Properties of fine Sr$^{2+}$-substituted hydroxyapatite synthesized using ultrasonication

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Abstract. This study investigated the properties of fine Sr$^{2+}$-substituted hydroxyapatite (SrHAp) synthesized using ultrasonication. SrHAp was synthesized by the addition of phosphoric acid to an ultrasonicated calcium hydroxide suspension containing strontium hydroxide. The X-ray diffraction peaks for SrHAp were shifted to low angle with increasing Sr/(Ca + Sr) atomic ratio. X-ray diffraction, energy dispersive X-ray spectroscopy and inductively coupled plasma spectroscopy measurements confirmed that HAp and strontium apatite (SrHAp) formed a complete solid solution. When the Sr/(Ca + Sr) atomic ratio was 0.3 or less, the (Ca + Sr)/P atomic ratio was 1.67 or less, and the specific surface area was also large. The bending strength of a SrHAp sintered body was increased and the bending strength of the SrAp sintered body became 40 MPa when the Sr/(Ca + Sr) atomic ratio was above 0.3. The ethanol conversion rate using SrAp as catalyst was 7% for 1 hour and was 40% of HAp reagent. However, selectivity of SrAp from ethanol to butanol was 70%.

1. Introduction

Apatite is represented by the general formula M$_i$(Zn)$_o$X$_2$, where the M$^{2+}$ ions are generally Ca$^{2+}$, Sr$^{2+}$, Cd$^{2+}$, or Pb$^{2+}$, ZnO$_3$ represents PO$_4$$_3^-$, or VO$_4$$_3^-$ and X is OH$, F$, or CI $[1]$. Hydroxyapatite (HAp) has a typical apatite structure and is represented by Ca$_{10}$(PO$_4$)$_6$(OH)$_2$. HAp can be used as a biomaterial substitute for teeth and bones, an ion-exchanger for repair heavy metals, a chromatographic filler for absorption of proteins and a catalyst for alcohol conversion $[2-11]$

HAp synthesis methods include dry and wet method, the microwave method and the ball-milling method $[12-18]$. We have been performing a series of studies on the synthesis of fine calcium compounds using ultrasonication. For example, calcium carbonate with specific surface area of 100 m$^2$/g was easily formed by direct ultrasonication $[19, 20]$. HAp with a specific surface area of 200 m$^2$/g or more was synthesized by reacting calcium hydroxide and phosphoric acid while irradiating with ultrasound $[21]$. Strontium-substituted hydroxyapatite (SrHAp) in which a portion of the Ca$^{2+}$ ions are replaced with Sr$^{2+}$ ions, is considered to have catalytic and ion-exchange performance similar to HAp. Furthermore, SrHAp is thought to be effective for improving the sinterability of HAp. SrHAp has been synthesized by urea hydrolysis, hydrothermal treatment, and addition of hydrogen phosphate at high temperature $[22-30]$. SrHAp has often been synthesized by addition of phosphate to nitrate containing Ca$^{2+}$ and Sr$^{2+}$ ions, and it was reported that SrHAp was produced directly, although the reaction process was unclear. Fine SrHAp particles were not obtained because it was slowly formed at high temperature.

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Onda et al. have conducted a series of studies on the conversion of alcohol using HAp, and examining the catalytic ability of apatite structure such as HAp and strontium apatite (Sr$_{(Ca+Sr)}$(PO$_4$)$_6$(OH)$_2$, SrAp) [9, 10]. It is expected that the catalytic ability could be improved by increasing the specific surface area. The purpose of the present study was to synthesize fine SrHAp and SrAp particles using ultrasonication, and investigate the relationship between the amount of Sr$^{2+}$ solid solution and the specific surface area, and the conditions for SrAp synthesis. The catalytic activity of synthesized HAp, SrHAp and SrAp was also investigated.

2. Materials and methods

2.1. Materials
Strontium hydroxide octahydrate, calcium hydroxide and phosphoric acid were used for the synthesis of SrHAp and SrAp. Strontium hydroxide octahydrate and phosphoric acid were special grade reagents obtained from Kanto Chemical, and calcium hydroxide (99.99%) was manufactured by Shiraishi Calcium Co., Ltd.

2.2. Experiment
SrHAp was synthesized by combining strontium hydroxide octahydrate and calcium hydroxide at a Sr / (Ca + Sr) atomic ratios in the range of 0.1 to 0.9 and suspending them in 60 cm$^3$ of pure water in a stainless beaker. The suspension was placed in a water tank and irradiated with ultrasound from the outside to make the suspension temperature 30 °C. This ultrasonication device (BJ-2566ST and S8580LP-5) was used at a frequency of 80 kHz with a power at 200 W, and five irradiation directions were used. 60 cm$^3$ of 0.1 mol/dm$^3$ phosphoric acid aqueous solution was then quickly added to the suspension during ultrasonication. The (Ca + Sr) / P atomic ratio was 1.67. The maximum reaction time was 10 min. The product was centrifuged at 10,000 rpm for 5 min and the precipitate was filtered using a membrane filter. The product was then kept in a vacuum dryer at 70 °C.

The synthesis of SrAp was conducted by reacting strontium hydroxide octahydrate in water and phosphoric acid aqueous solution with ultrasonication in the same way as the SrHAp synthesis. After the reaction, the resulting suspension was filtered, washed with pure water, and then dried under vacuum. SrHAp sintered body was obtained by molding SrHAp powder at 100 MPa and firing at 1000 °C for 3 h. The catalytic properties of SrHAp were studied by adding ethanol at 350 °C. The obtained sample was characterized using powder X-ray diffraction (XRD; Rigaku MultiFlex, Japan), infrared (IR) spectrometer (JASCO FT/IR-4600, Japan), field-emission electron microscopy (FE-SEM; Hitachi D-4500, Japan) and scanning transmission electron microscopy (STEM, JEOL JEM-F200). XRD was conducted at a scan rate of 8°/min, and IR absorption measurements were performed using the KBr disk method. SrHAp was dissolved using 3 mol/dm$^3$ HCl solution, and Sr$^{2+}$ and Ca$^{2+}$ in HAp particle were quantified using ICP. The catalytic activities of SrHAp and SrAp were examined for the conversion of ethanol to butanol at 350 °C.

3. Results and discussion

3.1. Synthesis of strontium-substituted hydroxyapatite
The specific surface area of HAp synthesized by the addition of phosphoric acid solution to a high-purity calcium hydroxide suspension with ultrasonication was 263 m$^2$/g. Since the radius of Ca$^{2+}$ ions is 0.099 nm and that of Sr$^{2+}$ ions is 0.112 nm, diffraction peaks of SrHAp shifted to low angle side when Sr$^{2+}$ ions incorporated in HAp structure.

Figure 1 shows XRD patterns for HAp and SrHAp synthesized at different Sr/(Ca+Sr) atomic ratio. The diffraction peaks for HAp with specific surface area of 263 m$^2$/g increased very low crystallinity. The (211) diffraction peak for HAp near 2θ = 32° shifted continuously to low angle with increasing Sr/(Ca+Sr) atomic ratio, and the crystallinity gradually increased. The diffraction peaks for SrAp without Ca$^{2+}$ ions indicated higher crystallinity than that for HAp. Figure 2 shows enlarged XRD patterns
around $\theta = 29 - 33^\circ$ to clarify the peak shift. It was confirmed that diffraction peak continuously shifted to a low angle of ca. $\theta = 1.5^\circ$ with the change in the composition from HAp to SrAP. Both HAp and SrAP crystal system are hexagonal. When the crystal system is the same and the difference in cation radius is small, a solid solution is formed. For this reason, it is assumed that HAp and SrAP form a solid solution.

The substitution ratio was calculated from the movement of the diffraction peak due to the (002) plane of HAp near $\theta = 26^\circ$ and was also obtained from EDX and ICP. Figure 3 shows the effect of the Sr/(Ca+Sr) atomic ratio on substitution ratio of Sr$^{2+}$ ion in HAp structure determined from X-ray diffraction peak, EDX and ICP measurements. The broken line shows the relationship between the Sr/(Ca+Sr) atomic ratio and the substitution ratio. If a point is on the line, it indicates that the substitution was successfully achieved according to the initial Sr/(Ca+Sr) atomic ratio. The substitution ratio of Sr$^{2+}$ ion in HAp determined from XRD was the same or slightly higher than this broken line, but was almost on the line. These results confirmed that HAp with any Sr$^{2+}$ content can be synthesized by changing the Sr/(Ca+Sr) atomic ratio. The ICP result also confirmed that substitute ratio increased with the Sr/(Ca+Sr) atomic ratio. The same results were obtained using EDX.
3.2. Properties of SrHAp and SrAp

The properties of synthesized SrHAp, such as the specific surface area, \((\text{Ca+Sr})/\text{P}\) atomic ratio, sinterability and catalyst activity, were investigated. Figure 4 shows the effect of the \(\text{Sr}/(\text{Sr}+\text{Ca})\) atomic ratio on specific surface area of SrHAp. The specific surface area of HAp was 263 m\(^2\)/g. However, the specific surface area rapidly decreased with increasing \(\text{Sr}/(\text{Ca+Sr})\) atomic ratio. The specific surface area for a \(\text{Sr}/(\text{Ca+Sr})\) atomic ratio of 0.3 was approximately 100 m\(^2\)/g, and no change was observed thereafter. XRD measurements indicated the crystallinity of SrHAp was increased by the addition of \(\text{Sr}^{2+}\) ions. The crystallinity of SrHAp gradually improved as the \(\text{Sr}^{2+}\)-substitution ratio was increased. Although the difference in the ionic radius between \(\text{Sr}^{2+}\) and \(\text{Ca}^{2+}\) ions is small, it was confirmed that SrHAp particles grow rapidly when \(\text{Sr}^{2+}\) ions were substituted into the HAp structure. The densities of HAp and SrAp were 3.16 and 4.08 g/cm\(^3\), respectively. Therefore, even when the particle size is the same, the specific surface area decreased when \(\text{Sr}^{2+}\) ions was replaced by HAp. However, due to the large decrease in specific surface area, it is considered that the particles produced with the substitution of \(\text{Sr}^{2+}\) ions became larger. The solubility of SrAp is greater than that of HAp; therefore, it was expected that SrAp with a small specific surface area would be generated. However, the specific surface area of the SrAp formed was 100 m\(^2\)/g. Such fine SrAp has never been obtained. The particle size can be determined by the following equation (1).

\[
\text{Particle size} = \frac{6}{(\text{specific surface area} \times \text{density})}
\]  

(1)

The SrAp particle size obtained from the calculation was 15 nm. Although this SrAp was ultrasonicated by the indirect method, SrAp with the same specific surface area was obtained by the direct method; therefore, the particles are smaller because the specific surface area is constant despite containing a large amount of \(\text{Sr}^{2+}\) ions.

Figure 4. Effect of the \(\text{Sr}/(\text{Ca+Sr})\) atomic ratio on specific surface area of SrHAp.

Figure 5. Effect of the \(\text{Sr}/(\text{Ca+Sr})\) atomic ratio on \((\text{Ca+Sr})/\text{P}\) atomic ratio of SrHAp.

Figure 6. Elution amount of Ca, Sr and P from SrHAp.
Figure 5 shows the effect of the Sr/(Ca+Sr) atomic ratio on the (Ca+Sr)/P atomic ratio for the products. The (Ca+Sr)/P atomic ratio for HAp was 1.52, which was smaller than the theoretical value of 1.67, i.e., the synthesized HAp was Ca defect HAp. The (Ca+Sr)/P atomic ratio increased with increasing Sr/(Ca+Sr) atomic ratio and was 1.68 when Sr/(Ca+Sr) atomic ratio was 0.4. Considering the specific surface area results, the specific surface area of the particles with defects was large, which suggested that stable particles were formed when the (Ca+Sr)/P atomic ratio approached the theoretical atomic ratio.

Figure 6 shows the result of a SrHAp powder dissolution. Ca$^{2+}$, Sr$^{2+}$ and PO$^{4-3}$ ions were measured using ICP spectroscopy. The eluate of HAp contained Sr$^{2+}$ ions, which was derived from the Ca(OH)$_2$ raw material. The amount of Ca$^{2+}$ ions in the eluate decreased linearly until a Sr/(Ca+Sr) atomic ratio of 0.7, whereas Sr$^{2+}$ and PO$^{4-3}$ ions increased linearly. The amount of each ion eluted decreased when the Sr/(Ca+Sr) atomic ratio was 0.7 or more. However, in the case of a Sr/(Ca+Sr) atomic ratio of 0.8, Sr$^{2+}$ and PO$^{4-3}$ ions were dissolved rapidly, while the Ca$^{2+}$ ions were almost insoluble. Figure 6(b) shows the change in the (Ca+Sr)/P atomic ratio at this time; the (Ca+Sr) atomic ratio was 1 when the Sr/(Ca+Sr) atomic ratio was in the range from 0.2 to 0.7.

Samples synthesized at each Sr/(Ca+Sr) atomic ratio were uniaxially pressed and then fired at 1000 °C to produce a sintered body for bending strength tests.

Figure 7 shows the effect of Sr/(Ca+Sr) atomic ratio on the bending strength of sintered bodies produced for each Sr/(Ca+Sr) atomic ratio. The bending strength of the HAp sintered body was 15 MPa. However, the bending strength decreased up until a Sr/(Ca+Sr) atomic ratio of 0.3. This was also related to the decrease in the specific surface area down to a Sr/(Ca+Sr) atomic ratio of 0.3, and the bending strength decreased as the SrHAp particle size increased. Above a Sr/(Ca+Sr) atomic ratio of 0.3, the bending strength increased linearly, and the bending strength of SrAp was 40 MPa, which was more than twice that of HAp. HAp particles containing Sr$^{2+}$ ions are considered to have improved strength due to easy sintering.

Figure 8 shows the solubility of each SrHAp sintered body in water. The amount of dissolved Ca$^{2+}$ ions was 0.09 ppm and a trace amount of Sr$^{2+}$ was detected. The existence of Sr$^{2+}$ ions depended on the raw material Ca(OH)$_2$. The amount of dissolved cations from the SrHAp sintered body was significantly reduced. By increasing the Sr/(Ca+Sr) atomic ratio of the sintered body, the amount of dissolved Ca$^{2+}$ ions was reduced, while the amount of dissolved Sr$^{2+}$ ions was slightly increased. The reason for the decrease in the amount of cations dissolved is presumed to be that structural distortion was eliminated by heating. It was also possible that heating caused grain growth, which reduced the amount of dissolution. The amount of Sr$^{2+}$ ions dissolved from the SrAp sintered body was 2.71 ppm. It was expected that SrAp shows high dissolution amount. It was expected that finer powders would
be easier to sinter, but in fact SrAp powders with larger particles were easier to sinter and the strength of the sintered body increased.

Onda et.al. investigated alcohol conversion using SrHAp or SaAp as a catalyst. The conversion from ethanol to butanol can be performed in two stages, but it can be performed in one stage using a catalyst such as HAp. Butanol has a 30% higher calorific value than ethanol, and it can be used by mixing with gasoline.

Figure 9 shows the effect of the Sr/(Ca+Sr) atomic ratio on the ethanol conversion rate over SrHAp or SrAp.

Figure 9 shows the effect of the Sr/(Ca+Sr) atomic ratio on the ethanol conversion rate over SrHAp or SrAp. The best conversion was obtained with ultrafine HAp. The total amount of ultrafine HAp was 1.3 times that of HAp reagent. Below that, the order of ethanol conversion rate was SrAp, SrHAp with a Sr/(Ca+Sr) atomic ratio 0.7, and SrHAp with a Sr/(Ca+Sr) atomic ratio of 0.5. The ethanol conversion rate over SrAp was 32% that of ultrafine HAp. When SrAp with specific surface area of 23 m²/g, ethanol conversion rate was 11.3% as reported by Onda et.al.[9]. An increase in the specific surface area of SrAp increased the ethanol conversion rate by 1.5 times. In addition, the selectivity toward butanol for HAp, SrHAp and SrAp were ca. 70%. The ethanol conversion rate could be increased by an increase in the specific surface area of HAp. Furthermore, It was thought that the reaction at a temperature lower than 350 °C will make the ethanol conversion rate of SrAp comparable to that of HAp reagent.

4. Conclusion
The aim of this study was to synthesize fine SrHAp and SrAp particles using ultrasonication and to examine their sintering and catalytic properties. XRD, EDX and ICP measurements indicated that HAp and SrAp formed a complete solid solution. Therefore, properties such as the specific were measured using SrHAp. The specific surface area of ultrafine HAp was 263 m²/g, and the specific surface area of SrHAp in the Sr/(Ca + Sr) atomic ratio range of 0.3 to 0.9 and that of SrAp was ca. 100 m²/g. The (Ca + Sr)/P atomic ratio for SrHAp in this range was 1.68, which was the same as the theoretical value. The (Ca + Sr)/P atomic ratio for SrHAp with a Sr/(Ca + Sr) atomic ratio of 0.4 – 1.0 was 1.7. Fine SrAp sinterability was better than that for HAp sintered body. The bending strength of the SrAp sintered body was 40 MPa. When the specific surface area of the HAp or SrAp catalysts was large, the ethanol conversion rate over ultrafine HAp and fine SrAp has improved.

5. References
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