used to prepare $CaCO_3$ from the raw material was as follows. The raw materials were ball-milled for 1 h until the particle size was less than 0.074 mm. The milled material was leached with 20 wt% hydrochloric acid by mechanical stirring at room temperature for 30 minutes to dissolve all of the dolomite grains. The main chemical composition of the solution was as follows (in mass): $C(CaO) = 62.43$ g/L $= 1.115$ mol/L, $C(MgO) = 55.97$ g/L $= 1.399$ mol/L. The chemical reaction that occurred mainly included

$$CaMg[CO_3]_2 + 4HCl \rightarrow CaCl_2 + MgCl_2 + 2H_2O + 2CO_2 \quad (1)$$

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After leaching and filtering, the second step was amination, which was performed by adding 18 wt% ammonium hydroxide dropwise into the solution to control the pH. Precipitation of magnesium hydroxide ($Mg(OH)_2$) occurred as the solution was mechanically stirred at room temperature. The $Mg(OH)_2$ precursor was calcined in air to produce MgO nanoballs. These results were reported in our previous paper (Li et al., 2011). The following equilibrium reactions occurred in the system:

$$MgCl_2 + 2NH_3 \cdot H_2O \rightarrow Mg(OH)_2\downarrow + 2NH_4Cl \quad (2)$$

$$Mg(OH)_2 \rightarrow MgO + H_2O \quad (3)$$

In this article, the preparation of $CaCO_3$ was studied, as shown in dashed boxes in Fig. 1. The reaction involved in the course of carbonization is given as Eq. (4).The reaction of the Gibbs free energy is −144.12 kJ/mol at 298 K. It is evident that the carbonation reaction can occur at 25 °C.

$$CaCl_2 + 2OH^- + CO_2 \rightarrow CaCO_3\downarrow + H_2O + 2Cl^- \quad (4)$$

A calcium-rich solution was obtained after filtration of the ammoniated mixture. CO_2 with a concentration of 40% was bubbled through the solution. The effects of carbonization temperature and time and aging time on the morphology of the resulting product were investigated.

2.2. Analysis methods

The chemical compositions of the prepared samples were determined by wet chemical analysis. The solid products were identified by powder X-ray diffraction (XRD), which was performed on a Rigaku D/Max-2500 diffractometer equipped with Cu Kα radiation. Diffraction data were collected over the 2θ range of 3–70 , with a step size of 0.01 . Surface morphology was investigated using a Hitachi S-4800 scanning electron microscope (SEM).

3. Results and discussion

3.1. Effect of carbonization time

CO_2 gas with a concentration of 40% was bubbled through the $CaCl_2$-NH_4Cl solution. The precipitated $CaCO_3$ was obtained after different carbonization times by filtration, and then washed three times with deionized water. A $CaCO_3$ cake was obtained by drying the precipitate at 105 °C overnight. The XRD patterns of $CaCO_3$ products prepared after different carbonization times are shown in Fig. 2.

When the carbonization time was 0.5 h, calcite (PDF05-0586) and vaterite (PDF33-0268) were obtained. However, the calcite phase transformed into aragonite (PDF41-1475) and vaterite (PDF33-0268) when the carbonization time was extended to 1–1.5 h. When the carbonization time was extended to 2 h, aragonite was the sole product.

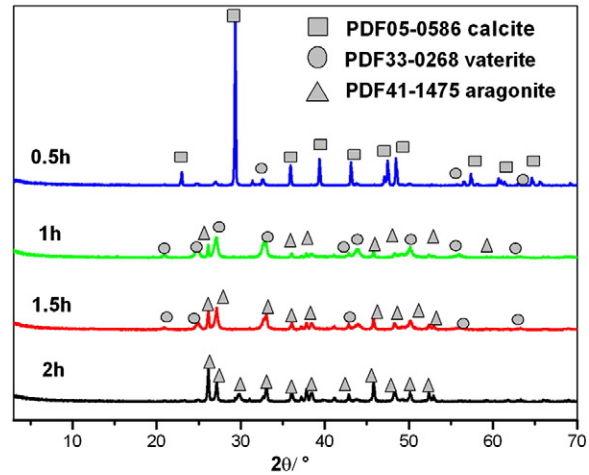

Fig. 2. XRD patterns of the $CaCO_3$ products prepared after various carbonization times.

Based on the characteristic diffraction peaks of each polymorph in the XRD spectra, the content of each polymorph was calculated. The formulas are as follows (Chen, and Xiang, 2009):

If only calcite and aragonite are present:

$$X_A = 3.157I_A^{221}/\left(I_C^{104} + 3.157I_A^{221}\right); \qquad X_C = 1 - X_A \quad (5)$$

If only vaterite and calcite are present:

$$X_V = 7.691I_V^{110}/\left(I_C^{104} + 7.691I_V^{110}\right); \qquad X_C = 1 - X_V \quad (6)$$

If calcite, aragonite, and vaterite are present:

$$X_A = 3.157I_A^{221}/\left(I_C^{104} + 3.157I_A^{221} + 7.691I_V^{110}\right); \quad X_C = I_C^{104} * X_A/3.157I_A^{221}; X_V = 1 - X_A - X_C \quad (7)$$

where X_A, X_V, and X_C, are the percentage content of aragonite, vaterite, and calcite, respectively; and I_A^{221}, I_C^{104}, and I_V^{110} represent the diffraction intensities of the aragonite (221) plane, calcite (104) plane, and vaterite (110) plane, respectively.

Fig. 3 shows the calculated contents of the three phases for different carbonization times obtained using formulas (5)–(7).

The aragonite content gradually increased, the vaterite content first increased and then decreased, and the calcite content decreased with increasing carbonization time. When the carbonization time reached 4 h, the aragonite content was 81.35%, calcite was 4.56%, and vaterite was 14.09%. Extending the carbonization time aids the formation of aragonite.

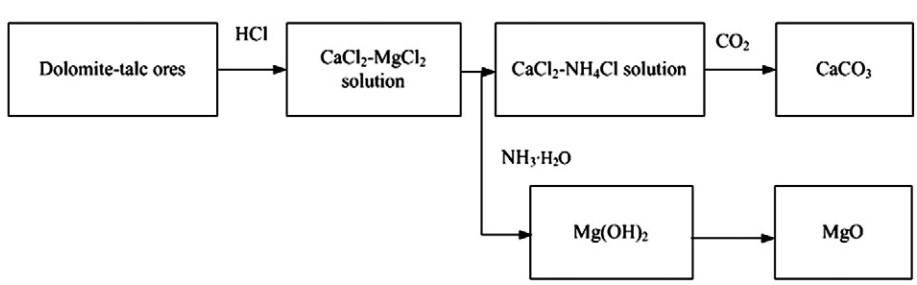

Fig. 1. Experimental procedure used to produce aragonite.

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