



# Carbonate-containing hydroxyapatite synthesized by the hydrothermal treatment of different calcium carbonates in a phosphate-containing solution



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## ABSTRACT

Carbonate-containing hydroxyapatite (CHA) particles were synthesized by the hydrothermal treatment of calcium carbonates in a phosphate-containing solution. Three types of calcium carbonates were synthesized: aragonite particles with rough surfaces, calcite particles with rough surfaces by heat treatment of aragonite particles with rough surfaces, and aragonite particles with smooth surfaces. The effects of the calcium carbonate crystal phase and morphology on the synthesized CHA were investigated and morphological changes in the formed CHA particles were observed. The reaction rates varied depending on the calcium carbonate crystal phase and morphology and this difference in reaction rates mainly affected the morphology of the synthesized CHA. On the other hand, the carbonate content and lattice constants of formed CHA were almost independent of the calcium carbonate crystal phase and morphology. This is because the equilibrium mainly governed the composition of the synthesized CHA. The characteristics of the starting material were highly important factors in controlling the morphology of the synthesized CHA.

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## 1. Introduction

Bone is an important organ that supports the body, protects internal organs, and stores ions. In order to repair damaged bones, artificial materials that are free from pathogen and available in unlimited amounts are required. Sintered stoichiometric hydroxyapatite (HA,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) ceramics are widely used as bone-repairing materials because they can bond to natural bone [1–4]. The sintered HA ceramics, however, show low bioresorbability and can hardly be replaced by new bone [5–7]. The ideal bone-repairing material should induce the regeneration of bone tissue and be resorbed permitting the bone formation. As such a bioresorbable bone-repairing material, carbonate-containing HA (CHA) has received attention because of its higher bioresorbability

compared to stoichiometric HA [8,9]. There are many reports about the synthesis of CHA from calcium carbonates by the reaction in the solutions containing phosphate ions [10–18]. We focused on the hydrothermal process because the morphology and composition of the formed HA can be controlled by the starting materials and synthetic conditions [19–22]. It has been reported that the properties of HA depend on the exposed crystal faces (*i.e.* the morphology of the HA crystal) [23]. The composition and morphology of the HA ceramics affect their biological behavior *in vivo* [24,25]. The mechanical properties of HA ceramics are also affected by the morphology of their constituent particles [26]. Therefore, the control of the composition and morphology is important for the synthesis of CHA. Moreover, in the case that calcium carbonate particles were used not only as the calcium sources but also as the template of the resultant CHA [12,14,17,18], the control of the CHA formation reaction is important. In the present study, we intended to investigate the effects of the types of calcium carbonates on the resultant CHA to obtain the fundamental knowledge for the CHA synthesis.

We previously synthesized CHA from calcium carbonate by hydrothermal treatment and revealed that the character of the starting material and the synthetic conditions were important factors to control the morphology and composition of the resultant

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CHA [27]. Although we previously reported that the crystal phase of the starting material, calcium carbonate, affected the morphology of the formed CHA, its formation mechanism and carbonate content were unknown. In the present study, we prepared different calcium carbonate particles with different crystal phases and morphologies. Calcite and aragonite were selected as crystal phases of the starting materials because the solubility of aragonite is higher than that of calcite [28]. It is speculated that the reactivity of starting materials governed by their crystal phases and morphologies affects the formed CHA. These calcium carbonates were hydrothermally treated in an aqueous solution containing phosphate ions, and the effects of the crystal phase and morphology of the calcium carbonates on the morphology and compositions of the formed CHA were investigated.

## 2. Materials and methods

### 2.1. Synthesis of calcium carbonate particles with different crystal phases and morphologies

Three types of calcium carbonates were synthesized: aragonite particles with rough surfaces, calcite particles with rough surfaces by heat treatment of aragonite particles with rough surfaces, and aragonite particles with smooth surfaces. The reagents, sodium carbonate, calcium nitrate tetrahydrate, calcium hydroxide, sodium hydroxide and diammonium hydrogen phosphate were obtained from Wako Pure Chemical Industries, Ltd., Japan.

Aragonite particles with rough surfaces (A\_R) were synthesized by a method detailed in a previous study [29]. A 0.10 mol dm<sup>-3</sup> sodium carbonate solution of 200 cm<sup>3</sup> was kept in a water bath at 80 °C and stirred for 30 min. Then, 20 cm<sup>3</sup> of a 1.0 mol dm<sup>-3</sup> calcium nitrate solution was preheated to 80 °C and added to the sodium carbonate solution at a rate of 5 cm<sup>3</sup> min<sup>-1</sup> by a pump. Stirring continued for 1 h after adding the calcium nitrate solution. The precipitates were collected by filtration, and washed with ethanol. The collected product was dried at 90 °C for 1 d. This sample was named A\_R.

It has been reported that aragonite transforms to calcite by a heat treatment [30]. In order to obtain calcite particles (CAL) with the same morphology as the obtained aragonite particles A\_R, the obtained A\_R sample was heated at 500 °C for 10 min. This sample was named CAL.

In order to investigate the effect of the morphology on the CHA formation by comparing A\_R sample, aragonite particles with smooth surfaces (A\_S) were also synthesized by the following method. A 1.5 mol dm<sup>-3</sup> of calcium hydroxide suspension of 50 cm<sup>3</sup> was mixed with 50 cm<sup>3</sup> of a 2.5 mol dm<sup>-3</sup> sodium hydroxide solution at 80 °C. A 0.50 mol dm<sup>-3</sup> sodium carbonate solution of 150 cm<sup>3</sup> was added at a rate of 3 cm<sup>3</sup> min<sup>-1</sup> by a pump and stirred for 3 h. The precipitates were collected by filtration, and dried at 90 °C for 1 d. This sample was named A\_S.

### 2.2. Hydrothermal synthesis of carbonate-containing HA from calcium carbonate particles

An amount of 3.3 mmol of each starting material (A\_R, CAL and A\_S) was put into a 50 cm<sup>3</sup> Teflon® vessel with 20 cm<sup>3</sup> of a 0.10 mol dm<sup>-3</sup> diammonium hydrogen phosphate solution. The vessel was tightly sealed in a stainless steel autoclave and then put in an oven at 160 °C for 24 h for the hydrothermal treatment. The final products were named CHA-A\_R, CHA-CAL, and CHA-A\_S, respectively. In order to examine the temporal changes, a number of autoclaves were used and taken out at the determined periods.

### 2.3. Characterization of materials

The crystal phases of the samples were examined by X-ray diffraction (XRD, RINT-2200VL, Rigaku Co., Japan). The internal standard method using silicon (640d, NIST, USA) was applied for determination of lattice constants. The diffraction lines between 25° and 53° were used for the determination of lattice parameters *a* and *c* using the software Jade 6 (Rigaku Co., Japan). The specific surface areas of the samples were examined by the N<sub>2</sub>-BET method using an Autosorb-iQ ASIQM0000-3 (Quantachrome Instruments, Florida, USA). The structure of the products was examined by Fourier transform infrared spectroscopy (FT-IR, FT/IR-6200, JASCO, Japan). For the FT-IR measurements, the samples were mixed with KBr and pressed into pellets before the transmittance method was applied. The morphology was observed by scanning electron microscope (SEM, SU8000, Hitachi, Japan) and transmission electron microscope (TEM, HF-2000, Hitachi, Japan). The carbonate content was calculated from the carbon content examined by CHNS/O elemental analysis (2400II, Perkin Elmer, USA).

## 3. Results and discussion

Figs. 1 and 2 show XRD patterns and SEM photographs of the starting materials, respectively. All the particles showed rod-like morphology. The crystal phase of samples A\_R and A\_S was composed mainly of aragonite with a small amount of calcite. Although the relatively large peaks of calcite were observed in the A\_S sample, the main crystal phase the A\_S sample was aragonite because the calcite provides higher intensity in XRD than aragonite. The crystal phase of the CAL sample was pure calcite. The CAL sample has almost same morphology as the A\_R sample. The A\_R sample has a slightly rougher surface whereas the A\_S sample has a relatively smooth surface. The specific surface areas measured by BET method of the CAL, A\_R and A\_S samples were almost same and about 2 m<sup>2</sup> g<sup>-1</sup>. Comparing the CAL and A\_R samples as well as A\_R and A\_S samples, the effects of crystal phase and morphology can be discussed, respectively.

The temporal changes in crystal phase and morphology were examined in order to reveal the mechanism of CHA formation from different calcium carbonates. The temporal changes in crystal phase and morphology are shown in Figs. 3 and 4, respectively. The crystal phases of the products after the reaction were only CHA and/or β-tricalcium phosphate (β-TCP, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>), and the patterns were shown in the range 2θ = 20–40° in Fig. 3. Fig. 5 shows TEM photographs of the samples after the hydrothermal treatment at 160 °C for 24 h.

Comparing the CHA-CAL and CHA-A\_R products, this difference might have appeared due to the differences in their crystal phases. From the SEM photographs of the products treated for 15 min, it can be seen that the reaction started from the surfaces of the particles for both the CAL and A\_R samples. Due to the treatment, however, the shape of the formed aggregates became different between the CAL and A\_R samples. For the product from the CAL sample, the flake-like nanoparticles were formed on the surfaces of the starting materials maintaining the original shape (rod-shape) to form agglomerates, as shown in SEM and TEM photographs. On the other hand, the original shape of the starting material was not retained for the product from the A\_R sample which formed globular agglomerates composed of flake-like nanoparticles. The morphologies depend on the crystal growth of CHA. The crystal growth conditions were changed by the differences in the crystal phase. The XRD patterns of the samples after the 6 h treatment showed that the transformation to CHA was almost completed for A\_R, unlike CAL in which calcium carbonate remained. These results indicate that the reaction rate of CAL was slower than that of A\_R.

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