Controllable preparation of hollow fibrous SrCO_3

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Abstract. A simple and economic CO_2 bubbling crystallization reactor for preparation of strontium carbonate (SrCO_3) was designed. Through monitoring pH and conductivity, hollow SrCO_3 fibres without any morphology control agents were successfully obtained. The effects of temperature and CO_2 flow rate on the morphology of SrCO_3 were analysed. This study presents a new method for carbonate crystal control and growth.

Keywords. Crystal growth; powder technology; crystallization reactor; hollow fibres; strontium carbonate.

1. Introduction

Strontium carbonate (SrCO_3) is a white powder and an important inorganic chemical raw material. It is widely used in electronic information, chemical industry, light industry, ceramics, metallurgy and other more than 10 industries [1–3], which is also used for high-dielectric materials, piezoelectric materials and coating [4]. The morphology control of SrCO_3 particles has been mostly accomplished by adding crystal shape control agents [5]. So far, research on the control of particle size and morphology of SrCO_3 has become a hot topic across the world [6–10]; SrCO_3 of various morphologies, including spherical, ribbon-like, helical, dumbbell-shaped, olive-like and flower-like products, have been synthesized. In the presence of CO_2 , spherical mesoporous SrCO_3 with a diameter of 200–400 nm was obtained by refluxing the solution of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and NaOH in 1,1,3,3-tetramethylguanidium lactate at 140°C [7]. SrCO_3 crystals with a ribbon-like shape were formed within thermally evaporated sodium bis-2-ethylhexylsulphosuccinate (aerosol OT, AOT) thin films by a process of Sr^{2+} ion entrapment followed by a reaction with CO_3^{2-} ions within the lipid matrix [6]. SrCO_3 grown in silica gel exhibited a variety of complex morphologies including sheet and spiral associated with biogenetic products. The non-crystallographic architecture had a hierarchical structure containing nano-scale needle-like building blocks wrapped with a silicate sheath [8]. An olive-like or flower-like SrCO_3 was synthesized in ethylene glycol or water solvent using $\text{Sr}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{CO}_3$ by a microwave-assisted method. The result showed that the solvent played an important role in the size and morphology of SrCO_3 [9]. A flower-like SrCO_3 nanostructure assembled using nanorods with a few hundred micrometres length and

several hundred nanometres width was successfully prepared by a simple hydrothermal process [10].

All the above materials with special morphologies have been synthesized by adding various crystal shape control agents. However, these control agents are relatively expensive and the preparation processes are also complex [11]. To this end, it is of particular desire to develop more easily controllable novel methods without the addition of any crystal control agent to prepare special-shaped SrCO_3 . It is well known that the fibrous materials with a hollow structure have promising application for drug encapsulation, catalyst loading and so on [12].

In this work, an easy and simple CO_2 bubbling crystallization reactor was designed referring to the preparation of calcium carbonate [13]. A strontium hydroxide solution and carbon dioxide were used directly to synthesize hollow fibrous SrCO_3 by an economic carbonization reaction without any crystal morphology control agent. In the process, hollow fibrous SrCO_3 was obtained only by reactor partitioning and control of reaction conditions. The method is simple and green, and to our knowledge, no report about the fabrication of the hollow SrCO_3 with this strategy has been published.

2. Experimental

All chemicals were of analytical grade, and water used in all experiments was deionized water which has a conductivity of $15.13 \mu\text{S cm}^{-1}$ at 25°C. Strontium hydroxide octahydrate ($\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$) was purchased from Aladdin with a purity of 99.5%. CO_2 gas was purchased from Guangzhou Sheng Ying with a purity of 99.0%.

Figure 1. Experimental device.

The crystallization of SrCO_3 occurred in a stirred tank reactor in a thermostatic water bath as shown in figure 1. The stirred tank reactor was filled with $\text{Sr}(\text{OH})_2$ solution, accompanying by a CO_2 bubbler, a mechanical stirrer, a conductivity probe and a pH meter in solution. The CO_2 gas was bubbled into the $\text{Sr}(\text{OH})_2$ solution from the CO_2 cylinder with a flow controller. At the same time, through the data display, pH and conductivity values could be detected at any time. The whole solution was divided into two regions by setting the height of the CO_2 bubbler and the agitator blade. The neighbourhood of CO_2 bubbles was regarded as ‘crystallization region’, where the crystal nucleus of SrCO_3 grew in. The area below the agitator blade was considered as ‘stabilization region’. The crystal nuclei of SrCO_3 were removed from the crystallization region into the stabilization region before aggregation or crystal growth. At last, they continued to grow to fibres and were dissolved into hollow structures.

The typical reaction conditions were as follows. $\text{Sr}(\text{OH})_2$ solution with a mass fraction of 0.05% was prepared by adding 1.2 g $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ into 1200 ml deionized water. The height of the CO_2 bubbler was 20 mm below the liquid level and the CO_2 flow rate was set to 10 ml min^{-1} . The height of the agitator blade was 30 mm below the liquid level. When $\text{Sr}(\text{OH})_2$ was fully dissolved and the solution reached a constant temperature, the CO_2 mass flow controller was turned-on to start reaction. The conductivity and pH were measured every minute by using a Rex DDS-307A conductivity meter and a Rex PHS-25 pH meter. At a certain time interval, a 5 ml sample from the stabilization region of the lower part solution was took out and centrifuged, followed by washing with deionized water and dried at 100°C in a vacuum for 10 h to obtain the SrCO_3 sample. The morphology of SrCO_3 was observed by using a scanning electron microscope (SEM-1530) and the length distribution statistics of SrCO_3 were analysed by using a Nano measurer.

3. Result and discussion

The change curves of pH and conductivity with the reaction time in the crystallization region are shown in figure 2A. The conductivity values decreased first and then increased, and there was a minimum value at 20 min. The pH values decreased continuously and had a rapid decrease rate at 20 min. The conductivity value and pH for the $\text{Sr}(\text{OH})_2$ solution were 1635 and $12.36 \mu\text{s cm}^{-1}$ at 30°C , respectively. In the process of reaction, CO_2 had a series of reactions [equations (1–4)] with H_2O and $\text{Sr}(\text{OH})_2$ as follows:

Figure 2. (A) The changes of pH and conductivity with the reaction time and (B) XRD patterns of the prepared samples at different pH values.

Figure 3. SEM images of samples at different reaction times: (A) 10, (B) 20, (C) 30 and (D) 50 min, corresponding to four points of (1)–(4) in figure 2A.

In the solution, OH^- was consumed with the generation of H^+ and pH decreased continuously. With the continuous consumption of Sr^{2+} and CO_3^{2-} , ion concentration decreased in the solution. So, the conductivity value becomes smaller and smaller. But, there was a minimum value at 20 min, and then the conductivity value slowly increased. At this stage, the following reaction [equation (5)] occurred:

Figure 2B shows the XRD patterns of the as-prepared samples at different pH values. The main diffraction peaks at 25.17° , 25.80° , 36.53° , 44.08° , 47.69° and 49.92° correspond to the (111), (021), (130), (221), (132) and (113) crystal planes of SrCO_3 (JCPDS #05-0418), respectively. At the same time, the height of characteristic peaks increased with the decrease of pH, indicating that the crystallinity of SrCO_3 increased with the reaction time increasing. No peaks for other impurities are found in the XRD patterns, revealing the high purity of all samples. Figure 3A–D shows the SEM images of the samples at different reaction times. In summary, the crystal nucleus of SrCO_3 grew firstly into fibrous SrCO_3 , and then the fibres started to dissolve through a further reaction of carbon dioxide and water, resulting in the formation of holes inside the fibres. At a suitable pH value (7.5–6.5) and conductivity

(150–300 $\mu\text{S cm}^{-1}$), we obtained hollow fibrous SrCO_3 as shown in figure 3C. Further prolonging the reaction time, the surface of fibres was corroded seriously (figure 3D).

Figure 4 shows the TEM images of samples at different reaction stages. Figure 4A and B shows the TEM images of solid fibrous SrCO_3 with a smooth surface at the first stage. The ends of the fibrous SrCO_3 are sealed and its middle appears solid. As the reaction process goes on, the ends of the fibrous SrCO_3 are etched as shown in figure 4C; a clear hollow structure can be found at the ends of the fibrous SrCO_3 . When the pH is 6.72 and conductivity is 291 $\mu\text{S cm}^{-1}$, we obtained hollow fibrous structure SrCO_3 as shown in figure 4D. The length of the hollow structure is about 5 μm and the width is about 0.5 μm . It indicates that the hollow structure comes from the etching of initially formed solid fibrous structure.

The effect of reaction temperature on the morphologies of hollow fibrous SrCO_3 was studied. The result shows the length of hollow fibrous SrCO_3 increases from 5.5 to 19.8 μm with the increase of temperature from 30 to 70°C, while its diameter is basically unchanged at 1 μm . With the temperature increasing, the Gibbs free energy of the system decreases which increases the driving force of crystallization and the SrCO_3 crystals grow longer.

According to the reaction mechanism, CO_2 dissolves in water to produce CO_3^{2-} and HCO_3^- , and then reacts with $\text{Sr}(\text{OH})_2$ to form SrCO_3 . So, the greater the CO_2 flow rate,

Figure 4. TEM images of samples at different reaction stages: (A) solid fibrous SrCO_3 , (B) HR-TEM solid fibrous SrCO_3 , (C) etched solid fibrous in the ends and (D) hollow structure fibrous SrCO_3 .

Table 1. The reaction time and average length for different CO_2 flow rates at 30°C and stirring rate 400 rpm.

CO_2 flow rate (ml min^{-1})	Reaction time (min)	Average length (μm)
10	30	5.47
20	25	5.54
30	15	5.48
40	10	5.71

the faster the carbonation reaction takes place. The results are shown in table 1. With the increase of the CO_2 flow rate, the reaction time for the $\text{pH} = 7$ became shorter and shorter, which

is strong proof that the reaction rate is accelerated. However, the average length of hollow fibrous SrCO_3 keeps basically unchanged at $5.5 \mu\text{m}$.

With the above similar device, we have also obtained hollow rice-like calcium carbonate (CaCO_3) and hollow fibrous barium carbonate (BaCO_3) as shown in figure 5. Under the experimental conditions of pH between 7.5 and 6.5 and the conductivity of $400\text{--}800 \mu\text{s cm}^{-1}$, the hollow rice-like CaCO_3 with a length of $1 \mu\text{m}$, a diameter of $0.3\text{--}0.5 \mu\text{m}$ and a hollow size of 200 nm can be prepared, as shown in figure 5A and B. Under the experimental conditions of pH between 8.0 and 7.0 and the conductivity of $300\text{--}400 \mu\text{s cm}^{-1}$, the hollow fibrous BaCO_3 can be produced as shown in figure 5C and D. Their average length is $50 \mu\text{m}$ and hollow size is $1 \mu\text{m}$. These hollow structures of alkaline earth

Figure 5. SEM images of (A, B) hollow rice-like CaCO_3 and (C, D) hollow fibrous BaCO_3 .

metal carbonate can be prepared by directly using metal hydroxide solution and carbon dioxide without any morphological control agent on a simple and convenient continuous carbon dioxide flow reactor. Therefore, the method provided in this work is a general strategy for making other carbonates as well.

4. Conclusions

When CO_2 were bubbled into strontium hydroxide solution, the pH value decreased continuously, and the conductivity decreased firstly and then increased. The crystal nuclei of SrCO_3 grow firstly into SrCO_3 fibres, and then were dissolved with HCO_3^- . By monitoring pH and conductivity, the hollow fibrous SrCO_3 materials were produced by a simple carbonization reaction of strontium hydroxide solution and carbon dioxide without any crystal morphology control agent. XRD patterns indicated that the prepared materials were in the strontianite form of SrCO_3 . With the reaction temperature increasing, the SrCO_3 fibres grow longer. The flow rate of CO_2 basically did not change the morphology of hollow fibrous SrCO_3 , but it could shorten the reaction time. At the same time, the method provided in this work was used successfully for the preparation of hollow rice-like CaCO_3 and hollow fibrous BaCO_3 .

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