

Synthesis of Barium Carbonate Using Phthalic Acid and Isophthalic Acid as Morphology Adjust Control Agent

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ABSTRACT

BaCO₃ were synthesized using phthalic acid (PA) and isophthalic acid (IPA) as morphology adjust control agent, respectively. The BaCO₃ powders were thoroughly characterized by XRD, and FT-IR spectroscopy. The morphologies of BaCO₃ crystals were investigated by scanning electron microscope (SEM). The morphologies of BaCO₃ crystals change from rod-shaped, shuttle-shaped to wire-shaped with the increase amount of PA. While IPA was used as adjuster, the morphologies of BaCO₃ crystals change from irregular block-like, flower-like to a mixture of irregular spherical-like and block-like particles with the increase amount of IPA. The result indicates that the morphology of BaCO₃ may be adjusted by the structure of carboxylic acid.

INTRODUCTION

The development of specific microstructure morphologies and controllable morphosynthes is of inorganic materials with specific shape has attracted research interest [1, 2] because the morphology of materials, their properties and applications are closely related[3].It is still one of the challenging issues in chemistry and materials science. Barium carbonate (BaCO₃) as a common alkaline earth metal

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mineral has orthorhombic, hexagonal and cubic three usual crystal phases. Orthorhombic (with erite BaCO_3), occurring in nature and being formed during conventional precipitation synthesis, is the only stable phase of BaCO_3 at room temperature [4-7]. Barium carbonate (BaCO_3) has some important applications in industry, for example, producing other barium salts, pigment, optical glass, electric condensers and barium ferrite. It also can be used as a precursor to produce superconductor and ceramic materials. It has been shown that the performance of BaCO_3 can be affected by certain parameters such as the specific surface area, size, morphology and crystal phase [5, 8]. For example, needle-like and superfine BaCO_3 crystals are used in microelectronics industry and the filler of plastic, rubber and dope [3]. Spherical BaCO_3 crystal can be used for the production of PTC thermistor, which makes capacitors with high dielectric constant and temperature characteristics so that it can exhibit the advantages of small PTC thermistor, high-frequency, high-capacity, and so on [9], which means that different morphologies often have different properties and applications even for the same substance. Therefore, controlled morphology, size and uniform distribution of ultrafine BaCO_3 powder have attracted more and more research interest [6, 10-12]. Control of nucleation, growth, organization of crystals to a superstructure can make their physical properties tunable, which are important for technical application. Various kinds of BaCO_3 crystals with morphologies, for example, candy-like, needle-like, olivary-like [5], spherical and rod [13] have been prepared and reported. To control and obtain distinct morphologies of BaCO_3 crystal, crystal growth modifiers, template of reversed micelles, organic additives et al. have been used extensively for control growth of BaCO_3 [14, 15].

It is well known that phthalic acid (PA) and isophthalic acid (IPA) can coordinate and have a strong electrostatic interaction with Ba(II) ion. Therefore, they may control the initial growth and further assemblies of BaCO_3 particles, at micro- and Nano-scale level, into target structured materials bearing the controlled size and tailored morphology [16]. Therefore, in this work, we report a facile and direct method for hierarchical BaCO_3 in presence of appropriate amount of phthalic acid (PA) and isophthalic acid (IPA) as morphology adjust control agent, using barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and anhydrous sodium carbonate (Na_2CO_3) as the starting materials. Investigating and dealing with the influence of structure of carboxylic acid on morphology of BaCO_3 .

Preparation Experimental

First, 0 mg (0 mmol), 34.2 mg (0.205 mmol), 62.0 mg (0.369 mmol) and 0.0885 g (0.533 mmol) phthalic acid (PA) were added into four beakers, respectively. 10.0 mL deionized water was slowly poured into beakers, respectively. Then 0 mg (0 mmol), 22.0 mg (0.205 mmol), 39.0 mg (0.369 mmol), 56.8 g (0.533 mmol) anhydrous Na_2CO_3 were added into corresponding beaker with stirring to neutralizing carboxylic acid. 48.9 mg (0.2 mmol) $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ powder was added

into each beaker and was stirred until the $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was solved completely. Final, 2.0 mL of 0.1 mol / L Na_2CO_3 was dropped into each beaker. The mixture solutions were stirred for another 10 minutes. The precipitates produced were centrifuged, washed three times with deionized water and anhydrous ethanol, and then vacuum dried at 40 °C for about 48 h.

To investigate the influence of carboxylic acid structure on the formation of BaCO_3 crystals, phthalic acid (PA) was replaced by isophthalic acid (IPA). But the procedure and amount of corresponding material are the same.

Results and Discussion

The phase structures of the obtained samples were characterized by X-ray powder diffraction (XRD) as shown in Fig. 1. Sample 1 shows the X-ray diffraction patterns of BaCO_3 synthesized without PA or IPA. The XRD pattern of BaCO_3 crystals obtained are pure orthorhombic BaCO_3 crystals because all the observed peaks can be perfectly indexed to a pure orthorhombic with erite phase and no characteristic peaks from other impurities have been detected in the synthesized products. The corresponding XRD pattern of the BaCO_3 crystals obtained displays the following diffraction peaks (2θ): 19.5, 24.0, 27.01, 34.5, 39.6, 42.1, 44.8, 46.9, 55.8, and 61.1°, which can be correlated to the (hkl) indices (110), (111), (112), (220), (221), (041), (113), (241), and (242) of orthorhombic with erite (PDF card number 05-0378). This is in agreement with the FT-IR results. It may also be seen that the peak (111) is the strongest in all the BaCO_3 crystals synthesized using different adjusters and adjuster concentration, suggesting that BaCO_3 crystals are well oriented and grew mainly along the (111) face [12].

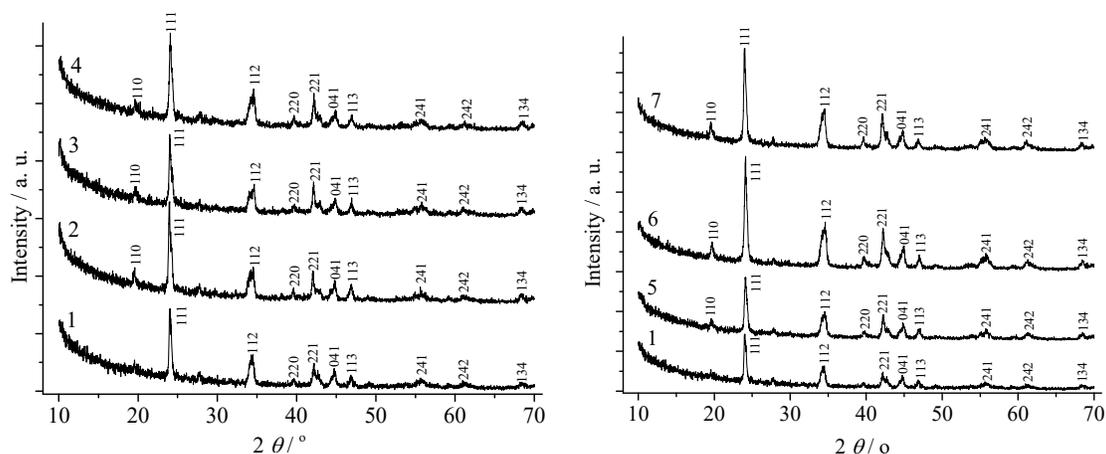


Figure 1. XRD patterns of samples without (1) and with the adding of PA (2-4) or IPA (5-7).

In order to further confirm the polymorphs of the as-prepared products in the presence of PA and IPA, the as-prepared products were characterized by FT-IR spectroscopy and the corresponding results are shown in Figure 2 respectively. The FT-IR spectra of the samples(Fig. 2)represent the characteristic absorbance of high purity BaCO₃particles. In general, isolated, planar CO₃²⁻ anion has D_{3h} symmetry. The absorption bands attributed to the vibrations in CO₃²⁻ anion are located within the1800-400 cm⁻¹region. The strong board absorption centered at about 1454 cm⁻¹is ascribed to the asymmetric stretching vibration and a strong sharp absorption band at about 856 and 693 cm⁻¹can be assigned to the bending out of plane vibrations and in plane vibrations, respectively[8]. The result is in agreement with the XRD.

The morphologies of the as-prepared sample without any adjuster and in the presence of PA and IPA were shown in Figure 3 respectively. Rod-shaped particles were produced without any additives as shown in Fig.3-1 and the average length is about 1-2 μm. When 34.2 mgPA was added to the preparation system, the shuttle-shaped particles were formed (Fig. 3-2). When the amount of PA was increased to 62.0 mg, there are thin wire-shaped and shuttle-shaped particles (shown in Fig. 3-3). Further, the amount of PA is up to 88.5 mg, the thin wire-shaped particles were formed (shown in Fig. 3-4). The differences in the morphologies become evident from their SEM micrographs when the concentration of PA rises. While in the presence of the 34.2 mg aqueous solution of IPA, the as-prepared BaCO₃ is the irregular block with average diameter of 3 μm (Fig. 3-5). In the presence of the 62.0 mg aqueous solution of IPA, the as-prepared BaCO₃ is the flower-like particle consisted of sheets (Fig. 3-6). However, when the concentration of IPA is increased to 88.5 mg, the as-prepared BaCO₃ are the mixture of irregular spherical and block particles (Fig. 3-7). According to the above description, we can conclude that the PA and IPA can regulate that morphology of BaCO₃ particle. Hence we conclude that the change in the morphology of BaCO₃ is influenced by the concentration of PA and IPA.

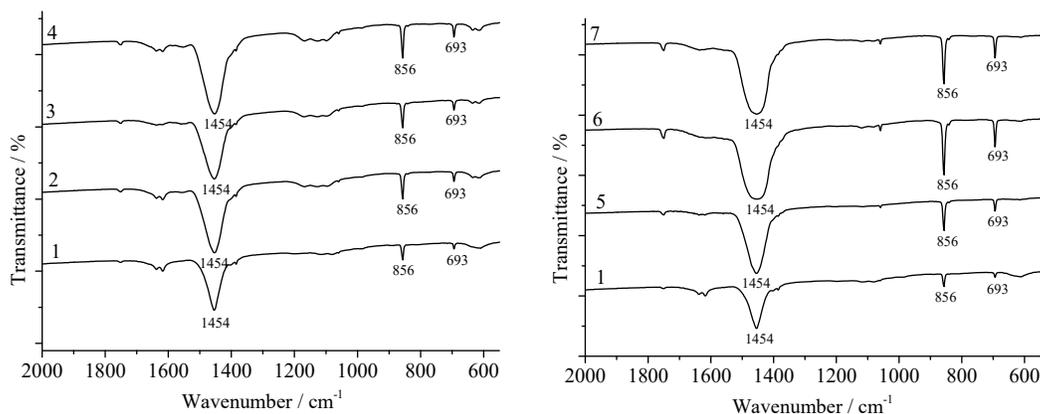


Figure 2. FT-IR of as-synthesized samples without (1) and with the adding of PA (2-4) or IPA (5-7).

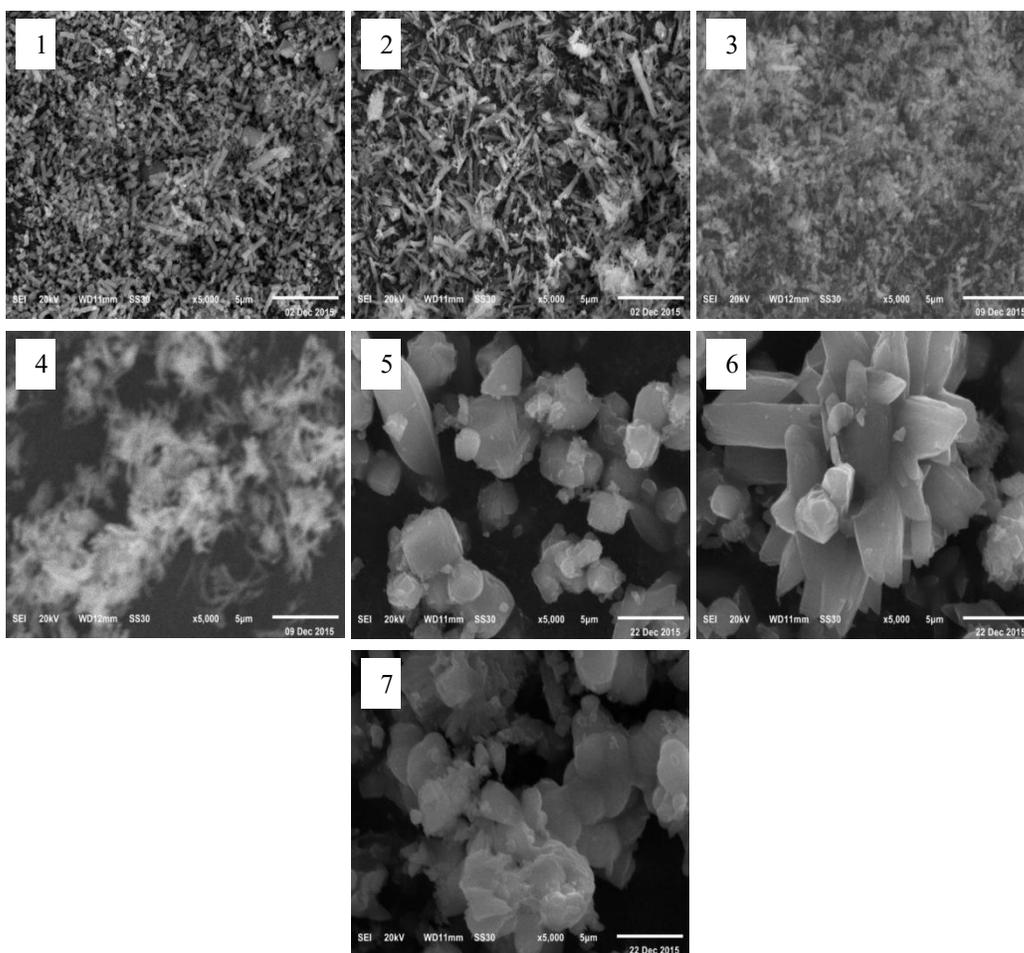


Figure 3. SEM images of samples without (1) and with the adding of PA (2-4) or IPA (5-7).

We know that the first stage of forming BaCO_3 is the nucleation process that is the initial reaction between Ba^{2+} and CO_3^{2-} ions leading to the formation of BaCO_3 nuclei. In the second stage, due to the presence of crystal growth modifying functional groups ($-\text{COO}^-$) in PA and IPA, carboxylate groups of IPA and PA act as capping agent through their coordination and static interactions with BaCO_3 particle surfaces, which can inhibit the incorporation rate of growth units onto the particle surfaces, change the surface free energies of different facets, and, thereby, change relative growth rates of the facets [17, 18], resulting in the modification of the final crystal shape [19].

In PA and IPA molecule, the distance of their two carboxylate groups is different. The distance between two carboxylate groups of IPA is larger than that of PA. Therefore, the carboxylate groups of PA can coordinate with $\text{Ba}(\text{II})$ ions with a chelating model. But the carboxylate groups of IPA cannot. They can coordinate

with Ba(II) ions with bridging model. These results suggest that IPA and PA may adsorb on different crystal faces, which give rise to different morphologies.

ACKNOWLEDGEMENTS

The authors are grateful to National Natural Science Foundation of China (41472047), Key projects of Anhui province university outstanding youth talent support program (gxyqZD2016327) for financial support of this work.

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