



Homogenous hydrothermal synthesis of calcium phosphate with calcium carbonate and corbicula shells



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ABSTRACT

In this work, we prepared calcium phosphate by a general homogenous hydrothermal process, either from commercial calcium carbonate and phosphoric acid, or from corbicula shells and phosphoric acid. The chemical composition and properties of the resulting products were also investigated. Commercial calcium carbonate and corbicula shells reacted with phosphoric acid to produce calcium hydrogen phosphate and hydroxyapatite via a homogeneous hydrothermal process. The chemical composition of the products was influenced by both processing temperature as well as time. The compositions themselves influenced the substitution of calcium with iron and the absorption of trimethylamine gas.

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1. Introduction

Interest in new means to effectively recycle and reduce waste has increased in recent years. With this goal in mind, researchers have previously attempted to use seashells as raw materials for various industrial materials [1,2]. Generally, the edible portion of shellfish is small, leaving a large amount of waste after processing the animal. Seashells are also easy to gather, a favorable trait of any raw material. At present, relatively light-toned seashells with little pigmentation (such as scallops) are used as a calcium source [3,4]. However, darker seashells with higher pigmentation (such as Corbicula, a common food clam in Japan about 3 cm in size) are more difficult to use in this manner.

Calcium phosphate is an important substance used for many applications, such as in ion exchangers and adsorbents [5,6]. Calcium phosphates have been previously prepared from sea urchin shells and artificial phosphorus waste fluids, where the main component of the obtained precipitate was $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ [7,8]. These precipitates contained organic coloring materials when sea urchin shells were pre-treated through heating at low temperatures. While the coloring in sea urchin shells is very strong, calcium phosphate produced with corbicula shells feature less coloring.

Therefore, we prepared calcium phosphate from corbicula shells and phosphoric acid in order to avoid issues related to pigmentation [9].

The addition of urea to a solution and subsequent heating increases its pH value, as urea decomposes to ammonia and carbon dioxide upon heating which then dissolve into the solution [10,11]. As a result, any precipitates are expected to form in a homogenous manner. In this work, this homogenous process was used to synthesize calcium phosphate using a hydrothermal method [12,13]. Calcium carbonate and corbicula shells were treated using this homogeneous hydrothermal process with phosphoric acid, and the obtained materials were examined in terms of chemical composition, iron substitution behavior, and trimethylamine adsorption.

2. Experimental

Commercial calcium carbonate powder (2 g) was mixed with urea (0, 0.6, 1.2, and 2.4 g) and phosphoric acid (25 mL; 0.1, 0.4, or 0.8 mol/L), and then placed in an airtight container with an inner tube (98 mL) composed of Teflon and an outer part composed of stainless steel. Mixtures were heated at 120, 140, 160 or 180 °C for 1, 3, or 6 h (homogeneous hydrothermal treatment), and the resulting precipitates were filtered and dried. Corbicula shells were washed and milled to form a powder and subjected to the same process for comparison with commercial calcium carbonate.

The chemical composition and condition of the powdered precipitates were determined using X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. The XRD patterns

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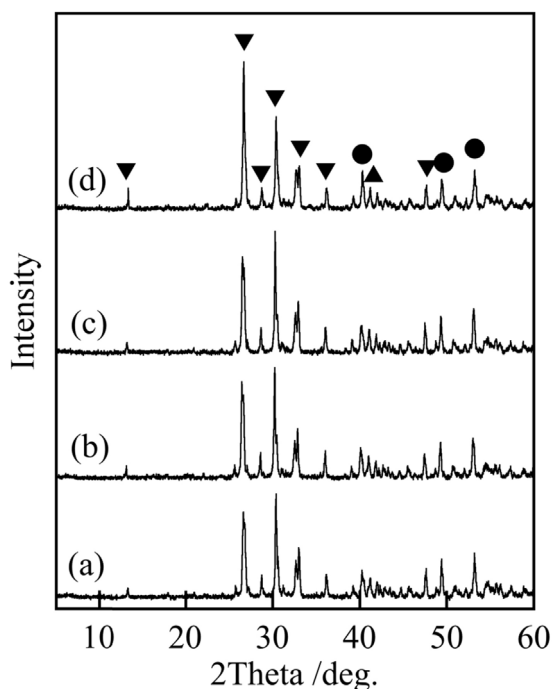


Fig. 1. XRD patterns of samples prepared from CaCO_3 at 160°C for 1 h with $\text{CO}(\text{NH}_2)_2$, (a) 0 g, (b) 0.6 g, (c) 1.2 g, (d) 2.4 g, ●: HAP, ▼: DCPA, ▲: CaCO_3 .

were recorded on a Rigaku MiniFlex X-Ray diffractometer using monochromated $\text{Cu K}\alpha$ radiation. SEM images were obtained using JSM-5510LV, JEOL Ltd. A portion of the solid sample was dissolved in hydrochloric acid and examined using inductively coupled plasma (ICP, SPS1500VR, Seiko Instruments, Inc.). The ratios of calcium and phosphorus in the samples were calculated from the ICP results of these solutions.

The substitution properties of the products were estimated using iron nitrate solutions. 0.1 g of the sample (prepared from 0.6 g urea, for 1 h at 160°C) was added to an iron (+III) nitrate solution (0.1 mol/L, 100 mL), and stirred for 0, 1, 2, 3, 6, or 24 h. The resulting precipitates were filtered and dried. A portion of the solid sample was also dissolved in hydrochloric acid and examined using ICP. The ratios of phosphorus and calcium in the samples were calculated from the ICP results of these solutions.

The adsorption properties of these phosphate products were estimated using trimethylamine gas at room temperature. 0.01 g of sample was placed in a gas bag (3000 cm^3) of polyethylene, which was then filled with trimethylamine gas (14.34 ppm). The concentration of trimethylamine gas after standing for 10 min was determined with a Kitagawa gas detector.

3. Results and discussion

3.1. Influence of urea concentration

Fig. 1 shows XRD patterns of samples prepared from commercial calcium carbonate and phosphoric acid with various amounts of urea. Patterns for all samples display peaks of di-calcium hydrogen phosphate anhydrate (DCPA; CaHPO_4), hydroxyapatite (HAP; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), and calcium carbonate. Because the Ca/P ratio in the original experiment with calcium carbonate was 1, DCPA is easily formed here. These DCPA peaks become more intense with increased amounts of added urea. Samples prepared from corbicula shells had peaks corresponding to DCPA and calcium carbonate, but HAP peaks were not observed in the XRD patterns of these samples. **Table 1** shows changes in sample solution pH for different

Table 1
pH changes of solutions using different preparation processes.

Urea/g	Temp./ $^\circ\text{C}$	Time/h	CaCO_3		Corbicula shell	
			Before	After	Before	After
0.6	160	1	3.05	6.08	1.82	2.39
1.2	160	1	3.37	6.23	1.95	3.53
2.4	160	1	3.08	7.17	1.69	5.79
0.6	120	3	3.60	6.74	1.79	6.07
0.6	140	3	3.18	7.30	2.09	6.56
0.6	160	3	3.16	7.80	1.87	6.42
0.6	180	3	3.20	8.29	1.77	6.42
0.6	160	6	3.13	7.29	2.19	6.65

Table 2
Ca/P ratios of samples prepared under various conditions.

Urea/g	Temp./ $^\circ\text{C}$	Time/h	CaCO_3	Corbicula shells
0	160	1	0.74	3.22
0.6	160	1	0.90	2.99
1.2	160	1	0.96	2.33
2.4	160	1	0.97	2.04
0.6	120	3	0.89	2.39
0.6	140	3	0.96	1.96
0.6	160	3	1.26	2.08
0.6	180	3	1.82	1.96
0.6	160	6	1.30	2.18

preparation conditions. Solutions prepared with corbicula shells had lower pH values than those made using calcium carbonate. Because HAP is a basic compound, HAP is difficult to form at this pH range. **Table 2** shows Ca/P ratios of samples prepared under various conditions. Samples prepared with calcium carbonate had low Ca/P ratios (0.74–0.97), but those prepared from corbicula shells had much higher ratios (2.04–3.22). The Ca/P ratios of DCPA and HAP are 1 and 1.67, respectively. When unreacted calcium carbonate or corbicula remain in solution, this ratio becomes larger. Samples prepared from corbicula shells, therefore, are believed to contain unreacted material. On the other hand, the formation of calcium di-hydrogen phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$) leads to a low Ca/P ratio in these products. Samples prepared from calcium carbonate contained both DCPA and calcium di-hydrogen phosphate. Because the ratio of calcium di-hydrogen phosphate was small in these samples, the above XRD patterns feature no peaks of calcium di-hydrogen phosphate.

3.2. Influence of temperature

Fig. 2 shows XRD patterns of samples prepared from commercial calcium carbonate and phosphoric acid at various temperatures. Samples prepared at 120°C and 140°C had strong DCPA peaks. On the other hand, samples prepared at 160°C and 180°C had strong HAP peaks. Solution after homogenous hydrothermal processing at 160°C and 180°C had higher pH values than those at 120°C and 140°C (**Table 1**). Because HAP contains hydroxyl (OH) groups, HAP is easy to form in solution at 160°C and 180°C . In **Table 2**, samples prepared at 160°C and 180°C had higher Ca/P ratios than those at 120°C and 140°C . This is related to the fact that the Ca/P ratios of DCPA and HAP are 1 and 1.67, respectively. **Fig. 3** shows SEM images of samples prepared from commercial calcium carbonate and phosphoric acid at various temperatures. Samples prepared at 160°C and 180°C had needle-like particles, while samples prepared at 120°C and 140°C had only small amounts of these needle-like particles, which are considered to be HAP based on the XRD and ICP results.

All samples prepared from corbicula shells at various temperatures display XRD peaks for DCPA ($\text{CO}(\text{NH}_2)_2$; 0.6 g, 3 h). The treatment temperature has less of an influence on the reaction

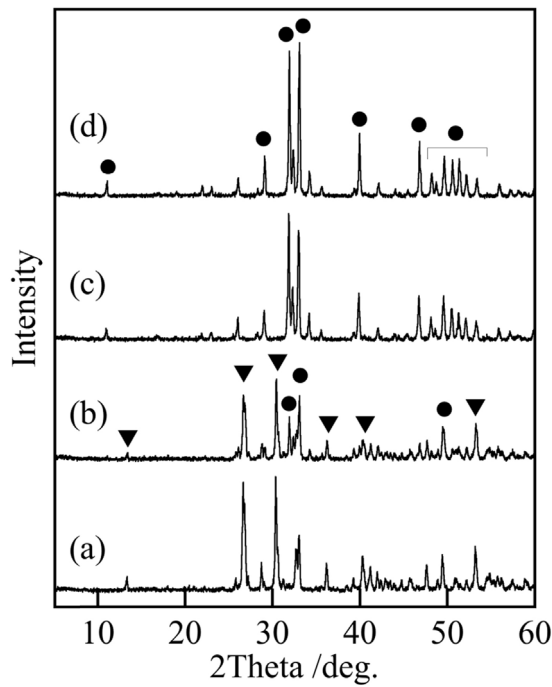


Fig. 2. XRD patterns of samples prepared from CaCO_3 at (a) 120 °C, (b) 140 °C, (c) 160 °C, (d) 180 °C for 3 h with $\text{CO}(\text{NH}_2)_2$ (0.6 g). ●: HAP, ▼: DCPA.

between corbicula shells and phosphoric acid. The preparation solutions indicated similar pH changes during these processes (Table 1). The obtained samples also had similar Ca/P ratios (Table 2).

3.3. Treatment time

Fig. 4 shows XRD patterns of samples prepared from commercial calcium carbonate and phosphoric acid for various time lengths (160 °C, $\text{CO}(\text{NH}_2)_2$; 0.6 g). The sample treated for 1 h had DCPA

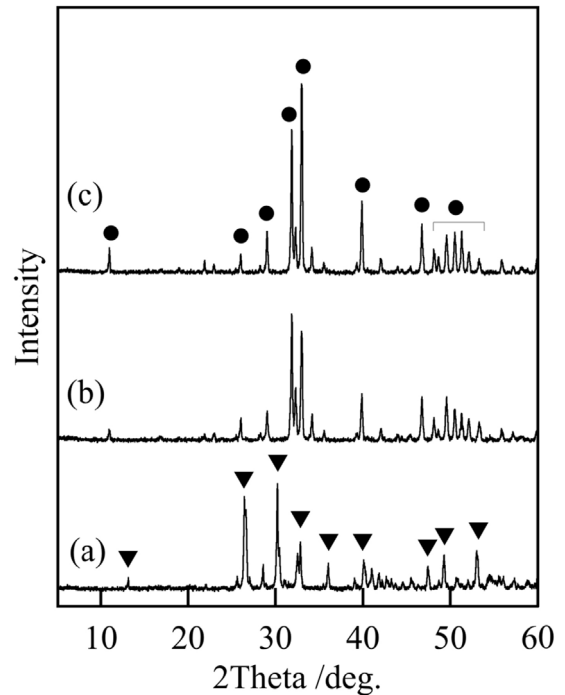


Fig. 4. XRD patterns of samples prepared from CaCO_3 with $\text{CO}(\text{NH}_2)_2$ (0.6 g) at 160 °C for (a) 1 h, (b) 3 h, (c) 6 h, ●: HAP, ▼: DCPA.

peaks, but samples treated for 3 and 6 h had HAP peaks, which were particularly strong in the sample treated for 6 h. Solutions after 3 and 6 h of treatment had higher pH values than the 1 h solution (Table 1). Samples treated for 3 and 6 h had Ca/P ratios between 1 (DCPA) and 1.67 (HAP) (Table 2).

Fig. 5 shows XRD patterns of samples prepared from corbicula shells and phosphoric acid for various time lengths (160 °C, $\text{CO}(\text{NH}_2)_2$; 0.6 g). All samples had peaks corresponding to DCPA, but as the processing time increased, these peaks became weaker and

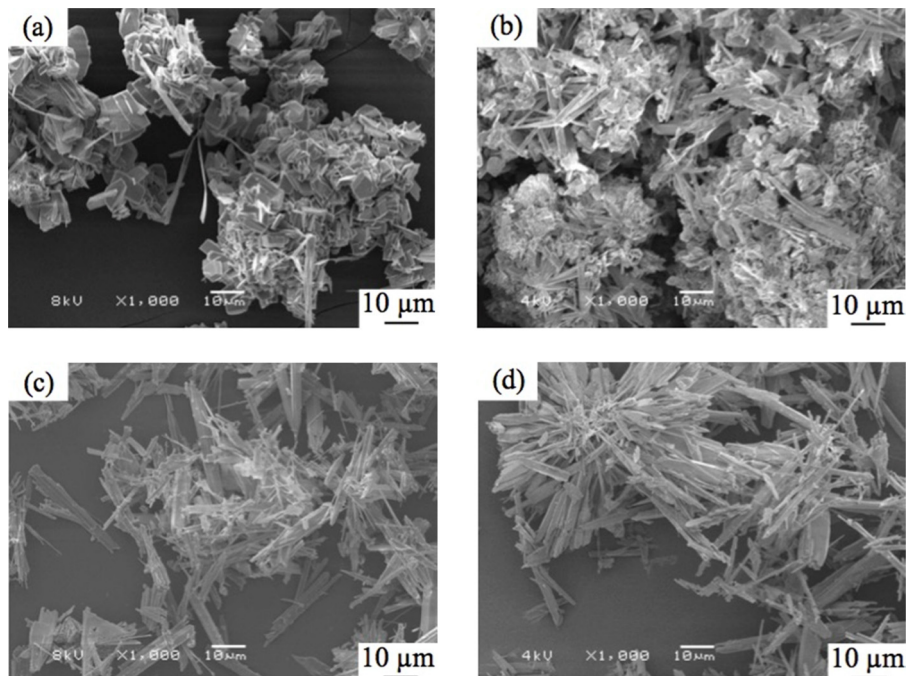


Fig. 3. SEM images of samples prepared from CaCO_3 at (a) 120 °C, (b) 140 °C, (c) 160 °C, (d) 180 °C for 3 h with $\text{CO}(\text{NH}_2)_2$ (0.6 g).

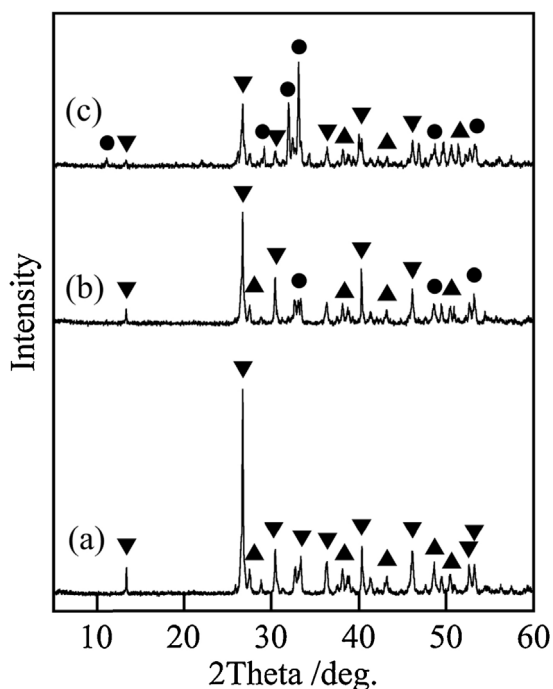


Fig. 5. XRD patterns of samples prepared from corbicula with $\text{CO}(\text{NH}_2)_2$ (0.6 g) at 160°C for (a) 1 h, (b) 3 h, (c) 6 h. ●: HAP, ▼: DCPA, ▲: CaCO_3 .

Table 3

Fe/(Fe + Ca) ratios of samples prepared at 160°C for 1 h with 0.6 g of urea and post-treatment with a 0.1 mol/L iron solution/%.

Time/h	CaCO_3	Corbicula shells
0	63.8	2.8
1	87.1	10.5
2	88.5	8.1
3	90.0	19.2
24	89.5	84.5

HAP peaks began to emerge. Solutions after 3 and 6 h of homogeneous hydrothermal processing had pH values ≥ 6 (Table 1). The Ca/P ratio of these samples was less affected by the processing time (Table 2).

3.4. Substitution with iron cation and adsorption of trimethylamine

To test one possible application of these materials, the obtained products were used to remove iron from pre-made solutions. Table 3 shows Fe/(Fe + Ca) ratios of samples prepared at 160°C for 1 h with 0.6 g of urea and post-treated in a 0.1 mol/L iron solution. A sample prepared from commercial calcium carbonate and then treated for 1 h had a Fe/(Fe + Ca) high ratio ($>80\%$). This means that the calcium in these samples was easily substituted with iron. On the other hand, samples prepared from corbicula shells had lower Fe/(Fe + Ca) ratios ($< 20\%$) after 3 h iron treatment, implying less favorable iron substitution.

The gas adsorption properties of the obtained materials were estimated using trimethylamine gas. Table 4 shows adsorption

Table 4

Adsorption ratios of trimethylamine on samples prepared using various conditions/%.

Temp./ $^\circ\text{C}$	Time/h	CaCO_3	Corbicula shells
120	3	23	3
140	3	36	4
160	3	19	30
180	3	23	26
160	1	3	17
160	6	23	30

ratios of trimethylamine on samples prepared under various conditions. Samples prepared from commercial calcium carbonate at 140°C had a high adsorption ratio, likely due to the formation of the more acidic DCPA. Samples prepared from commercial calcium carbonate at 160 and 180°C had lower adsorption ratios; because trimethylamine is basic, samples with higher amounts of HAP have less favorable absorption. Samples prepared from corbicula shells at 160°C and 180°C had higher adsorption ratios, related to the formation of DCPA. The adsorption ratio of trimethylamine was strongly influenced by the presence of DCPA and HAP in the samples.

4. Conclusion

Calcium hydrogen phosphate and hydroxyapatite were synthesized by a homogeneous hydrothermal process, using both commercial calcium carbonate and corbicula shell precursors. Hydroxyapatite was easily formed under these high-temperature conditions, because the addition of urea increased the pH of the reaction solution. The crystalline phase changed from calcium hydrogen phosphate to hydroxyapatite in samples prepared from commercial calcium carbonate at 160°C for 3 h. Samples prepared from corbicula shells had weaker XRD peaks for hydroxyapatite than those prepared from commercial calcium carbonate. These results were related to the pH of the solution after processing. Samples prepared from commercial calcium carbonate more easily underwent iron substitution. The adsorption ratio of trimethylamine was greatly affected by the formation of calcium hydrogen phosphate anhydrate and hydroxyapatite in these samples.

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