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Characteristic reaction processes in the system brushite–NaOH solution

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Abstract

The reaction of brushite ($CaHPO_4{\cdot}2H_2O$, DCPD) with NaOH solutions ranging in concentration from 0 to 40 mass% were investigated at 25 °C. At low NaOH concentrations below 20 mass%, hydroxyapatite (HAp) formed directly through the reaction (1) DCPD → HAp. At middle concentrations of 20–27 mass%, DCPD changed once into $Ca(OH)_2$ and then into HAp, i.e., through the consecutive reaction (2) DCPD → $Ca(OH)_2$ → HAp. At high concentrations above 27 mass%, the consecutive reaction (3) DCPD → HAp → $Ca(OH)_2$ was concluded. The boundary concentrations, i.e., singular points, between the first/second and the second/third reactions were estimated to be ca. 20 and 27 mass%, respectively. HAp particles obtained were platelet aggregates of very fine HAp microcrystals. The platelet form was compatible to the original platelet DCPD form. HAp samples prepared in this reaction system were structurally low crystalline and compositionally stoichiometric, and had a feature of large heating weight losses below 400 °C.

Keywords: Apatite; Brushite

1. Introduction

Since hydroxyapatite (stoichiometrically $Ca_{10}(PO_4)_6(OH)_2$, HAp) had been clarified to be an excellent candidate for the restoration of bone and tooth defects, numerous studies on chemical reactions and preparations of HAp have been done[1–6] and sometimes reviewed.[7] Recently, the authors have elucidated that tricalcium phosphate ($Ca_3(PO_4)_2$), which has been thought to be stable in high pH solutions,[8] transforms easily into hydroxyapatite (stoichiometrically $Ca_{10}(PO_4)_6(OH)_2$, HAp) or $Ca(OH)_2$ in concentrated NaOH solutions.[9,10] And a solubility singular point between HAp and $Ca(OH)_2$ as a function of NaOH concentration was determined to be 32 mass% at 90 °C. In the present paper, we have investigated reaction details of calcium hydrogenphosphate dehydrate (mineral name: brushite, $CaHPO_4{\cdot}2H_2O$, DCPD) in NaOH solutions, compared with the case of $Ca_3(PO_4)_2$. The reaction modes forming HAp and $Ca(OH)_2$ could be stoichiometrically given as follows.

$$CaHPO_4{\cdot}2H_2O + 1.2NaOH + 1.8H_2O \rightarrow 0.1HAp + 0.4Na_3PO_4{\cdot}12H_2O \quad (1)$$

$$\begin{aligned} &CaHPO_4{\cdot}2H_2O + 3.0NaOH + 1.8H_2O \\ &\rightarrow Ca(OH)_2 + Na_3PO_4{\cdot}12H_2O + 7.2H_2O \\ &\rightarrow 0.1HAp + 0.4Na_3PO_4{\cdot}12H_2O + 1.8NaOH \end{aligned} \quad (2)$$

$$\begin{aligned} &CaHPO_4{\cdot}2H_2O + 3.0NaOH + 1.8H_2O \\ &\rightarrow 0.1HAp + 0.4Na_3PO_4{\cdot}12H_2O + 1.8NaOH \\ &\rightarrow Ca(OH)_2 + Na_3PO_4{\cdot}12H_2O + 7.2H_2O \end{aligned} \quad (3)$$

$$CaHPO_4{\cdot}2H_2O + 3.0NaOH + 9.0H_2O \rightarrow Ca(OH)_2 + Na_3PO_4{\cdot}12H_2O \quad (4)$$

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2. Experimental

Batch style reaction runs were carried out by dispersing DCPD powder of 2.5 g (0.0145 mol) in 0–40 mass% NaOH solutions using a sealed Teflon vessel, and then keeping at 25 °C with continuous stirring for appropriate reaction times. The NaOH solutions were prepared by dissolving 0–0.5 mol of reagent NaOH in 50–30 ml of distilled water. Reaction products were analyzed by XRD in a sample state of wet filter cakes before water-washing. Reaction products after brief water-washing, acetone-washing and drying were characterized by TG-DTA, SEM, and FT-IR. The reaction was followed by the relative XRD intensity (R_x) of reaction products according to the following equation,

$$R_x = \frac{I_x}{I_{\mathrm{HAp}} + I_{\mathrm{DCPD}} + I_{\mathrm{Ca(OH)_2}}} \tag{5}$$

where x means $Ca_3(PO_4)_2$ or $Ca(OH)_2$ or HAp, and I_x diffraction intensity at 2θ (Cu Kα radiation) = 11.6° for DCPD, 18.0° for $Ca(OH)_2$, and 31.8° for HAp. Another style of reaction runs, i.e., flow style, was conducted by passing a 50 ml NaOH solution kept 25 °C through a DCPD powder bed of 2.5 g put on a glass filter with a diameter of 30 mm. In the flow style, passing time of the reactant solution through the bed was ca. 10 s.

3. Results and discussion

3.1. Reaction details

When DCPD was supplied to a 30 mass% NaOH solution at 40–100 °C, DCPD disappeared within 5 min, and HAp or a mixture of HAp and $Ca(OH)_2$ was formed instead. As the reactions were too fast to examine the initial events, reaction temperature was lowered to 25 °C. Table 1 shows reaction products at various NaOH concentrations and reaction times, where reaction time of 10 s was a passing time through the DCPD bed in the flow style runs, and the existence of water-soluble $Na_3PO_4{\cdot}12H_2O$ in products was considered to be due to the brief water-washing operation. The reaction of DCPD with concentrated NaOH solutions was extremely fast. Figs. 1–3 show XRD patterns of products obtained in the

Table 1
Reaction products in the system DCPD–NaOH–H_2O at 25 °C

Reaction time	NaOH solution (mass%)	Products by XRD
10 s	10	DCPD
	20	DCPD ≫ HAp
	30	HAp, $Na_3PO_4{\cdot}12H_2O$
	40	HAp, $Ca(OH)_2$, $Na_3PO_4{\cdot}12H_2O$, Na_3PO_4
15 min	10	DCPD > HAp
	20	HAp
	30	$Ca(OH)_2$ > HAp
	40	$Ca(OH)_2$ ≫ HAp
2 h	10	HAp
	20	HAp ≫ $Na_3PO_4{\cdot}12H_2O$
	30	$Ca(OH)_2$ ≫ HAp, $Na_3PO_4{\cdot}12H_2O$, Na_3PO_4
	40	$Ca(OH)_2$, Na_3PO_4, U[a]

[a] Unidentified phase.

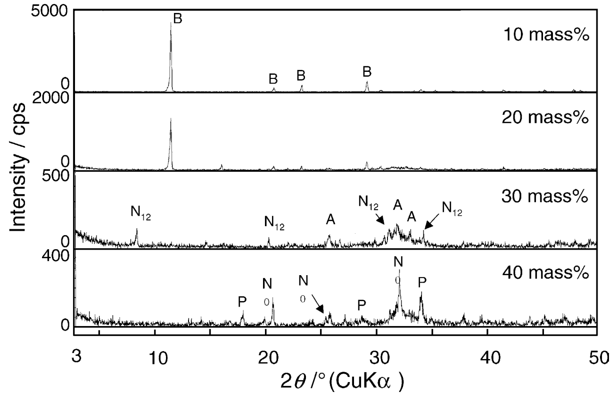


Fig. 1. XRD patterns of products at various NaOH concentrations at 25 °C after 10 s. B: $CaHPO_4{\cdot}2H_2O$, A: HAp, P: $Ca(OH)_2$, N_{12}: $Na_3PO_4{\cdot}12H_2O$ and N_0: Na_3PO_4.

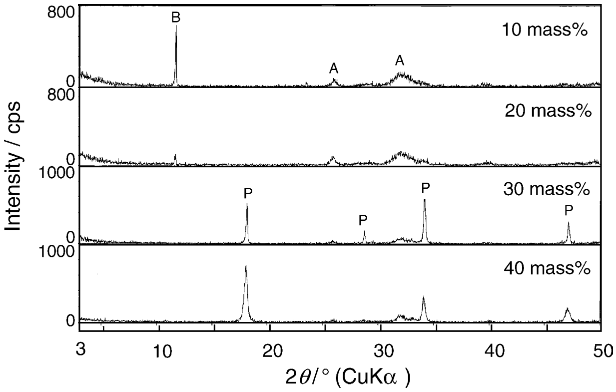


Fig. 2. XRD patterns of products at various NaOH concentrations at 25 °C after 15 min. B: $CaHPO_4{\cdot}2H_2O$, A: HAp and P: $Ca(OH)_2$.

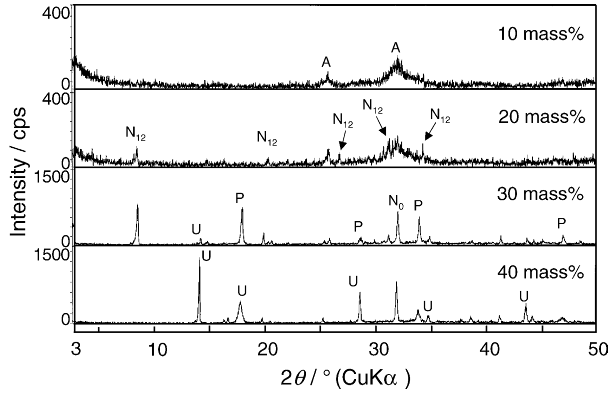


Fig. 3. XRD patterns of products at various NaOH concentrations at 25 °C after 2 h. A: HAp, P: $Ca(OH)_2$, N_{12}: $Na_3PO_4{\cdot}12H_2O$, N_0: Na_3PO_4 and U: unidentified.

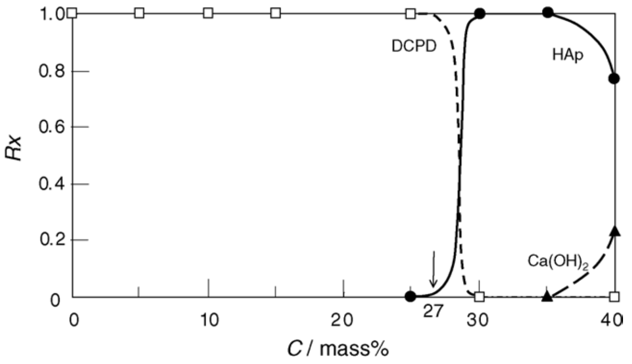


Fig. 4. Changes in R_x with NaOH concentration (C) at 25 °C after 10 s.

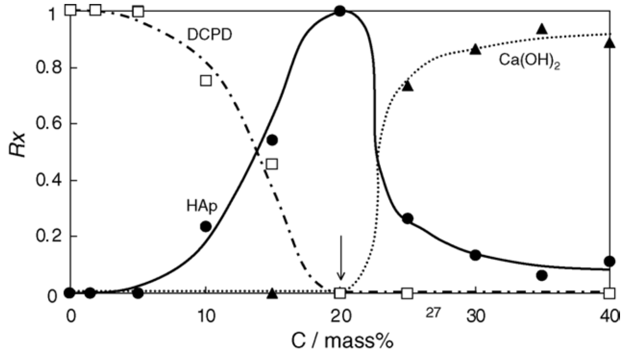


Fig. 5. Changes in R_x with NaOH concentration (C) at 25 °C after 15 min.

flow style (10 s) and batch style (15 min and 2 h), respectively. From the changes in relative amount of constituents in products with reaction time, simple reaction (1) below 20 mass% and consecutive reaction (3) above 30 mass% were seen. Although the resulting HAp products were low crystallinity similar to that of so-called calcium deficient HAp, no thermal destruction of the apatite structure as described in Section 3.3 suggested that the HAp in the products had the stoichiometric composition.

Next, further runs were conducted in order to investigate reaction modes depending on NaOH concentration.

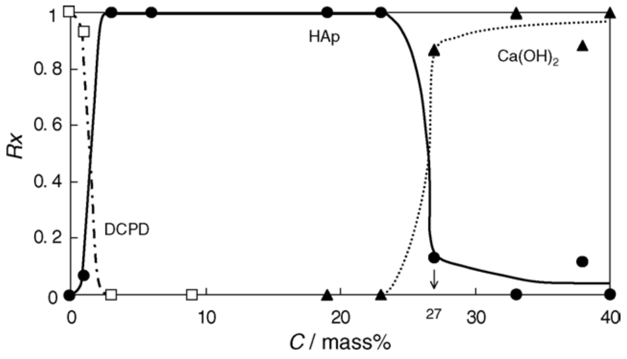


Fig. 6. Changes in R_x with NaOH concentration (C) at 25 °C after 2 h.

Table 2
Reaction modes in the system DCPD–NaOH–H_2O at 25 °C

NaOH solution (mass%)	Reaction mode	Remarks
0	DCPD	
0.8–20	DCPD → HAp	Reaction (1)
20–27	DCPD → $Ca(OH)_2$ → HAp	Reaction (2)
27–40	DCPD → HAp → $Ca(OH)_2$	Reaction (3)

Figs. 4–6 shows changes in R_x with NaOH concentration. Increasing or decreasing tendencies in amount of each product with reaction time suggested that ca. 20 mass% was a boundary concentration between simple reaction (1) and consecutive reaction (2), and ca. 27 mass% was another boundary between reactions (2) and (3). Consequently, the reaction modes depending on NaOH concentration were summarized as shown in Table 2. 20 mass% is a singular point, at which solubilities of corresponding two DCPD and $Ca(OH)_2$ phases become equal, and 27 mass% is another singular point between $Ca(OH)_2$ and HAp phases.

3.2. *Schematic solubility diagram for DCPD, HAp and Ca(OH)$_2$*

Reaction modes in Table 2 are illustrated as Fig. 7 using schematic drawings of solubilities of DCPD, HAp and $Ca(OH)_2$. The two singular points of ca. 20 mass% for DCPD/$Ca(OH)_2$ and ca. 27 mass% for HAp/$Ca(OH)_2$ determined at 25 °C were in comparable to 23 mass% for β-$Ca_3(PO_4)_2$/$Ca(OH)_2$ and 32 mass% for HAp/$Ca(OH)_2$ determined at 90 °C.[10] In other words, singular points and solubility relationships among these calcium phosphates and $Ca(OH)_2$ in NaOH solution were comparable to be little affected by the kind of calcium phosphates and also reaction temperature.

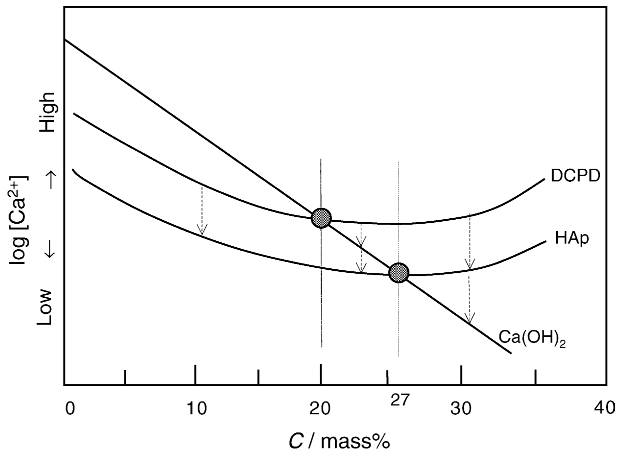
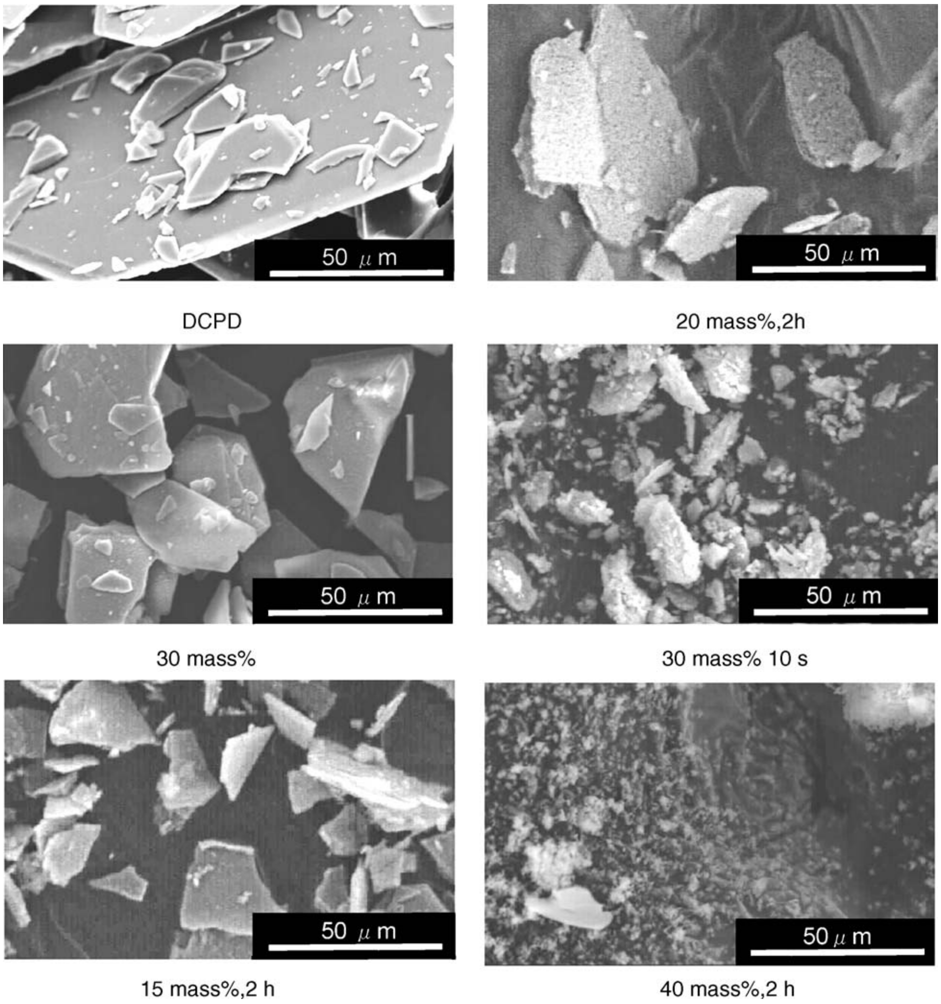


Fig. 7. Schematic solubility isotherms for DCPD, $Ca(OH)_2$ and HAp as a function of NaOH concentration (C).



DCPD 20 mass%,2h

30 mass% 30 mass% 10 s

15 mass%,2 h 40 mass%,2 h

Fig. 8. SEM photographs of starting DCPD and HAp products after water-washing.

3.3. Characteristics

Fig. 8 shows SEM images of DCPD and HAp products. HAp particles formed below 20 mass% are considered to be platelet aggregates of very fine HAp crystals, since the products were identified to be low crystalline HAp by XRD. The platelet form seems to take over the original DCPD platelet form. While, above 30 mass% DCPD platelets are assumed to converted into HAp with rupture due to, probably, an increase in reaction rate.

Fig. 9 shows TG curves of HAp products after thoroughly water washing. The loss between 400 and 600 °C is characteristic of the decomposition of $Ca(OH)_2$. The loss at 700–850 °C is characteristic of calcium-deficient HAp,[8] however the product after heating 1000 °C was only HAp. Therefore, the loss at 700–850 °C was imagined to be due to the decomposition of a trace $CaCO_3$ which formed possibly from $Ca(OH)_2$ exposed to air. In other words, thus obtained HAp products were low crystalline as shown in Figs. 1–3, compositionally stoichiometric, and had a feature of large heating losses below 400 °C.

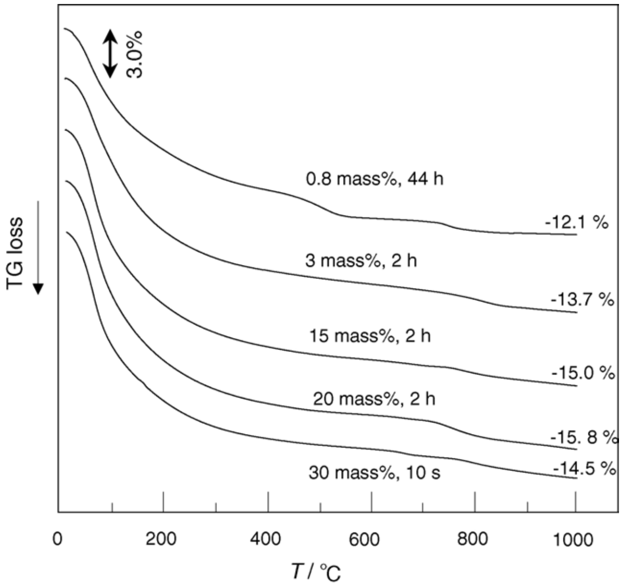


Fig. 9. TG curves of HAp products after water-washing (20 °C/min, in quiescent air).

4. Conclusions

The reaction modes of brushite ($CaHPO_4 \cdot 2H_2O$, DCPD) with NaOH solutions at 25 °C were as follows; (1) DCPD → HAp below 20 mass%, (2) DCPD → $Ca(OH)_2$ → HAp at 20–27 mass% and (3) DCPD → HAp → $Ca(OH)_2$ above 27 mass%. The boundary concentration, i.e., singular point, between the DCPD/$Ca(OH)_2$ was estimated to be ca. 20 mass%, and $Ca(OH)_2$/HAp was ca. 27 mass%. HAp particles obtained were platelet aggregates of very fine HAp microcrystals. The platelet form was compatible to the original platelet DCPD form. HAp products prepared in this reaction system were structurally low crystalline and compositionally stoichiometric, and had a feature of large heating weight losses below 400 °C.

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