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Porous hydroxyapatite monoliths from gypsum waste

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Porous hydroxyapatite (HAp) monoliths were synthesized from gypsum mold waste with diammonium hydrogen phosphate solution by hydrothermal treatment at 50–190 °C and their properties studied. Gypsum waste samples could be completely converted to HAp with 0.5 mol dm^{-3} $(NH_4)_2HPO_4$ at 50 °C in 15 days and 100 °C in 2 days. This paper describes the effect of hydrothermal reaction conditions such as reaction temperature, time and concentration of $(NH_4)_2HPO_4$ on the formation of new HAp monoliths and their porous properties.

1 Introduction

Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$], which is well known as a main component of bone and teeth, has been used widely in many industrial applications and in the medical field. For example, HAp has been found to have cation-exchange properties where Ca^{2+} ions of HAp can be exchanged with poisonous heavy metal ions.[1,2] HAp also has the ability to adsorb organic chemicals.[3,4] Generally, HAp powder is synthesized by several routes such as precipitation from solution containing Ca^{2+} and PO_4^{3-} ions[5,6] and hydrolysis of $CaHPO_4$ or $CaHPO_4{\cdot}2H_2O$ at room temperature[7] and hydrothermal synthesis of $Ca_3(PO_4)_2$ at 200 °C.[8] One of the problems with these processes is that HAp monoliths such as bone or tooth, *etc.* can not be obtained from these chemicals by an *in situ* method. Therefore, synthetic HAp powder is molded and then sintered at 1000–1250 °C.[9]

A large amount of gypsum plaster ($CaSO_4{\cdot}2H_2O$) is used as molds for slip or pressure casting in the ceramic industry. These gypsum molds wear out after repeated use (*ca.* 100 times) and are then discarded as waste. Gypsum is a sparingly soluble calcium salt, and has never been used previously as the source material to prepare HAp. Here we develop a novel process for preparing porous HAp monoliths directly from gypsum waste by *in situ* crystallization using the following chemical reaction.

$$10CaSO_4{\cdot}2H_2O + 6(NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 6(NH_4)_2SO_4 + 4H_2SO_4 + 18H_2O$$

This concept will alleviate the environmental problem from the following two standpoints: (1) effective recycling of industrial waste materials, and (2) use of this new porous HAp as a purification system of waste water containing heavy metal ions or organic chemicals.

In this study, porous HAp monoliths were produced by *in situ* crystallization from gypsum mold waste by a conventional hydrothermal treatment and its characteristics were investigated.

2 Experimental

Gypsum waste mold was washed and cut into rectangular pieces of 5 × 10 × 20 mm. The surface layer of gypsum mold was removed since small amounts of some impurities such as Na and Si components from the ceramic raw materials are deposited on the surface of the repeatedly used gypsum mold. The gypsum and 0.5 mol dm^{-3} diammonium hydrogen phosphate [$(NH_4)_2HPO_4$] solution were placed in a 50 ml Teflon vessel of a stainless steel hydrothermal reactor. The initial pH of the $(NH_4)_2HPO_4$ solution was *ca.* 7.5. The hydrothermal reactor was introduced into a drying oven which was heated in the range 50–100 °C for 1–15 days. After hydrothermal treatment, reacted samples were washed with distilled water to remove residual ions such as SO_4^{2-}, NH_4^+ and PO_4^{3-} and were dried. The drying temperature was kept below 50 °C so that unreacted gypsum crystals would not be decomposed during the drying treatment. To promote the formation rate of HAp, 1.0 mol dm^{-3} $(NH_4)_2HPO_4$ was used as the starting solution and the reaction temperature was increased to 190 °C. The conversion of gypsum to HAp was estimated from the ratio of X-ray intensities of the peaks of gypsum ($hkl = 020$, $2\theta = 11.62°$) and HAp ($hkl = 211$, $2\theta = 31.77°$) by powder X-ray diffraction (XRD, Model RAD-2B, Rigaku Co., Japan). The HAp samples were dissolved in Na_2CO_3–H_3BO_3 solution, and the chemical composition of HAp was analyzed by ICP emission spectrometry (ICPS-2000, Shimadzu Co., Japan). The crystal morphology of the synthetic samples was observed by scanning electron microscopy (SEM, Model JXA-840, JEOL Co., Japan) and transmission electron microscopy (TEM, Model 2010, JEOL Co., Japan). The pore diameter, porosity and pore size distribution of products were investigated by mercury porosimetry (Pore Sizer 9310, Micromeritics Co., USA) and the surface area was measured by the BET method with N_2 gas adsorption (Autosorb 1, Quantachrome Co., USA).

3 Results and discussion

3.1 Synthesis of HAp from gypsum waste

Gypsum waste used in this study was composed of fine needle-like crystals of length 5–10 µm and 1–2 µm thickness as shown in Fig. 1. This gypsum has a porous structure with 2.4 µm median pore diameter, 60% porosity and 1.6 m^2 g^{-1} surface area. The effect of reaction temperature on the formation of HAp was investigated with 0.5 mol dm^{-3} $(NH_4)_2HPO_4$. Fig. 2 shows XRD patterns of the as-received gypsum and the samples synthesized for 1, 2 and 3 days at 100 °C, and Fig. 3 shows XRD patterns of the samples synthesized at 50, 75 and 100 °C for 6–15 days. Fig. 4 summarizes the conversion rate from gypsum to HAp based on the calculation from XRD intensity ratios of gypsum and HAp. At 100 °C, *ca.* 58–59 mass% gypsum was hydrothermally converted into HAp after 1 day, and the conversion of the gypsum to HAp reached 100 mass% after 2 days. HAp monoliths could be hydrothermally prepared by *in situ* crystal growth from gypsum waste

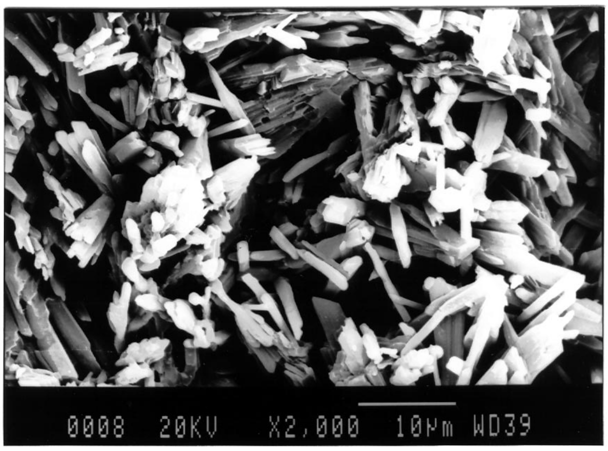

Fig. 1 Morphology of gypsum waste.

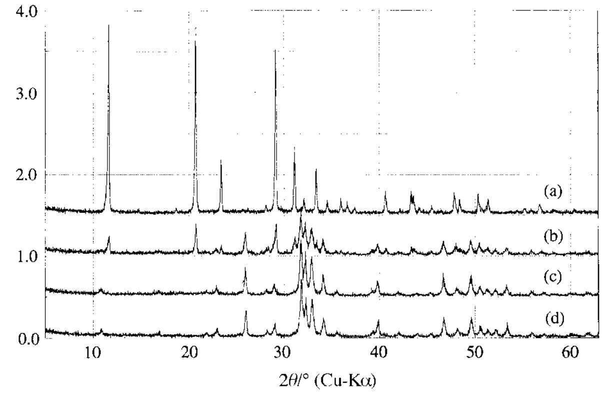

Fig. 2 XRD patterns of (a) gypsum waste and samples synthesized by hydrothermal reaction with 0.5 mol dm^{-3} $(NH_4)_2HPO_4$ at 100 °C for (b) 1 day, (c) 2 days and (d) 3 days.

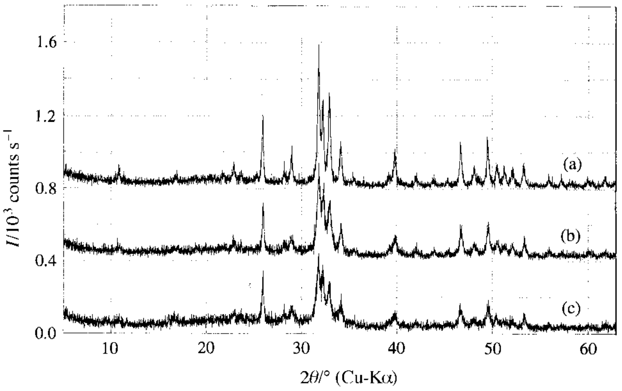

Fig. 3 XRD patterns of HAp synthesized from gypsum waste and 0.5 mol dm^{-3} $(NH_4)_2HPO_4$ under the following hydrothermal reaction conditions: (a) 100 °C, 6 days; (b) 75 °C, 7 days; (c) 50 °C, 15 days.

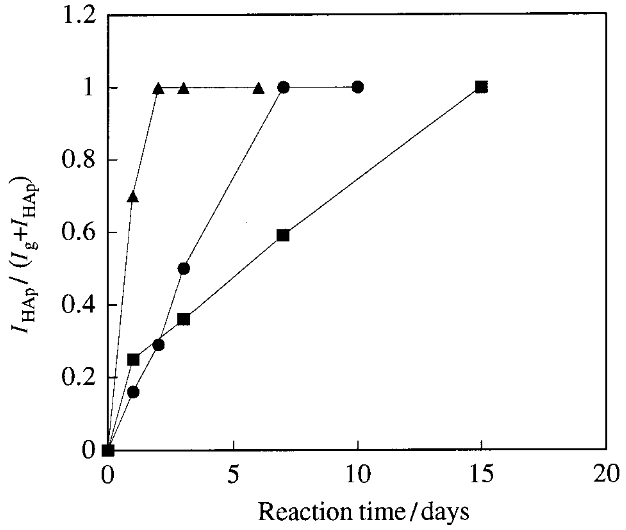

Fig. 4 The conversion rate of gypsum to HAp based on the calculation from the X-ray intensity ratio under the hydrothermal reaction with 0.5 mol dm^{-3} $(NH_4)_2HPO_4$. ■: 50 °C, ●: 75 °C and ▲: 100 °C.

and $(NH_4)_2HPO_4$ at 100 °C in 2 days. To prepare smaller HAp crystals, the growth of HAp was examined at lower temperatures. The conversion of gypsum to HAp was 100 mass% at 75 °C after treatment for 7 days and after 15 days at 50 °C.

Monoliths of HAp resulted under all reaction conditions, and the size of the HAp monoliths were the same size as the starting gypsum piece in all cases. During this preparation process, HAp is produced in a solution under neutral or mildly alkaline condition with the solubility product $[Ca^{2+}]^5[PO_4^{3-}]^3[OH]$ exceeding that of HAp.[6] The solubility of $CaSO_4 \cdot 2H_2O$ in water in the present reaction is *ca.* 0.16–0.21% at 50–100 °C.[10] The mechanism of HAp formation involves slight leaching of Ca^{2+} ions from gypsum crystals and these ions then react with PO_4^{3-} and OH^- ions in solution to form HAp until all the gypsum crystals are converted.

These results show that the novel HAp monoliths can be synthesized by *in situ* crystallization of gypsum waste with $(NH_4)_2HPO_4$ solution under conventional hydrothermal treatment at 50–100 °C.

3.2 Properties of new HAp crystals

To characterize the chemical composition of synthesized HAp crystals, the Ca/P molar ratio of the crystals was analyzed by ICP. The Ca/P molar ratios of crystals obtained at 50 °C for 15 days and 100 °C for 6 days were calculated to be 1.25 and 1.30, respectively. These new HAp crystals were non-stoichiometric compared to theoretical hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$ whose Ca/P ratio was 1.67. HAp is known to be a stable substance even though its composition is non-stoichiometric. There are several previous reports[11–13] on explaining why the Ca/P ratio of apatite can be varied over a wide range: (1) other crystal phases such as $CaH(PO_4)_3 \cdot 2H_2O$ and $Ca_4H(PO_4)_3 \cdot 3H_2O$ can co-exist,[11] (2) phosphoric acid can be adsorbed on the surface of HAp,[12] (3) there may be a deficiency of Ca^{2+} in the crystal lattice of apatite.[13] In our study, only the HAp phase was observed by XRD after complete conversion. Thus it is considered that residual phosphoric acid is adsorbed on the surface of HAp because the concentration of $(NH_4)_2HPO_4$ in the starting solution is stoichiometrically higher than that of gypsum. The crystallinity of the HAp crystals increased with reaction temperature as can be deduced from peak widths of the XRD patterns in Fig. 3.

Fig. 5 and 6 show the morphology of HAp synthesized at 50, 75 and 100 °C. After reaction at 50 °C for 7 days, unreacted gypsum crystals were still present within the body of the monolith, but the surface was coated with fine HAp crystals of diameter 10–30 nm as shown in Fig. 5(b). Almost all gypsum crystals were completely converted into the HAp phase after 15 days leading to an HAp monolith which was composed of crystals of 80–120 nm. With increasing reaction temperature, the crystal growth of HAp was enhanced and the crystals grew to 3–8 μm in length at 100 °C for 3 days.

To promote the formation rate of HAp, the gypsum waste was reacted with 1.0 mol dm^{-3} $(NH_4)_2HPO_4$ at 190 °C. However, under these conditions the gypsum could not be completely converted into the HAp phase because the surface

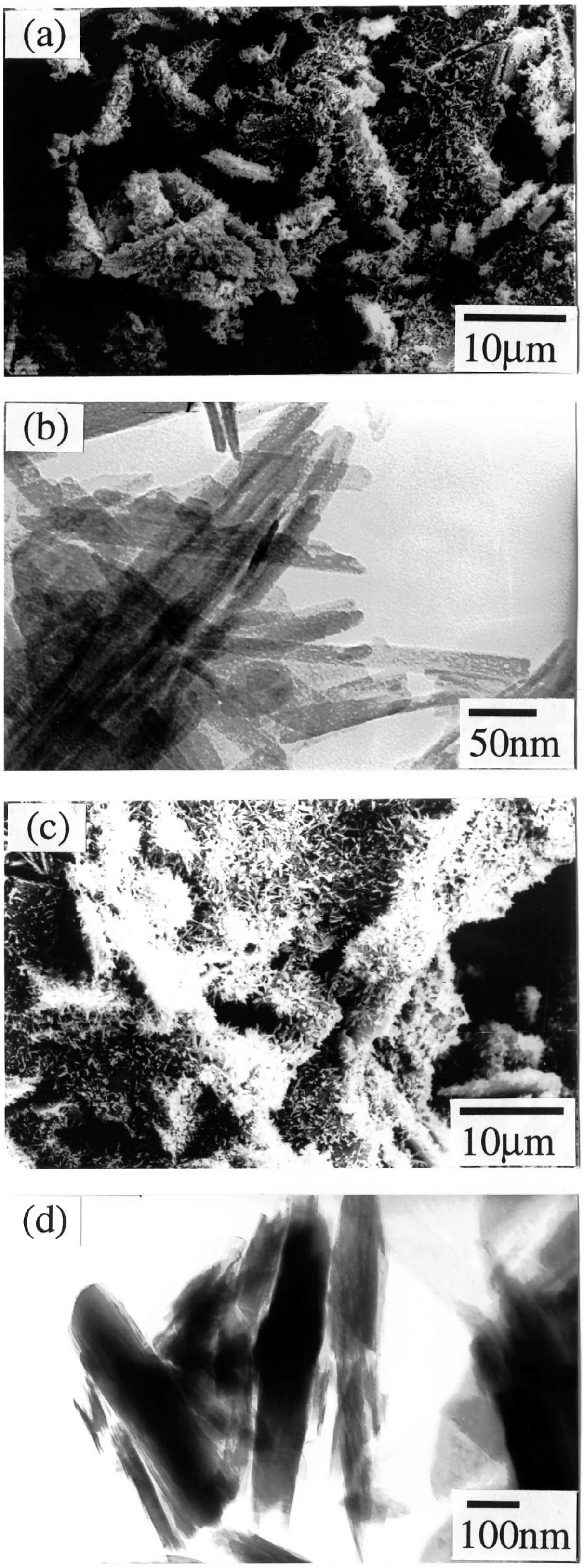

Fig. 5 Morphology of HAp crystals synthesized from gypsum waste and 0.5 mol dm^{-3} $(NH_4)_2HPO_4$ by hydrothermal reaction. (a) and (b): 50 °C, 7 days; (c) and (d): 50 °C, 15 days.

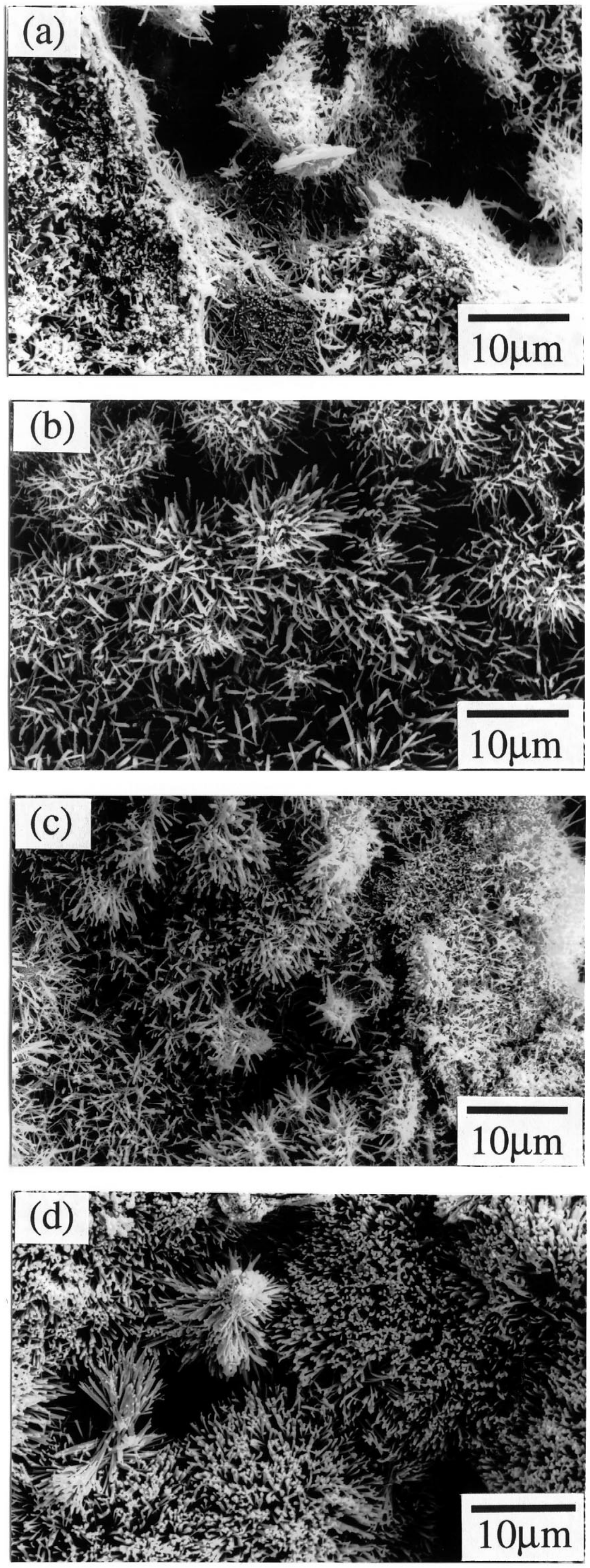

Fig. 6 Morphology of HAp crystals synthesized from gypsum waste and 0.5 mol dm^{-3} $(NH_4)_2HPO_4$ by hydrothermal reaction. (a) 75 °C, 3 days; (b) 75 °C, 7 days; (c) 100 °C, 1 day; (d) 100 °C, 3 days.

of gypsum rapidly reacted with $(NH_4)_2HPO_4$, and a tight HAp layer of about 1 mm thickness was formed on the surface after reaction for 3 days and prevented further conversion of gypsum crystals to HAp. Therefore, unreacted gypsum crystals remained within the body of the monolith. Further reactions were thus not carried out using this concentration of $(NH_4)_2HPO_4$.

3.3 Porous properties of HAp monoliths

In this study, novel HAp monoliths were easily synthesized from the reaction of gypsum waste with $(NH_4)_2HPO_4$ and it

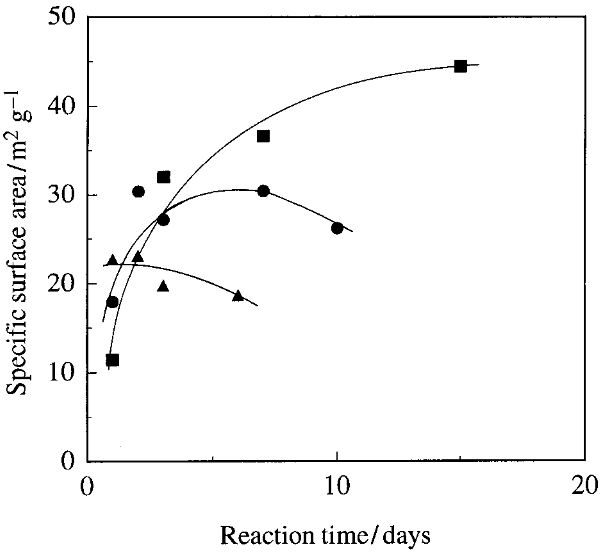

Fig. 7 The surface area of synthesized HAp with 0.5 mol dm^{-3} of $(NH_4)_2HPO_4$. ■: 50 °C, ●: 75 °C and ▲: 100 °C.

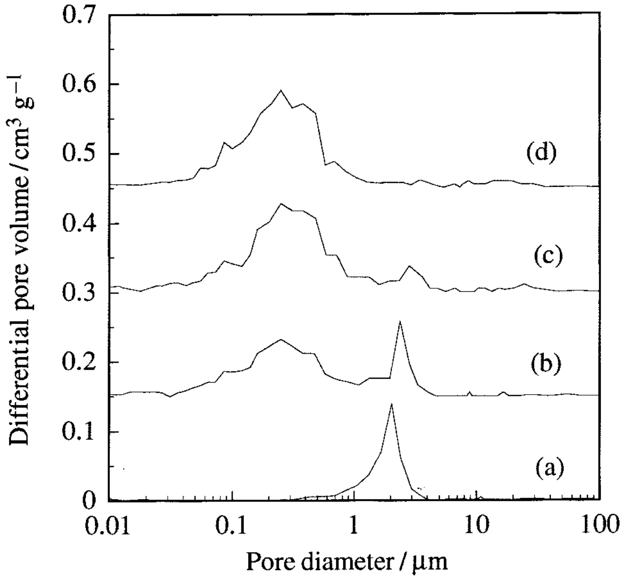

Fig. 8 The pore size distributions of (a) starting gypsum and HAp synthesized with 0.5 mol dm^{-3} $(NH_4)_2HPO_4$ at 75 °C for (b) 1 day, (c) 7 days and (d) 10 days.

was composed of fibrous or needle-like crystals. To determine the value of such HAp monoliths for applications, porous properties such as porosity, pore diameter and the surface area are important and therefore, these were investigated.

Fig. 7 shows the effect of reaction temperature and time on the surface area of HAp monoliths. The surface area of products at 75 °C for 2–10 days and at 100 °C for 1–6 days ranged from 26–30 and 19–23 $m^2\ g^{-1}$, respectively. However, these values increased to 35–45 $m^2\ g^{-1}$ at 50 °C when the gypsum was reacted for 7–15 days due to the formation of smaller HAp crystals as can be seen in Fig. 5. Upon *in situ* synthesis of HAp monoliths from gypsum waste, the surface area increased from 20 to 45 $m^2\ g^{-1}$ upon lowering the temperature from 100 to 50 °C and this is related to the morphology of HAp crystals. From the observation of HAp crystals by TEM and SEM (Fig. 5 and 6), the crystals were of length 100–300 nm long and thickness 10–30 nm at 50 °C for 7 days, 2–5 μm long at 75 °C for 3 days, and 3–8 μm long at 100 °C for 3 days. The surface area strongly depends on the morphology of HAp, and decreased with increased crystal size.

The porosities of the HAp samples which were synthesized using 0.5 mol dm^{-3} $(NH_4)_2HPO_4$ at 75 °C for 1–10 days were in the range 75–78% while the porosity of starting gypsum waste was 60%. Pore size distributions of the starting gypsum and products at 75 °C are shown in Fig. 8. The bimodal pore distribution in Fig. 8(b) and (c) is attributed to the different pore sizes of gypsum waste and HAp. Pore diameters of products obtained after treatment for 1–7 days centered at 2–3 μm were apparently from unreacted gypsum, and the pore distribution of HAp aggregates was between 0.01 and 1 μm with a median pore diameter of around 0.3 μm. The pore size distribution of gypsum centered at 2–3 μm remained in the sample treated up to 7 days at 75 °C, and the sample had double-pore structures, one from gypsum and the other from HAp. A single pore distribution derived from HAp crystals was obtained after 10 days at 75 °C. While it was not possible to obtain a single pore structure at 50 °C over short times, the sample prepared at 100 °C for 2 days showed only the pore size distribution of HAp.

Conclusion

In this study, porous HAp monoliths were synthesized and characterized from gypsum mold waste and $(NH_4)_2HPO_4$ solution by hydrothermal reaction. The main results are as follows.

(1) The conversion of gypsum to HAp was affected by reaction time and temperature taking about 2 weeks for complete conversion at 50 °C, but only 2 days at 100 °C when 0.5 mol dm^{-3} $(NH_4)_2HPO_4$ was used. The crystallinity of the synthesized HAp was enhanced by increasing the reaction temperature. SEM observation revealed that HAp monoliths formed at 50 °C in 15 days and were composed of fine crystals of HAp of 80–120 nm diameter and 0.5–1 μm length while HAp formed at 100 °C for 3 days showed larger crystals of size 3–8 μm.

(2) The surface area of synthesized HAp monoliths ranged from 20–45 $m^2\ g^{-1}$ at 50–100 °C and was related to the morphology of the HAp crystals. The pore size distribution of gypsum was *ca.* 2–3 μm and decreased in intensity during the hydrothermal reaction while the pore size distribution of HAp, which was between 0.01 and 1 μm, increased. Under appropriate conditions of time and temperature of reaction, porous HAp monoliths with single pore structure resulted from the reaction of gypsum waste and $(NH_4)_2HPO_4$.

References

1 T. Suzuki, T. Hatsushika and Y. Hayakawa, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1059.
2 S. Suzuki, T. Fuzita, T. Maruyama and M. Takahashi, *J. Am. Ceram. Soc.*, 1993, **76**, 1638.
3 E. C. Moreno, M. Kresak and A. Gaffar, *J. Colloid Interface Sci.*, 1994, **168**, 173.
4 T. Akazawa, M. Kobayashi, T. Kanno and K. Kodaira, *J. Mater. Sci.*, 1998, **33**, 1927.
5 A. L. Bosky and A. S. Posner, *J. Phys. Chem.*, 1976, **80**, 40.
6 H. Mcdowell, T. M. Gregory and W. E. Brown, *J. Res. Natl. Bur. Stand., Sect. A*, 1977, **81**, 273.
7 E. J. Duff, *J. Chem. Soc. A*, 1971, 917.
8 M. Yoshimura, H. Suda, K. Okamoto and K. Ioku, *J. Mater. Sci.*, 1994, **29**, 3399.
9 J. G. Peelen, B. V. Rejda and K. De Groot, *Ceram. Int.*, 1978, **4**, 71.
10 H. F. W. Tayler, *The Chemistry of Cements*, 1964, vol. 1, p. 321.
11 D. McConnel, *Arch. Oral Biol.*, 1965, **10**, 421.
12 A. S. Posner and S. R. Stephenson, *J. Dent. Res.*, 1952, **31**, 371.
13 G. Kuhl and W. E. Nebergall, *Z. Anorg. Allg. Chem.*, 1963, **24**, 313.

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