SYNTHESIS OF WHISKER-LIKE HYDROXYAPATITE BY AQUEOUS AMMONIA NEUTRALIZATION USING NITROGEN CARRIER

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Abstract Whisker-like hydroxyapatite (HAp) was synthesized by an aqueous ammonia neutralization method using nitrogen carrier. Acidic-aqueous solutions containing 0.167 mol·dm⁻³ Ca(NO₃)₂ and 0.1 mol·dm⁻³ (NH₄)₂HPO₄ were heated at three different temperatures (70°C, 75°C and 80°C) for 24h and then at 95°C for 24h; during this process the solutions were neutralized with nitrogen-carrier gases saturated with various concentrations of aqueous ammonia. The flow rate of nitrogen carrier was 0.1 dm³·min⁻¹. The obtained whisker-like HAp had Ca/P ratios of 1.59 to 1.62, which were non-stoichiometric compositions. The products were whisker-like and/or tape-like and/or acicular crystals. In the above three conditions, the mean values of long-axis size distribution and aspect ratio of whisker-like HAp were 14.5µm and 14.2 at 70°C, 18.1µm and 19.3 at 75°C, and 12.9µm and 13.2 at 80°C, respectively.

INTRODUCTION

Hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂] whiskers are expected to be used for new materials such as porous biomaterial ceramics, ion-exchangers of heavy-metal ions and absorbents for separation of proteins. We already synthesized HAp fibers¹, HAp whiskers², and fluorapatite whiskers³ containing carbonate by a homogeneous precipitation method using urea. In this work, whisker-like products of HAp were

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synthesized by aqueous ammonia neutralization using nitrogen carrier, which is a new method resembling the homogeneous precipitation method but not using urea.

EXPERIMENTAL

SYNTHESIS: A 400 cm$^3$ volume of the solution (0.1 mol·dm$^{-3}$HNO$_3$) containing 0.167 mol·dm$^{-3}$ Ca(NO$_3$)$_2$ and 0.1 mol·dm$^{-3}$ (NH$_4$)$_2$HPO$_4$ (Ca/P = 1.67) was taken in a round-bottom flask with a condenser. Each solution was heated at one of three different temperatures (70°C, 75°C and 80°C) for 24h and then heated at 95°C for 24h in the silicone-oil bath. Hereinafter, the data are shown in temperature conditions, e.g., as 70°C-95°C. During this process, the solutions were very slowly neutralized with nitrogen carrier gases saturated with various concentrations of aqueous ammonia ($6.4 \times 10^{-1}$, 2.2 and 4.4 mol·dm$^{-3}$). The ammonia which was adsorbed on the nitrogen gas was introduced through a glass tube (ID: 9mm) in the reaction system by bubbling the nitrogen gas into the aqueous ammonia solution at room temperature. The flow rate of nitrogen carrier was 0.1 dm$^3$·min$^{-1}$.

MEASUREMENTS OF XRD AND IR SPECTRA: Products were studied on an X-ray powder diffractometer (Rigaku Denki RAD-II A, CuKa radiation) and an FT-IR spectrometer (JOEL JIRFX3001) using KBr.

X-RAY FLUORESCENCE SPECTROMETRY: The contents of Ca and P in the products were determined by X-ray fluorescence spectrometry (Shimazu SXF-1200).

SEM OBSERVATION: The morphology of the products was observed by a scanning electron microscope (SEM; S-430, Hitachi Ltd.). Aspect ratio in HAp was determined by the measurements of the long-axis and short-axis of 100 whiskers in a SEM photograph.

RESULTS AND DISCUSSION

EFFECT OF REACTION CONDITIONS: Figure 1 shows pH changes in solutions during the reactions, when the reactions were carried out by two methods. The dotted line shows pH changes in the solution when the homogenous method using urea was carried out$^{11}$. By this method, we could produce fiber-like hydroxyapatite containing carbonate. On the other hand, the solid line shows pH changes in this work. When the pH was changed along the dotted line, whisker-like
and/or acicular hydroxyapatite(s) were obtained.

During the reaction, products with two morphologies were formed; these separated into two layers at the initial stage in the range of pH 3.3 to 4.5: whisker-like CaHPO$_4$ at the bottom of the flask and the agglomerates of HAp aciculae in the upper solution. Between the middle stage up to pH about 7 at 70°C, and the final stage in the range of pH 7 to 5.5 at 95°C for 24h, CaHPO$_4$ was hydrolyzed to form HAp. Figure 2 (a) and (b) show for example a typical XRD pattern and an IR spectrum of the product at 70°C-95°C. The XRD pattern$^4$ and the IR spectrum$^5$ accorded with those of calcium-defect hydroxyapatite; its crystal system was hexagonal. In the conditions at 75°C for 24h and 80°C for 24h, the reactions and pH changes were similar to the above results and progressed at higher temperatures.

The yields and Ca/P ratios of HAp are shown in Table 1. The total yields were 84% to 88% and Ca/P ratios were 1.59 to 1.62. Since the above values of Ca/P ratio are lower than 1.67 of stoichiometric composition of HAp, all products are non-stoichiometric HAp. Therefore, when the Ca/P of obtained HAp is 1.60, its composition can be represented by the following formula: Ca$_{9.6}$(HPO$_4$)$_{0.4}$(PO$_4$)$_{5.6}$(OH)$_{1.6}$. 

![FIGURE 1 pH changes in solutions during the reactions.](image)

Conditions: 70°C-24h and 95°C-24h;
Concentrations of aq. NH$_3$: (1), (3) 2.2 mol·dm$^{-3}$, (2) 4.4 mol·dm$^{-3}$, (3) 6.4 mol·dm$^{-3}$

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MORPHOLOGY, LONG-AXIS SIZE DISTRIBUTION AND ASPECT RATIO: Figure 3 shows SEM photographs of products in three conditions. Figure 4 (a) and (b) show long-axis size distributions and aspect ratio distributions of obtained HAp at 75°C-95°C as typical data. In Figure 3, the morphologies of HAp were tape-like at 70°C-95°C, whisker-like at 75°C-95°C and aciculae at 80°C-95°C. The mean values of long-axis size distribution and aspect ratio are provided in Table 1.

![XRD pattern and FT-IR spectrum](image)

**Figure 2** XRD pattern (a) and FT-IR spectrum (b) of synthesized HAp(70°C-24h, 95°C-24h).

**Table 1: Yields and Ca/P ratios of HAp**

<table>
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<th>Temperature Range</th>
<th>Total Yield/%</th>
<th>Ca/P</th>
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<th>Total Yield/%</th>
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</table>

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FIGURE 3 Morphologies of synthesized HAp.

FIGURE 4 Long-axis size distributions (a) and Aspect ratio distributions (b) of synthesized HAp.
and aspect ratio of bottom products were larger than those of upper products. In the bottom products, the mean values of long-axis size and aspect ratio distributions were 14.5µm and 14.2 at 70°C-95°C, 18.1µm and 19.3 at 75°C-95°C, and 12.9µm and 13.2 at 80°C-95°C, respectively. The above results suggest that the optimum condition of whisker-like HAp synthesis is 75°C-95°C.

CONCLUSION

The results obtained were as follows: (1) All products obtained in three conditions (70°C-95°C, 75°C-95°C and 80°C-95°C) were non-stoichiometric HAp which had Ca/P ratio = 1.59-1.62. When Ca/P was 1.6, its composition was represented in this formula: Ca₉.₆(HPO₄)₀.₄·(PO₄)₅.₆(OH)₁.₆. (2) The products were whisker-like and/or tape-like crystals which were well-crystallized. The total yields of products were 84-88%. (3) The mean values of long-axis distribution and aspect ratio of whisker-like HAp were 14.5µm and 14.2 at 70°C-90°C, 18.1µm and 19.3 at 75°C-95°C, and 12.9µm and 13.2 at 80°C-90°C, respectively. Therefore, the optimum condition among the three conditions was at 75°C for 24h and then 95°C for 24h.

REFERENCES

4) JCPDS card No.24-33.