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Hydroxyapatite Formation Reaction between Calcium Carbonate and Diammonium Hydrogenphosphate

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Calcium carbonate powder was placed in a solution of diammonium hydrogenphosphate and the reaction between them was studied at temperatures ranging from 60 to 100 ℃ for 1 min to 24 hrs. X-ray diffraction patterns after the reaction showed the existence of calcium carbonate and hydroxyapatite. Scanning electron micrographs of powder after reaction indicated needle-like hydroxyapatite on the surface of calcium carbonate. Using the values for the fraction reacted of calcium carbonate, various types of rate equations are fitted. From the results, it was considered that rate-determining step for the formation of hydroxyapatite in the aqueous solution was the dissolution of calcium carbonate or the deposition of hydroxyapatite on calcium carbonate.

Keywords: Hydroxyapatite, Calcium carbonate, Diammonium hydrogenphosphate,

1. INTRODUCTION

There are various types of methods to prepare the hydroxyapatite. They include solid state reaction, hydrothermal reaction, hydrolysis, precipitation from calcium hydroxide, and so on. Most of them need several hundreds temperature or over thousand temperature. However, there is a demand to prepare the hydroxyapatite at lower temperature. It was reported that the hydroxyapatite was made from the reaction between calcium carbonate and phosphoric acid or phosphate at low temperature [1, 2]. Ueda et al. [1] used the slurry of calcium carbonate (calcite, aragonite, and vaterite) in a solution of phosphoric acid or diammonium hydrogenphosphate or ammonium dihydrogenphosphate to prepare the hydroxyapatite at the temperature of 40 ~85 ℃. They concluded that the shape of hydroxyapatite depended on the source of calcium carbonate. Kasahara et al. [2] prepared the spherical hydroxyapatite using the colloids of calcium carbonate in a solution of phosphoric acid or phosphate. However, the formation reaction of hydroxyapatite was not studied in detail. Especially kinetic of the reaction was not known yet. Therefore, the aim of the present study was to understand the formation reaction of hydroxyapatite from the reaction of calcium carbonate with diammonium hydrogenphosphate at temperatures ranging from 60 to 100 ℃ as a function of time.

2. EXPERIMENTAL PROCEDURE

Calcium carbonate powder from Kanto Chemical was used. The particle size of calcium carbonate powder was about 10 μm and was uniform. The solution of diammonium

hydrogenphosphate at the concentration of 2 mol · dm^{-3} was heated to experimental temperatures ranging from 60 to 100 ℃ using oil bath. After reaching the experimental temperature, the calcium carbonate powder was added to the solution. They were allowed to react for 1 minute to 24 hrs. After the reaction, the solution was quenched in deionized water. Then the remaining powder was filtered, washed with deionized water, and dried at 85 ℃ over night. The powder was analyzed using X-ray diffraction.

As a first step a working curve was made from X-ray diffraction analysis. The powders of calcium carbonate and hydroxyapatite were mixed at the ratio of 20, 40, 60, 80, and 100 wt%. The mixed powder was examined by X-ray diffraction. One peak of calcium carbonate at (104) of obtained peaks was used to calculate integrated intensity, because it was difficult to measure the amount of hydroxyapatite for X-ray diffraction. The amount of non-reacted calcium carbonate was obtained using the working curve, and then assuming that calcium carbonate that was lost reacted to form hydroxyapatite, fraction reacted of calcium carbonate was calculated.

Finally, the powders after reaction were observed by scanning electron microscopy.

3. RESULTS AND DISCUSSION

The powder of calcium carbonate reacted with the solution of diammonium hydrogen phosphate. After the reaction, the powder sample was examined by X-ray diffraction. The results are shown in Fig. 1. They are the results after the reaction at 60 ℃. The X-ray diffraction patterns after the reaction showed the existence of calcium carbonate and hydroxyapatite. The intensity of peaks for hydroxyapatite increased as the reaction time increased. To the contrary, the intensity of peaks for calcium carbonate decreased as the reaction time increased. Therefore, it is clear that the hydroxyapatite was formed with increasing reaction time. At 80 and 100 ℃, the X-ray diffraction patterns showed also the existence of both calcium carbonate and hydroxyapatite, the intensity of which became stronger with increasing reaction time.

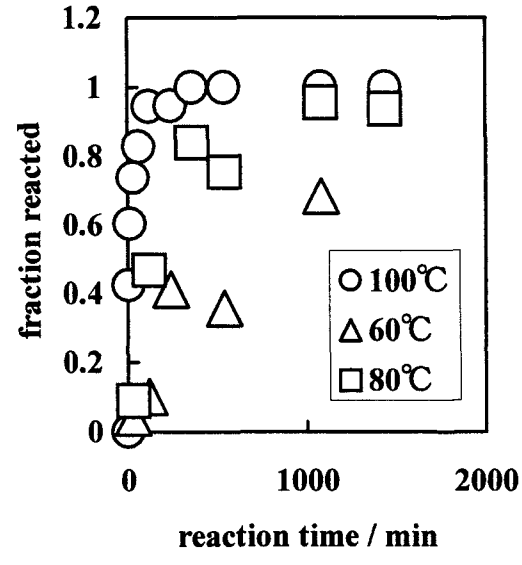


Fig. 1 The relation between fraction reacted of $CaCO_3$ and reaction time.

The scanning electron micrographs of samples before and after reaction at 60 ℃ are shown in Fig. 2. The particles of non-reacted calcium carbonate are uniform in shape and size. With the progression of the reaction time, the shape of particles became irregular, and the hydroxyapatite was formed on the surface of calcium carbonate. The hydroxyapatite formed was a needle-like in shape. In the case of short time reaction (0-2 hrs), both calcium carbonate and hydroxyapatite coexisted. However, after long time reaction, a needle-like hydroxyapatite was mainly observed. This needle-like shape was similar to the products of other hydroxyapatite formation reaction reported in

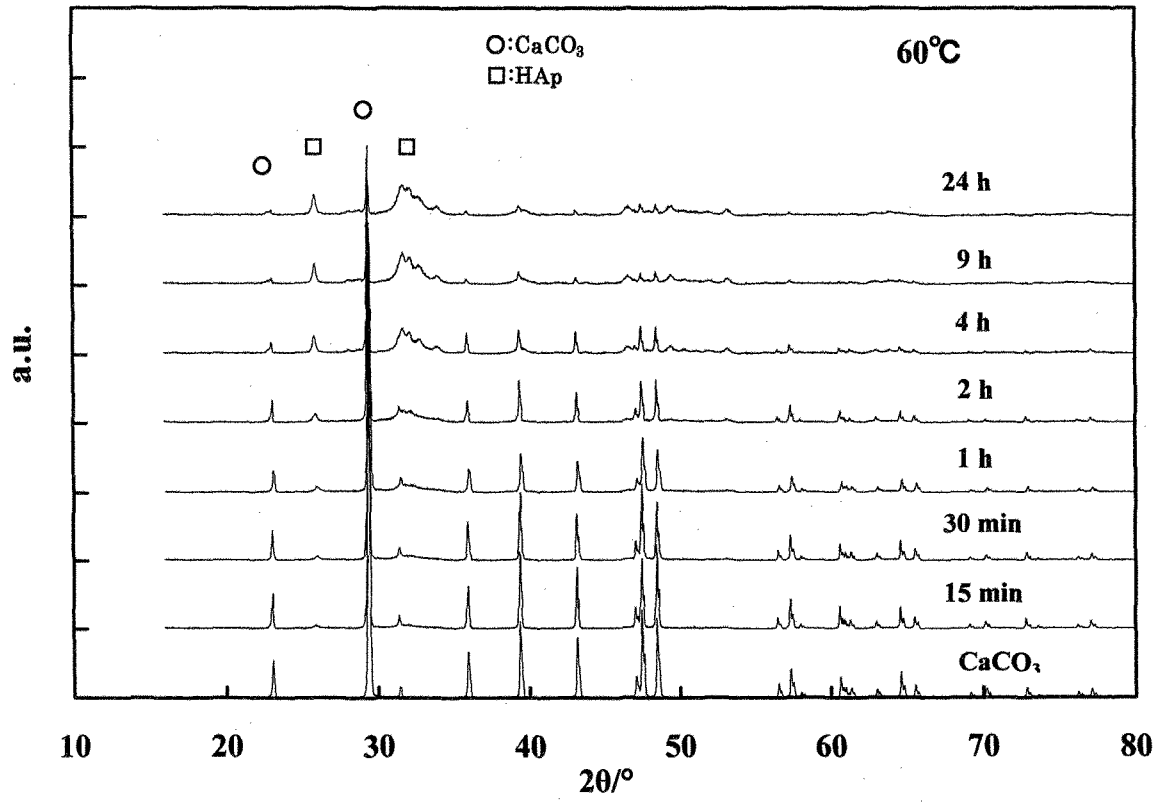


Fig. 2 The X-ray diffraction patterns before and after reaction between $CaCO_3$ and diammonium hydrogenphosphate at 60 ℃.

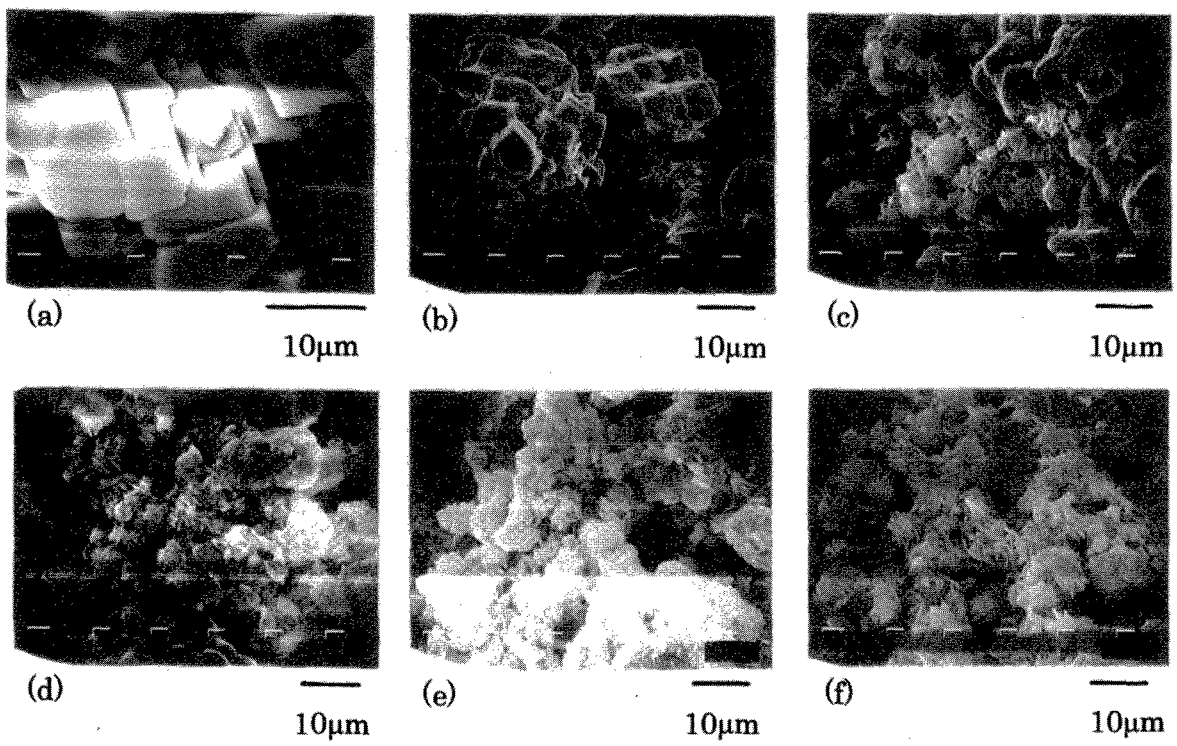


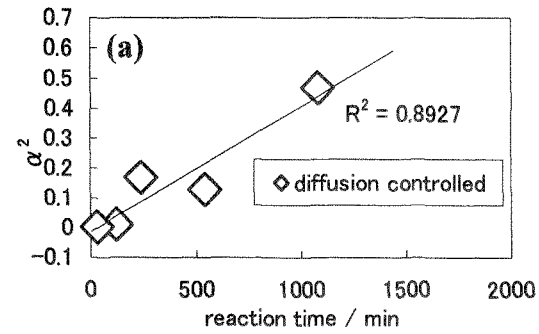
Fig. 3 SEM micrographs before and after reaction at 60 ℃ for (a) non-reacted $CaCO_3$, (b) 15 min, (c) 1 hr, (d) 4 hrs, (e) 9 hrs, and (f) 24 hrs.

the literature [2]. The hydroxyapatite was formed even in shorter time at 80 and 100 ℃.

To examine the rate-determining step for the formation reaction of hydroxyapatite, the amount of non-reacted calcium carbonate was calculated using a working curve. The fraction reacted was calculated using the equation:

$$\alpha = 1 - C_r \qquad [1]$$

where, α is the fraction reacted, and C_r is the amount of non-reacted calcium carbonate calculated from a working curve. The results of calculation are shown in Fig. 3. The fraction reacted increased with increasing temperature and increasing reaction time. Using these values of fraction reacted, various types of rate equations, such as solid diffusion controlled reaction, first-order reaction, interfacial rate-controlled reaction, zero-order reaction, and Avrami equation, were fitted. A good agreement between calculated values and experimental data was observed just when solid diffusion controlled reaction and first-order reaction equations were used. These results are shown in Fig. 4. It was difficult to consider that the solid phase formation reaction in aqueous solution was solid diffusion controlled reaction. Therefore, it can be concluded that rate-determining step for the formation of hydroxyapatite in the aqueous solution was the dissolution of calcium carbonate or the deposition of hydroxyapatite on calcium carbonate.



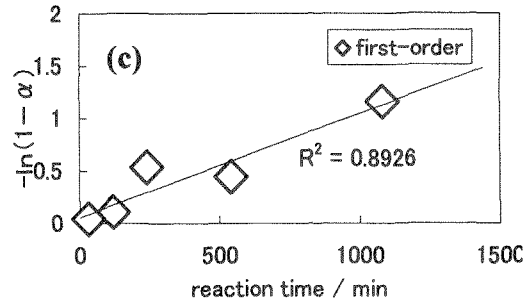


Fig. 4 The results of fitting for rate equation; (a) diffusion controlled, (b) diffusion controlled, and (c) first-order.

4. CONCLUSION

The reaction between calcium carbonate and diammonium hydrogen phosphate was studied at various temperatures. After the reaction, the powder samples were examined by X-ray diffraction and scanning electron microscopy. From the results it was found:

1. The products were hydroxyapatite which had the needle-like shape.
2. The rate-determining step for this reaction was thought to be the dissolution of calcium carbonate or the deposition of hydroxyapatite on solid.

5. REFRENCES

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