Preparation and Characterization of Spherical Calcium Hydroxyapatite

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The preparation of spherical calcium phosphate particles by aging a solution containing $CaSO_4$ and NaH_2PO_4 at 80 and 100 °C in the presence of urea (1 mol/dm^3) and a surfactant [cetyltrimethylammonium chloride; CTAC] (1.0×10^{-2} mol/dm^3) has been investigated, and their properties were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR), scanning and transmission electron microscopy (SEM and TEM), N_2 and H_2O adsorption measurements, and thermogravimetric–differential thermal analyses (TG-DTA). The size and shape of the particles produced strongly depended on the concentration of the reactants and the aging temperature. Spherical calcium hydroxyapatite particles were precipitated only within a narrow concentration domain of reactants after aging at 100 °C for 3 h. The spherical calcium hydroxyapatite particles produced at $[CaSO_4] = 2.0 \times 10^{-3}$ mol/dm^3 and $[NaH_2PO_4] = 7.9 \times 10^{-4}$ mol/dm^3 were agglomerates of small platelet particles and were B-type carbonate hydroxyapatite in which 4.8 wt % of CO_3^{2-} ions are substituted for PO_4^{3-} ions. The results of chemical analysis and TG identified the formula of the particles as $Ca_{8.5}Na_{1.5}(PO_4)_{5.4}(CO_3)_{0.8}(OH)_{0.7}\cdot 1.2H_2O$. The texture and crystallinity of the spherical calcium hydroxyapatite particles were sustained up to 1000 °C, and the particles showed the selective adsorption of H_2O molecules. This selective adsorption was more pronounced after calcining the samples in air.

Introduction

To produce high-quality materials, studies on the preparation and characterization of uniform, spherical, metal phosphate particles have been extensively carried out.[1–5] Recently, we investigated the formation and characterization of uniform spherical cobalt and nickel phosphate particles,[6–8] prepared by aging a solution containing $CoSO_4$ or $NiSO_4$ and NaH_2PO_4 at 80 °C in the presence of urea and sodium dodecyl sulfate (SDS). These studies indicated that the cobalt phosphate particles possess thermally unstable slit-shaped micropores and exhibit a high selectivity for H_2O adsorption by the molecular sieve effects of these micropores.[6,8] On the other hand, it was found that, differing from the cobalt phosphate particles, the nickel phosphate particles are agglomerates of fine, primary, spherical particles with a high mesoporosity.[7]

Recently, calcium hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, CaHAP] has attracted a great deal of attention due to its affinity to biopolymers such as proteins and enzymes and the fact that this material is a major inorganic crystalline constituent in human-calcified hard tissues such as bone and teeth. Therefore, many studies have employed CaHAP with high-performance liquid chromatography (HPLC) for separating biopolymers.[9–11] Spherical CaHAP can be expected to attain a high separation efficiency with HPLC due to its large packing fraction. However, to our knowledge, spherical CaHAP has been produced only by a spray drying technique.[12] Therefore, development of a new technique for producing spherical CaHAP particles with a narrow size distribution from an aqueous solution phase is desired. In the current study, we extended our investigation on the preparation and characterization of metal phosphate particles obtained by a homogeneous precipitation method to produce spherical CaHAP. The spherical CaHAP particles obtained by aging a mixed solution of $CaSO_4$–NaH_2PO_4 in the presence of urea and a surfactant were characterized in terms of their structure, composition, crystallinity, specific surface area, and ultramicroporosity.

Experimental Section

All the chemicals used were a guaranteed reagent grade from Wako Co. Ltd. and were used without further purification. Calcium phosphate particles were prepared using a solution of $CaSO_4$, NaH_2PO_4, urea (1 mol/dm^3), and CTAC (1.0×10^{-2} mol/dm^3) in a 20 cm^3 Teflon-lined screw-capped Pyrex test tube aged in a turbulent air circulation oven at 80 and 100 °C for 1 h to 6 days, using essentially the same recipe for

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cobalt and nickel phosphate particle production.[5-8] The concentration of $CaSO_4$ was varied from 31.6×10^{-5} to 5×10^{-3} mol/dm^3. The concentration of NaH_2PO_4 was varied from 31.6×10^{-5} to 31.6×10^{-3} mol/dm^3. The precipitates produced were washed thoroughly with distilled water and finally dried in vacuo at room temperature for 16 h.

X-ray diffraction measurements were taken using a diffractometer (XRD, Rigaku UO-200B) using Cu Kα radiation (30 kV, 15 mA). Infrared spectra of CaHAP in KBr pellets were measured using a Fourier transform intrared spectrometer (FTIR; Horiba FT-200). The CO_3^{2-} ion concentration in the particle was estimated using a calibration curve which was made using the intensity of the IR bands of the CO_3^{2-} ions of $CaCO_3$ as a standard material. The accuracy of this method was ±0.2 wt %. Additional IR spectra were recorded *in situ* using an FTIR spectrophotometer (Degilab FTS15E) with a PbSe detector having a high sensitivity in the near-IR region. The particles were pasted on a glass plate and were pretreated in a vacuum cell at temperatures varying from 25 to 400 °C for this measurement.

Ca and P contents of the particles were assayed respectively using inductively coupled plasma spectroscopy (ICP, Seiko SPS1200VR) and using the molybdenum blue method.[13] Scanning and transmission electron microscopy (SEM, JEOL JSM-840A, TEM; JEOL 1200) was used to ascertain the morphology of the particles. The adsorption isotherms of N_2 were measured at liquid N_2 temperature using a computerized volumetric apparatus constructed in our laboratory with the error of ±0.2 wt %.[14] A computerized automatic gravimetric instrument designed in our laboratory was employed for determining the adsorption isotherms of H_2O at 25 °C, the sensitivity being 10 μg.[15] Before any gas adsorption measurements were taken, the samples were pretreated at 10^{-2} Pa at temperatures varying from 25 to 400 °C for 2 h. Before outgassing at 100 °C for 2 h, several samples were treated in air at temperatures varying from 200 to 1000 °C for 2 h. TG-DTA measurements were carried out with a thermobalance (Seiko TG-DTA 220) connected to a data station (SSC/5200H). Sensitivity of the equipment was determined to be ±0.2 μg for TG and ±0.06 μV for DTA.

Results and Discussion

Morphology of Precipitated Particles. The size and shape of the particles strongly depended on the concentration of the reactants in the starting solution and aging temperature. Figure 1 gives the morphology of the precipitates at various concentrations of $CaSO_4$ and NaH_2PO_4 produced after aging at 80 and 100 °C. A precipitate was not obtained at concentrations of $CaSO_4$ below 1.0×10^{-3} mol/dm^3. It was seen that changing the aging temperature remarkably controlled the morphology of the precipitates. Platelet and needle aggregated particles were produced at 80 °C while the spherical particles appeared at 100 °C in addition to the platelet and needle aggregated particles. Typical TEM and SEM micrographs of platelet, needle aggregated and spherical particles are given in Figure 2. It must be noted that the spherical particles were produced only at 100 °C. The high-magnification SEM picture of the spherical particles in Figure 2E seems to indicate that these particles are formed by the aggregation of smaller platelet particles. Since the aim of this study is to develop a preparation method for spherical CaHAP particles, we employed the spherical particles formed at $[CaSO_4] = 2.0 \times 10^{-3}$ mol/dm^3, $[NaH_2PO_4] = 7.9 \times 10^{-4}$ mol/dm^3, [urea] = 1 mol/dm^3 and $[CTAC] = 1.0 \times 10^{-2}$ mol/dm^3 as displayed in Figure 2E for the following experiments.

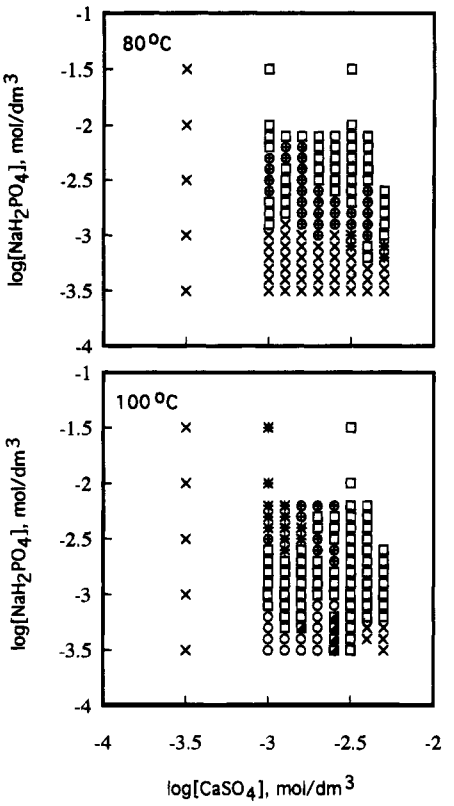

Figure 1. Concentration domains of solutions containing different concentrations of $CaSO_4$ and NaH_2PO_4 in the presence of urea (1 mol/dm^3) and CTAC (1.0×10^{-2} mol/dm^3). Aging time was 3 h. (×) no precipitates, (*) aggregated needles, (⊕) aggregated needle and platelets, (□) platelets, (○) spheres, (◪) spheres and platelets.

Characterization of Spherical Calcium Phosphate Particles. The spherical particles produced exhibited the characteristic peaks of CaHAP in their XRD patterns as shown in Figure 3a. The spherical particles have a broad size distribution from 3 to 15 μm and their average diameter is 9.6 ± 3.1 μm. It should be noted that the spherical particles are agglomerates of small platelet particles. The mean edge length of these platelet particles, assuming square plates, is estimated to be $1.8 \times 2.0 \times 0.2$ μm^3. The average crystallite sizes of the (300), (211), and (002) planes of the particles estimated from XRD patterns by using the Scherrer equation were 40, 57, and 47 nm, respectively. These values were not only smaller than the size of the spherical particles but also smaller than that of the agglomerated platelet particles, indicating that the particles are polycrystalline. Figure 4 shows the change of pH during preparation of the spherical CaHAP particles aged at 100 °C. The pH steeply increased up to 9.5 within 3 h of aging through the decomposition of urea and became almost constant at 9.8 after aging for 4 h. This fact corresponds with the fact that CaHAP

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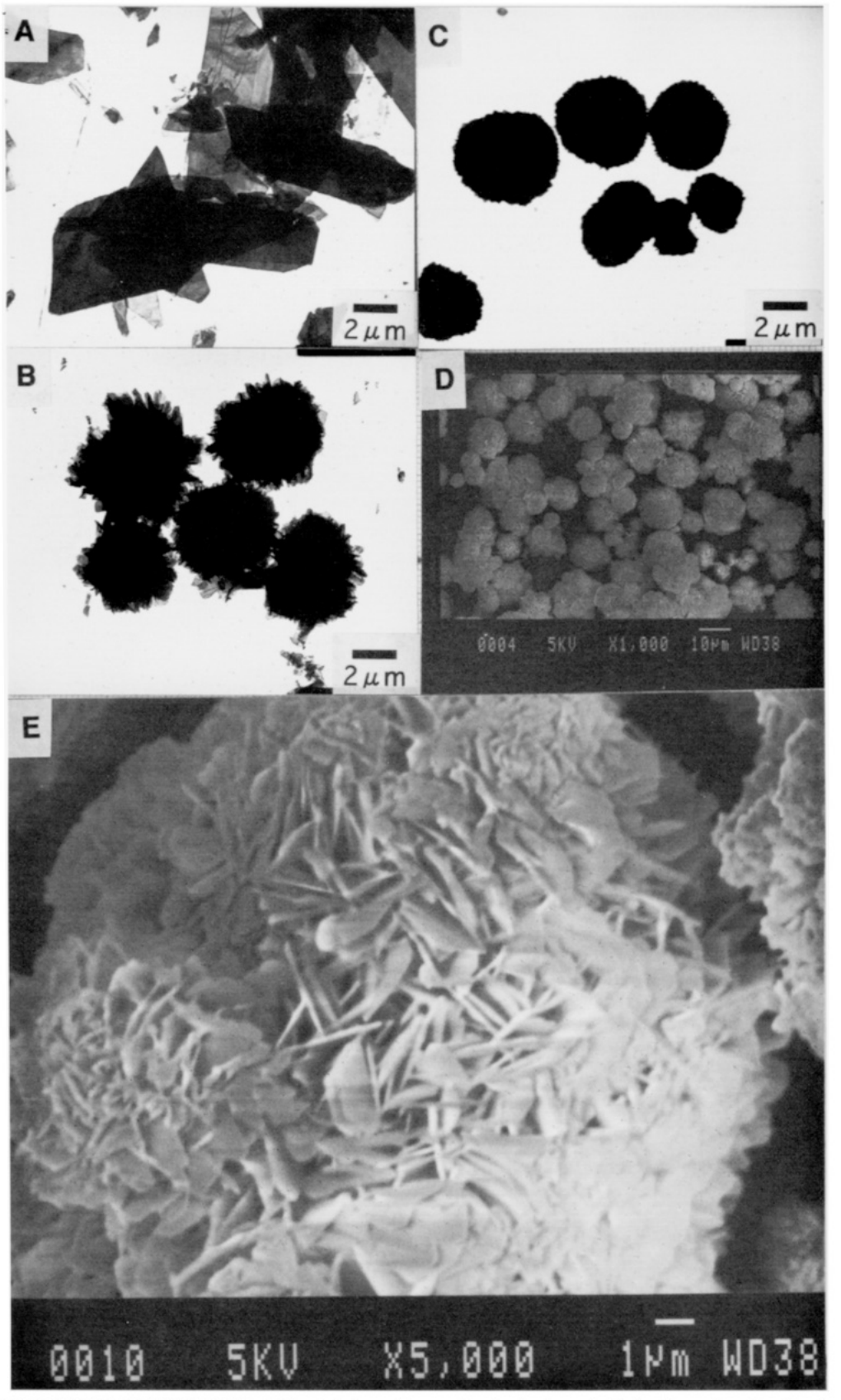

Figure 2. Electron micrographs of platelets, aggregated needles and spherical precipitates formed under fixed concentration of urea (1 mol/dm^3) and CTAC (1.0×10^{-2} mol/dm^3). Aging temperature was 100 °C. (A) Platelets precipitated at $[CaSO_4] = 3.2 \times 10^{-3}$ mol/dm^3 and $[NaH_2PO_4] = 6.3 \times 10^{-3}$ mol/dm^3. (B) Aggregated needles precipitated at $[CaSO_4] = 1.3 \times 10^{-3}$ mol/dm^3 and $[NaH_2PO_4] = 4.0 \times 10^{-3}$ mol/dm^3. (C) Spheres precipitated at $[CaSO_4] = 2.0 \times 10^{-3}$ mol/dm^3 and $[NaH_2PO_4] = 7.9 \times 10^{-4}$ mol/dm^3. (D) SEM micrograph of sample (C). (E) High magnification SEM micrograph of sample (C).

particles are produced at a pH > 8.0 as reported by many investigators.[16-20] Bosky and Posner, in their study of the precipitation of calcium phosphates from the reaction of Ca^{2+} and PO_4^{3-} ions in aqueous media, reported that CaHAP is precipitated directly from solution when the product of the molar concentrations

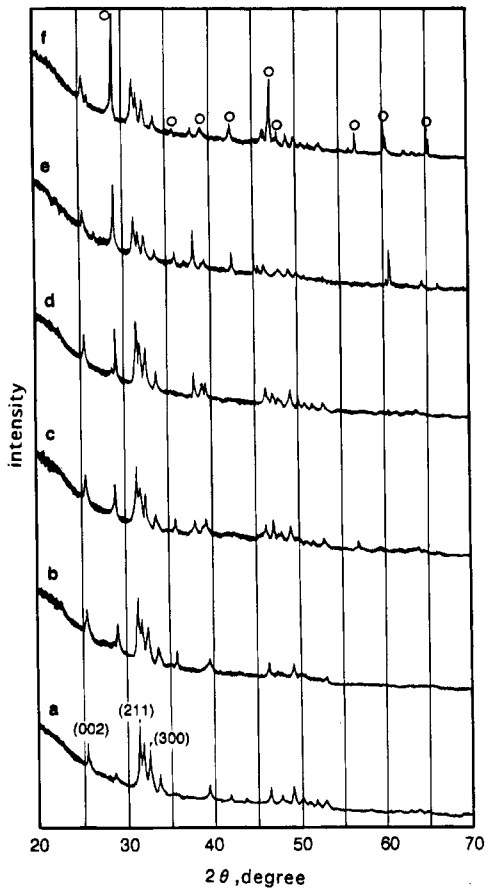

Figure 3. XRD patterns of spherical calcium phosphate particles precipitated at various aging periods. Aging temperature was 100 °C. $[CaSO_4] = 2.0 \times 10^{-3}$ mol/dm^3, $[NaH_2PO_4] = 7.9 \times 10^{-4}$ mol/dm^3, [urea] = 1 mol/dm^3, and [CTAC] $= 1.0 \times 10^{-2}$ mol/dm^3. Aging periods: (a) 3 h, (b) 6 h, (c) 1 day, (d) 2 days, (e) 4 days, (f) 6 days. The open circle represents the characteristic peaks of $CaCO_3$ (calcite).

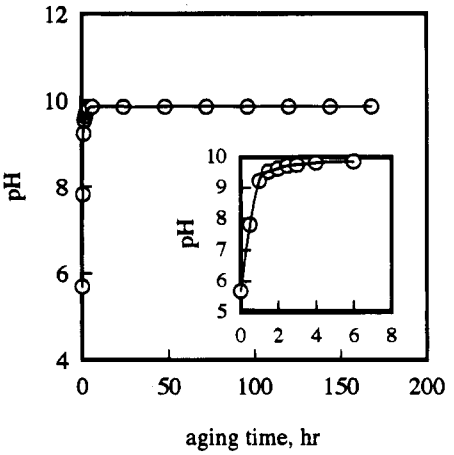

Figure 4. Change in the solution pH with aging time. $[CaSO_4] = 2.0 \times 10^{-3}$ mol/dm^3, $[NaH_2PO_4] = 7.9 \times 10^{-4}$ mol/dm^3, [urea] = 1 mol/dm^3 and [CTAC] $= 1.0 \times 10^{-2}$ mol/dm^3.

of Ca^{2+} and PO_4^{3-} ions, $[Ca^{2+}][PO_4^{3-}]$, ranges from 0.25×10^{-6} to 1.67×10^{-6} (mol/dm^3)^2.[21] The product of $[Ca^{2+}][PO_4^{3-}]$ in the present study is 1.58×10^{-6} (mol/dm^3)^2, which is consistent with the results of Bosky and Posner. Also Aoki and Kato found that CaHAP particles are formed at pH > 6.0 and 100 °C,[22] supporting our observations.

In the course of studying the formation mechanism of the spherical CaHAP particles, SEM studies were performed on the samples that had precipitated after various aging periods. The photos are shown in Figure 5. No precipitation was observed when the aging time was less than 40 min. After aging for 1 h, the spherical particles in the 3–15 μm diameter range appeared abruptly without observation of fine primary particles and maintained their shape and size until 3 h of aging had passed. This fact implies that the primary particles aggregated rapidly reducing the interfacial free energy. After aging for 6 h, however, needlelike and cubic particles appeared. Comparing to the XRD patterns of these samples as shown in Figure 3b–f, these needlelike and cubic particles can be assigned to $CaCO_3$ (calcite). The characteristic peaks of $CaCO_3$ marked by the open circles emerged after the sample had been aged for 4 h. Since the decomposition of urea produces CO_2, it is understandable that $CaCO_3$ particles are formed by the reaction of dissolved CO_2 in basic medium with Ca^{2+} ions dissolved from the precipitated spherical CaHAP particles and/or with residual Ca^{2+} ions. Therefore, particular attention should be given to the effect of CO_2 when forming CaHAP.

It is known that there are two kinds of biological apatites containing CO_3^{2-} ions in different sites;[23–25] one is the A-type carbonate hydroxyapatite (CAP) in which CO_3^{2-} ions are substituted for OH^- ions, and the other is the B-type CAP in which CO_3^{2-} ions are substituted for PO_4^{3-} ions. The IR spectra of CaHAP in KBr after calcination of samples in air at 25, 100, 200, 400, 600, 800, and 1000 °C are shown in Figure 6. The spectra contain the 1035, 960, 603, and 565 cm^{-1} bands of PO_4^{3-} ions and the 1458, 1421, and 873 cm^{-1} bands of CO_3^{2-} ions along with a broad peak of adsorbed water centered at 3400 cm^{-1}. By increasing the pretreatment temperature, the intensity of the bands of the CO_3^{2-} ions decreased, and these bands completely disappeared with heat treatment at 1000 °C. Since these three bands of the CO_3^{2-} ions are characteristic to the B-type CAP,[26] the present synthetic CaHAP has been assigned to the B-type CAP.

TG-DTA curves of the spherical CaHAP particles are shown in Figure 7. Weight loss is observed up to 250 °C with a small endothermic peak in DTA, implying the elimination of adsorbed water. Furthermore, the weight loss continues until 1000 °C with a substantial weight loss at 635–675 °C accompanied by many endothermic peaks. Comparing the TG curve to the IR spectra in Figure 6, this weight loss of 7 wt % from 250 to 1000 °C is consistent with the elimination of CO_3^{2-} ions and bound water. It has been reported that the composition of B-type CAP is $Ca_{10-x}Na_x(PO_4)_{6-y}(CO_3)_{4y/3}(OH)_{2-x+y/3}$.[23] The carbonate content in the spherical particles used in the present study has been estimated to be 4.8 wt % by FTIR measurement in a KBr pellet. Also, the calcium to phosphorous molar ratio of the particles was calculated to be 1.59. Because the difference between the weight loss of 7 wt % and carbonate content of 4.8 wt % is the bound water, the formula of this CaHAP

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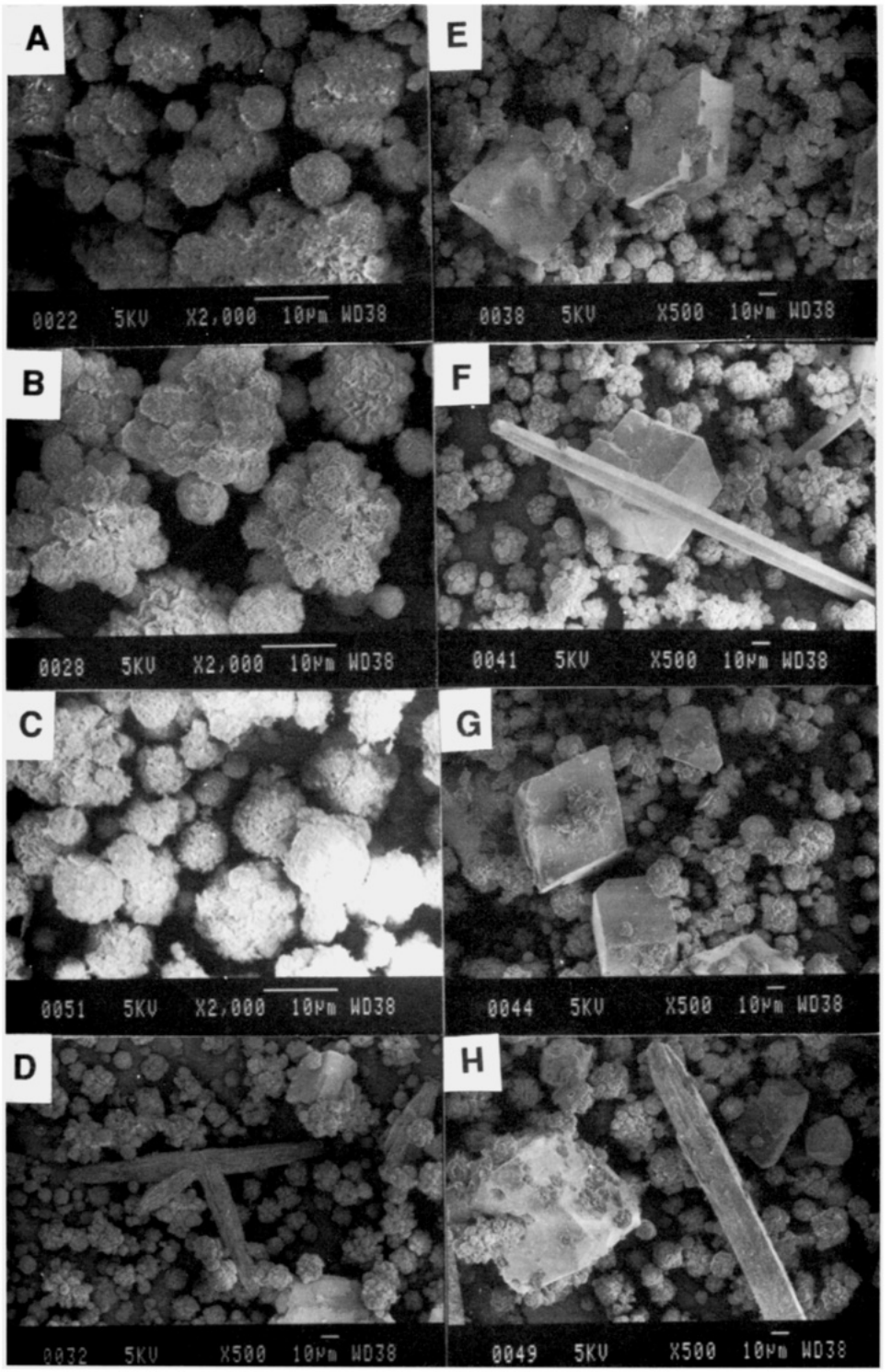

Figure 5. SEM micrographs of precipitates formed at various aging periods. Aging temperature was 100 °C. $[CaSO_4] = 2.0 \times 10^{-3}$ mol/dm^3, $[NaH_2PO_4] = 7.9 \times 10^{-4}$ mol/dm^3, [urea] = 1 mol/dm^3 and $[CTAC] = 1.0 \times 10^{-2}$ mol/dm^3. Aging periods: (A) 1 h, (B) 2 h, (C) 3 h, (D) 6 h, (E) 1 day, (F) 2 days, (G) 4 days, (H) 6 days.

specimen could be given as $Ca_{8.5}Na_{1.5}(PO_4)_{5.4}(CO_3)_{0.8}$-$(OH)_{0.7}$·$1.2H_2O$.

The morphology and crystal structure of the spherical CaHAP particles were sustained up to 1000 °C, suggesting a high thermal stability of the CaHAP. It can be seen from Figure 6 that a sharp peak at 3568 cm^{-1} increased in intensity with increasing calcination temperature in air. Ishikawa et al. have assigned the peak at 3570 cm^{-1} to the lattice OH^- ions in the CaHAP particles.[27] Hence, the 3568 cm^{-1} band can be presumed to be of the same origin. For confirmation, we measured *in situ* IR spectra of the spherical CaHAP particles pasted on a glass plate set in a vacuum cell, and a hydrogen–deuterium isotope exchange was carried out with five cycles of adsorption of heavy water into the sample at 1.33×10^{-3} Pa and 25 °C for 5 min. From this H–D isotope exchange, the 3568-cm^{-1} band slowly changed to a band at 2630 cm^{-1}. The agreement of the isotope ratio of this band (3568/2630 = 1.357) to the theoretical isotope ratio (1.374) provides evidence that

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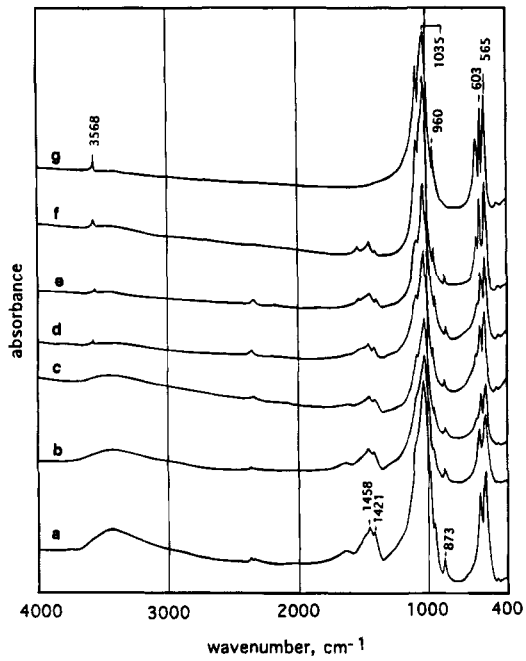

Figure 6. FTIR spectra of spherical calcium hydroxyapatite particles calcined at various temperatures in air for 2 h. Pretreatment temperature (°C): (a) 25, (b) 100, (c) 200, (d) 400, (e) 600, (f) 800, (g) 1000.

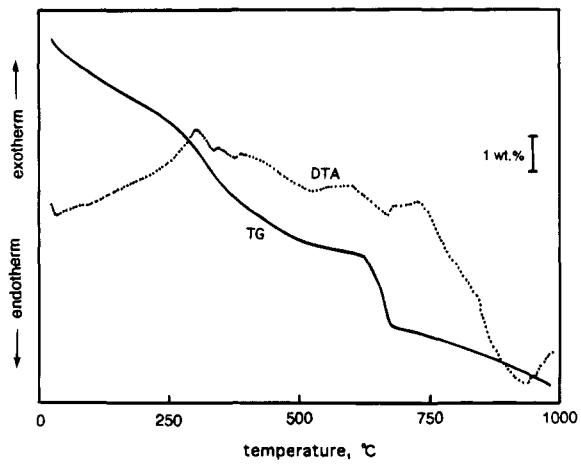

Figure 7. TG-DTA curves of spherical calcium hydroxyapatite particles. $[CaSO_4] = 2.0 \times 10^{-3}$ mol/dm^3, $[NaH_2PO_4] = 7.9 \times 10^{-4}$ mol/dm^3, [urea] = 1 mol/dm^3, and [CTAC] = 1.0×10^{-2} mol/dm^3.

the 3568-cm^{-1} band corresponds to the lattice OH^- ions.

We found in previous work that cobalt phosphate particles have slit-shape micropores and adsorb H_2O molecules selectively over N_2 molecules.[6] Therefore, we were interested to know whether the spherical CaHAP particles produced in this study exhibit a similar adsorption selectivity or not. To determine this, we performed adsorption experiments with N_2 and H_2O. Type II isotherms of the BDDT classification[28] were obtained for both adsorptive molecules. Figure 8 displays the typical adsorption isotherms of N_2 for the particles, pretreated at 25, 50, and 150 °C in vacuo and 200 and 600 °C in air, and their pore-size distribution curves computed from these isotherms using the Cranston–Inkley method, respectively.[29] The steep increase of the

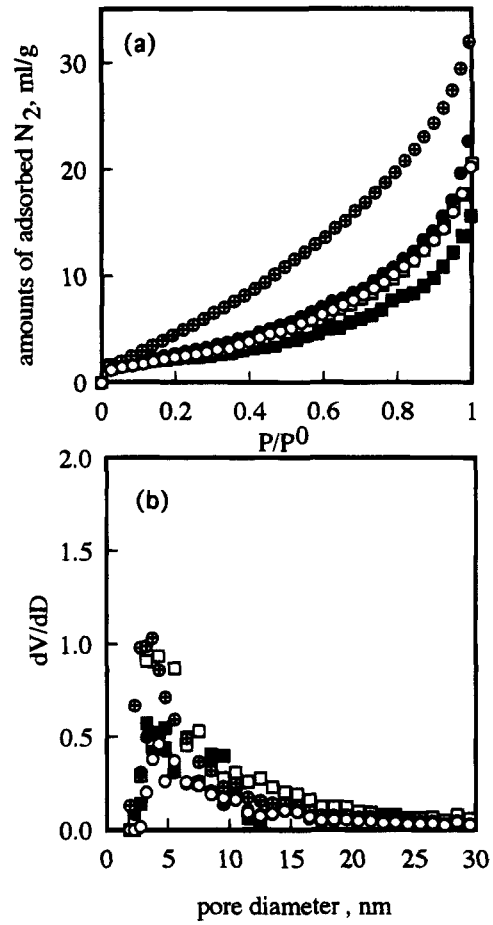

Figure 8. Adsorption isotherms of N_2 (a) and pore-size distribution curves (b) for spherical hydroxyapatite particles pretreated at various conditions. Pretreatment temperature: (○), 25, (⊕) 50, (●) 150, (□) 200, (■) 600 °C, (○, ⊕, ●) in vacuo, (□, ■) in air.

adsorption isotherms of N_2 at higher relative pressure indicates the existence of macropores.[30] Figure 8b also leads us to conclude that there are a few mesopores of diameter ranging from 2 to 20 nm, but no micropores have been produced with any pretreatment conditions. Since the specific surface areas measured by the N_2 BET method are in fair agreement with the specific surface area estimated by the size of platelet particles as will be shown in the next paragraph, these meso- and macropores seem to be produced mainly by the interstices of agglomerated platelet particles. To quantitatively investigate the microporosity of the particles, we evaluated the specific surface areas of the particles from the adsorption isotherms of N_2 and H_2O (abbreviated respectively as S_n and S_w) by fitting the data to the BET equation.[30] In this calculation, we assumed the cross-sectional areas of N_2 and H_2O molecules to be 0.162 and 0.108 nm^2, respectively.[30] The obtained S_w, S_n, and S_w/S_n ratios are plotted in Figure 9 as a function of the pretreatment temperature.

The S_n values of the particles pretreated in vacuum ranged from 9.0 to 25.8 m^2/g and show a maximum at a pretreatment temperature of 50 °C. These values are much larger than the specific surface area of 0.1 m^2/g expected for spherical particles but are close to that of

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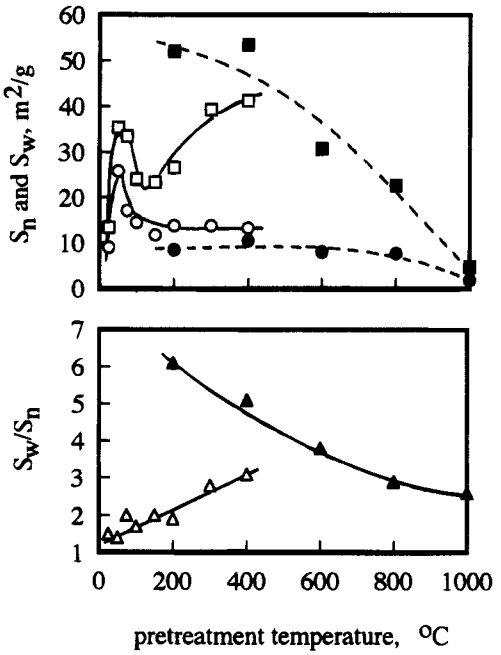

Figure 9. Plots of S_n and S_w (upper) and S_w/S_n ratio (lower) vs pretreatment temperature for spherical calcium hydroxyapatite particles. (○, ●) S_n, (□, ■) S_w, (△, ▲) S_w/S_n, (○, □, △) in vacuo, (●, ■, ▲) in air.

the 4.2 m^2/g of platelet particles which were estimated from their mean particle sizes assuming the density of CaHAP to be 3.16 g/cm^3. This is clear evidence that the spherical CaHAP particles are agglomerates of the small platelet particles as ascertained by the SEM and XRD measurements described before. A similar maximum is observed for the S_w values when aged at 50 °C. However, the S_w values are larger than S_n values and increase above 150 °C. Another interesting finding is that the S_w/S_n ratio gradually increased with elevating pretreatment temperature from 25 to 400 °C. Since the S_w/S_n ratio is a measure of the number of ultramicropores into which can take H_2O molecules but not N_2 ones, this result indicates that the formation of ultramicropores in the small platelet particles is enhanced by an increase in the pretreatment temperature in vacuo. The rod-shaped CaHAP particles with dimensions of 24 × 72 nm^2 that were produced by aging the precipitates from a reaction of $Ca(OH)_2$ and H_3PO_4 have no such selectivity.[27] More pronounced selectivity of H_2O adsorption was observed for the particles calcined in air as shown in Figure 9. The S_w/S_n ratio of 6.1 when pretreated at 200 °C decreased to 2.6 with increasing calcination temperature up to 1000 °C. This large S_w/S_n ratio implies that the formation of ultramicropores is enhanced by calcination in air. The reduction of the S_w/S_n ratio would be due to pore closure of ultramicropores by sintering. Because the S_n values represent the platelet particles as described before, it seems reasonable to consider that the ultramicropores were produced in each platelet particle. Here it should be restated that the highest ultramicroporosity is obtained for the spherical CaHAP particles by calcining in air at 200 °C. Owing to this characteristic ultramicroporosity, the spherical CaHAP particles could be used in applications such as adsorbents, catalyst carriers, fillers, etc.

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