REACTIVITY OF MECHANOCHEMICALLY-TREATED
β-TRICALCIUM BIS (ORTHOPTHOSPHATE)

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Abstract. β-tricalcium bis (orthophosphate) [Ca₃(PO₄)₂] (β-TCP) was mechano-
chemically treated with mortar grinder. The ground β-TCP was hydrolyzed in
organic-aqueous binary systems (octane-H₂O, and octanol-H₂O) to give
Ca-deficient hydroxyapatite (HAp) involving small amount of CO₃²⁻ ions. The
rate of the hydrolysis in octane-H₂O binary system was faster than that in
ammonium aqueous solution, however, shape of the products in the binary
system did not so much differ from that in the aqueous system. Fluorination of
the ground β-TCP proceeded much faster than that of β-TCP to form fluoridated
hydroxyapatite (FHAp).

INTRODUCTION

We reported shape-controlled synthesis of hydroxyapatite (HAp) by hydrolysis
of α-TCP in hydrophobic organic solvent-aqueous binary system¹. In the binary
system, hydrophobic nature of the organic solvent affected the crystal growth to
afford well-crystalline HAp. For example, in octanol-H₂O binary system well-
crystalline long needles were formed by hydrolysis of α-TCP with similar reaction
rate to hydrolysis in ammonium aqueous solution.

Recently, it was found that β-TCP mechanochemically treated by ball-milling,
which was transformed into amorphous calcium phosphate, may be subject to
hydrolysis². We found that β-TCP ground with mortar grinder, which remained the
parent structure, was also subject to hydrolysis³. The shape of the hydrolysis
products depended on the grinding time of β-TCP. Especially, well-crystalline
Ca-deficient HAp was obtained from β-TCP ground for 7 hours.

We report herein hydrolysis of β-TCP ground with mortar grinder in the
organic-aqueous binary systems and fluorination of the ground β-TCP in aqueous
solution.

EXPERIMENTAL PROCEDURE

β-TCP (Taihei Chemical Industrial Co. Ltd.)⁴ was ground for 7, 24, and 72
hours by mortar grinder (Nitto Kagaku ANM-1000)³.

Hydrolysis in an organic-aqueous binary system; The ground β-TCP (2.0 mmol)
was hydrolyzed, with stirring, for 3 hours up to 48 hours at 90 °C in organic solvent
(25 cm³) and 0.1 M ammonium aqueous solution (20 cm³). The organic solvents used
were 1-octanol and n-octane (Wako Pure Chemical Ind.). The initial pH was about 11.0 in all cases.

Fluorination of the ground β-TCP: The ground β-TCP (2.0 mmol) was reacted with ammonium fluoride aqueous solution (0.35 mmol of NH₄F in 20 cm³ of water) under stirring for 3 hours up to 24 hours at 70 °C. The reaction products were collected by filtration, washed with distilled water, and air-dried at 50 °C for 5 hours.

The products obtained in this procedure were studied by an X-ray diffractometry (XRD; Rigaku Geigerflex RAD- I A) using a graphite monochromater (CuKα, λ= 0.15405 nm), a differential thermal analysis-thermogravimetric analysis (DTA-TG; Shimadu DTG-60), and a Fourier transform infrared spectrometry (FT-IR; Bruker IFS-112V). Infrared absorption spectra were measured in KBr pellets. The conversion ratio of β-TCP to apatite was estimated from the intensity ratio of the (217) and (211) XRD peaks due to β-TCP and HAp, respectively. Crystallinity (β₁/₂⁻¹) of apatite was estimated based on the reciprocal of the half-value width of (002) and (300) XRD peaks due to HAp. The morphology of the β-TCP and hydrolysis products (coated with Pt) were investigated by scanning electron microscopy (SEM; Hitachi S-4700).

**RESULTS**

Hydrolysis of the ground β-TCP in organic-aqueous binary system

The ground β-TCP was easily hydrolyzed in organic-aqueous binary system to form Ca-deficient HAp involving small amount of CO₃²⁻ ions, which was similar product to the hydrolysis product in H₂O system 3). The formation of Ca-deficient HAp was confirmed by measurements of XRD and FT-IR.

Fig. 1 shows the relationship between reaction time and the conversion ratio of the ground β-TCP to Ca-deficient HAp by hydrolysis in H₂O system and octane-H₂O system. With increasing the grinding time, the ground β-TCP was easily hydrolyzed in both systems. The hydrolysis in octane-H₂O system was much faster than that in H₂O system; β-TCP ground for 72 hours was completely converted to Ca-deficient HAp after 7 hours in octane-H₂O system, whereas in H₂O system 16 hours was required for the completed conversion. The rate in octanol-H₂O system was almost the same as that for H₂O system.

In octane-H₂O system, crystallinity of hydrolysis products, from β-TCP ground for certain time, did not differ from those in another system. In each system, the crystallinity (β₁/₂⁻¹) of the products decreased with increasing the grinding time (Table 1).

Fig. 2 shows SEM photographs of the hydrolysis products from β-TCP ground for 7 hours and 74 hours in octanol-H₂O system, and octane-H₂O system. In all systems; H₂O, octanol-H₂O, and octane-H₂O system, there was not substantial difference among the SEM photographs of the hydrolysis products from β-TCP ground for the same time. The product from β-TCP ground for 7 hours in each system was needle-like crystals. In contrast, the product from β-TCP ground for 72 hours was micro-crystals.
Fig. 1  Relation between reaction time and the conversion ratio of the ground β-TCP to apatite at 90°C in water system and octane-aqueous binary system. Grinding time of β-TCP: ■; 7 hours, ▲; 24 hours, ●; 72 hours.

Fig. 2  SEM photographs of hydrolysis products from the products obtained by grinding of β-TCP for (a) 7 hours and (b) 72 hours in octanol-water system, and for (c) 7 hours and (d) 72 hours in octane-water system.
Table 1  Crystallinity and particle size of hydrolysis products from the ground β-TCP in organic solvent-water systems at 90°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity (θ_{101}^{-1})</th>
<th>Particle size μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>water-system</td>
<td></td>
<td></td>
</tr>
<tr>
<td>grinding time; 7 hours</td>
<td>1.00</td>
<td>5</td>
</tr>
<tr>
<td>grinding time; 72 hours</td>
<td>0.86</td>
<td>0.5</td>
</tr>
<tr>
<td>octanol-water system</td>
<td></td>
<td></td>
</tr>
<tr>
<td>grinding time; 7 hours</td>
<td>1.14</td>
<td>5</td>
</tr>
<tr>
<td>grinding time; 72 hours</td>
<td>0.83</td>
<td>0.5</td>
</tr>
<tr>
<td>octane-water system</td>
<td></td>
<td></td>
</tr>
<tr>
<td>grinding time; 7 hours</td>
<td>1.03</td>
<td>5</td>
</tr>
<tr>
<td>grinding time; 72 hours</td>
<td>0.87</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 2  Crystallinity and particle size of fluoridated apatite from the ground β-TCP at 70°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity (θ_{101}^{-1})</th>
<th>Particle size μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>grinding time; 0 hours</td>
<td>1.25</td>
<td>2 ~ 5</td>
</tr>
<tr>
<td>grinding time; 7 hours</td>
<td>1.25</td>
<td>1</td>
</tr>
<tr>
<td>grinding time; 72 hours</td>
<td>0.98</td>
<td>0.5 ~ 0.8</td>
</tr>
</tbody>
</table>

Fig. 3  Relation between reaction time and the conversion ratio of the ground β-TCP or β-TCP to FHAp at 70 °C.
- ○; β-TCP ground for 72 hours,
- ■; β-TCP ground for 7 hours,
- ○; β-TCP

Fig. 4  SEM photographs of fluorination products from the products obtained by grinding of β-TCP for (a) 7 hours and (b) 72 hours with mortar grinder.
Fluorination of the ground β-TCP

By the fluorination, Ca-deficient fluoridated hydroxyapatite (FHAp) involving small amount of CO$_3^{2-}$ ions was formed, which was confirmed by measurements of XRD and FT-IR. As shown in Fig. 3, fluorination of the ground β-TCP proceeded much faster than that of β-TCP$^5$. The reaction rate of β-TCP ground for 7 hours did not differ from that of the β-TCP ground for 72 hours. The crystallinity ($\beta_{1/2}$) of obtained Ca-deficient FHAp decreased with increasing the grinding time (Table 2). As shown in Fig. 4, shape of the FHAp after grinding for 7 hours did not differ from that after 72 hours so much, compared with those of the hydrolysis products mentioned above.

DISCUSSION

In hydrolysis of TCP dissolution-precipitation process is involved as depicted in Scheme 1.

![Scheme 1](image)

In the organic-aqueous binary system, shape-controlled hydrolysis of HAp from α-TCP was achieved$^1$. Hydrophobic nature of the organic solvent may affect the dissolved cluster growth and gives long needles. In the present case of hydrolysis of the ground β-TCP, hydrophobicity did not affect the shape of the product. The resulting calcium phosphate cluster from the ground β-TCP differ from the cluster from α-TCP and may not be interacted with the organic solvents. On the other hand, shape of the hydrolysis product from the ground β-TCP depended on the grinding time. By the grinding, H$_2$O was incorporated into β-TCP, which may cause the lattice defect and/or distortion$^3$. Depending on the degree of the lattice defect and/or distortion, the structure of a dissolved cluster may be different among those from the ground β-TCPs. Accordingly, the shape and the crystallinity of the hydrolysis product from β-TCP ground for 7 hours differ from that for 72 hours.

The enhancement of rate of the hydrolysis in octane-H$_2$O system might be derived from prevention of crystal deposition of HAp on β-TCP with octane.

In the fluorination of β-TCP itself, β-TCP was predominantly attacked by F$^-$ ions to form FHAp$^5$. In fluorination of the ground β-TCP, F$^-$ ions and OH$^-$ ions attack the ground β-TCP to yield the dissolved cluster, which does not change the cluster structure so much and precipitate FHAp. By the grinding of β-TCP, the dissolution process proceeded much faster than that without the treatment.

Compared with β-TCP the enhancement of fluorination rate of the ground β-TCP should have been observed with increase of the grinding time. However, under the present condition the fluorination of the ground β-TCP proceeded so fast that substantial difference of the rate could not be observed.
CONCLUSION

β-TCP Mechanochemically-treated with mortar grinder was hydrolyzed to give Ca-deficient HAp involving small amount of CO$_3^{2-}$ ions. Enhancement of the reaction rate was found in octane-aqueous binary system, however, distinct shape-controlled syntheses with organic solvents were not recognized. In fluorination of the ground β-TCP, enhancement of the reaction rate was found.

REFERENCES