

Synthesis of vaterite CaCO_3 by direct precipitation using glycine and L-alanine as directing agents

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Abstract

We report room temperature synthesis of calcium carbonate (CaCO_3) vaterite phase by the reaction of calcium chloride and sodium carbonate with glycine or L-alanine as directing agents. The compound crystallize in the hexagonal symmetry, $P6_3/mmc$ with $a = 4.1304(8) \text{ \AA}$ and $c = 8.4770(2) \text{ \AA}$.

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1. Introduction

Calcium carbonate is one of the most abundant materials present in nature, and it exhibits three polymorphic modifications, namely calcite, aragonite and vaterite [1–4]. The crystal structure, size and shape are the major concerns in crystallization especially for CaCO_3 , which has recently received a great deal of attention due to its applications in the paper, paints, plastics, adhesive and rubber industries. Interest has been shown on controlling crystal properties by modifying the reaction medium using surfactants, suspensions, additives and templates [5] instead of varying the precipitation conditions such as pH, temperature and agitation. Despite this, the preparation of pure vaterite calcium carbonate under ambient condition is a challenge.

Dupont et al., reported the synthesis of monocrystalline hexagonal platelets of vaterite by using hydroxyethylidene-1,1-phosphonic acid surfactant and ultrasonic waves at 95°C [6]. Recently Wentao and Qingling [7] reported precipitation of vaterite CaCO_3 by using CO_2 diffusion method which takes 24 h. Extensive studies on phase stabilization and habit modification of CaCO_3 crystal growth under Langmuir monolayers and in presence of organic, biological and inorganic additives have been reported [8–12].

Here we describe a simple and innovative method for the synthesis of single phase vaterite at room temperature involving the use of glycine. The use of glycine ($\text{H}_2\text{NCH}_2\text{COOH}$) for the above purpose was motivated by its ability to associate with ions in solution and thus acting as a directing agent.

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2. Experimental

About 6 g of glycine (AR grade) was dissolved in 100 ml of water (pH \sim 6) to which 10 ml of 0.5 M Na₂CO₃ (pH \sim 7.5) solution was added and stirred for 30 min at constant rate followed by the addition of 10 ml of 0.5 M CaCl₂·2H₂O solution (pH \sim 6.5). The solution was stirred continuously for 1 h when slow precipitation of milky white CaCO₃ takes place. The pH of the medium during precipitation was 7.5. The product was filtered, washed and vacuum dried. White powder of vaterite calcium carbonate was obtained. CaCO₃ precipitation has been studied by varying the amount of glycine and pH of the solution (using HCl).

To understand precipitation of different carbonate polymorphs, experiments were carried out by varying the concentration of glycine and also with yet another amino acid viz., L-alanine (H₂NCH(CH₃)COOH). Preparation conditions and concentration are given in Table 1.

X-ray diffraction (XRD) of the products were carried out using Philips X'pert Pro diffractometer with Cu K α ($\lambda = 1.5418 \text{ \AA}$) with graphite monochromator to filter the K β lines. FT-IR (Perkin-Elmer FT-IR Spectroscopy Spectrum 1000) was used to confirm the characteristic vibrational bands of different CaCO₃ polymorphs. Scanning electron micrographs were recorded using Sirion FESEM.

3. Results and discussion

The indexed powder X-ray diffraction pattern of CaCO₃ (from experiment 4 of Table 1) is shown in Fig. 1(a). All the reflections could be indexed to the vaterite phase (JCPDF: 33-0268). The crystal structure was refined by Rietveld method with the space group *P6₃/mmc*. There is good agreement between observed and calculated patterns. The lattice parameters $a = b = 4.1304(8) \text{ \AA}$, $c = 8.4770(2) \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ obtained from the refinement agree well with the reported values [13–15].

The product obtained without glycine (pH 7) was pure calcite (experiment 2 of Table 1) matching with (JCPDF-47-1743) shown in Fig. 1(b). The product obtained at pH \sim 5 (experiment 3 of Table 1) was observed to be mixed phase containing both calcite and vaterite modification as can be seen from Fig. 1(c) [16].

SEM images of calcite and vaterite phases agree with rhombohedral and spherical morphologies as shown in Fig. 2(a) and (b).

All the products obtained were examined by infrared spectroscopy and FT-IR spectra are shown in Fig. 3(a)–(c). In pure calcite phase, characteristic CO₃²⁻ peak at 1417 cm⁻¹, and C–O stretching at 1084 cm⁻¹ and at 713 cm⁻¹ are present. In pure vaterite characteristic CO₃²⁻ at 1417 cm⁻¹ splits into 1478 and 1406 cm⁻¹. In vaterite characteristic C–O stretching appears at 744 cm⁻¹. The common C–O stretching at around 1084 and 713 cm⁻¹ is present in the mixed-phase [17]. In vaterite phase the peak at 1084 and 671 cm⁻¹ are more prominent compared to that in calcite where it occurs as a shoulder.

Precipitation of CaCO₃ is pH dependent and takes place in the pH range 6–8. The role of amino acid in the precipitation of vaterite phase is very important and it is confirmed by our experimental results that when concentration ratio of amino acid to calcium chloride is 2 or above precipitation of pure vaterite calcium carbonate takes place. When the concentration ratio is below 2, calcite and vaterite mixed phase are precipitated. This can be

Table 1
Experimental condition for precipitation of calcite and vaterite phase of CaCO₃ at 30 °C

Experiment	pH	Glycine (M)	L-Alanine (M)	CaCl ₂ (M)	Na ₂ CO ₃ (M)	Phase (CaCO ₃)
1	\sim 5	0.0	0.0	0.04	0.04	Mixed phase (calcite + vaterite)
2	7–7.5	0.0	0.0	0.04	0.04	Calcite
3	\sim 5	0.08	0.0	0.04	0.04	Mixed phase (calcite + vaterite)
4	6.5–7.5	0.08	0.0	0.04	0.04	Vaterite
6	6.5–7.5	0.09	0.0	0.04	0.04	Vaterite
7	6.5–7.5	0.07	0.0	0.04	0.04	Mixed phase (calcite + vaterite)
8	>7.5	0.0	0.0	0.04	0.04	No precipitate
9	<5.5	0.0	0.0	0.04	0.04	No precipitate
10	6.5–7.5	0.0	0.08	0.04	0.04	Vaterite
11	6.5–7.5	0.16	0.0	0.08	0.08	Vaterite

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