Synthesis and characterization of calcium hydroxyapatite (Hap) and Ti(IV)-substituted Hap particles by forced hydrolysis of $\text{Ca}(\text{OH})_2\text{-Na}_4\text{P}_2\text{O}_7$ solution

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The productions of calcium hydroxyapatite (Hap) and Ti(IV)-doped Hap (TiHap) particles were examined by forced hydrolysis reaction of $\text{Ca}(\text{OH})_2$ -pyrophosphate (pp: $\text{P}_2\text{O}_7^{4-}$) and $\text{Ca}(\text{OH})_2$ -pp- TiCl_4 mixed solutions under 100 and 140°C, respectively, and precipitated particles were characterized by various physicochemical techniques. The degree of hydrolysis of pp ions was remarkably improved and the yields of the precipitates by using the pp ions was increased rather than the tpp one. No particles were produced at higher concentration of pp ions. On the other hand, ellipsoidal aggregated and rod-like particles were produced at other concentration domains. The Hap particles produced were ellipsoidal secondary particles with ca. 210–240 nm in the particle length which were composed by aggregation of small primary single crystal particles with ca. 20–50 nm in length. The TiHap particles facilitated at atomic ratio of $\text{Ti}/(\text{Ca}+\text{Ti})$ [$X_{\text{Ti}} \leq 0.20$] were ellipsoidal secondary particles with ca. 240–380 nm in length composing by aggregation of small primary particles with ca. 30–100 nm in length, while they were changed to very fine particles with ca. 5–10 nm in diameter along with small amounts of large rod-like particles at $X_{\text{Ti}} = 0.3$. The highly crystallized pure TiHap particles were produced at $X_{\text{Ti}} \leq 0.15$, while the Hap structure was almost disappear at $X_{\text{Ti}} = 0.2$. All the TiHap particles produced at $X_{\text{Ti}} \leq 0.2$ were phosphorus deficient. The diffuse reflectance UV spectra of TiHap particles revealed that these particles have a UV absorption property, especially fabricated at $X_{\text{Ti}} = 0.05$. The highly crystallized TiHap particles ($0.05 \leq X_{\text{Ti}} \leq 0.15$) had also large specific surface area.

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1. Introduction

Calcium hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, designated as Hap, is a major inorganic component of animal hard tissues and is used in bio-ceramics, chromatographic adsorbents, acid and base catalysts, tooth paste and other products.^{1)–4)} Further, Wakamura has developed Ti(IV)-doped Hap (expressed as TiHap). The TiHap particle possesses a photocatalytic activity for decomposition of acetaldehyde and albumin under ultra violet (UV) irradiation.⁵⁾ Recently, the authors also reported on the decomposition behaviors of proteins by TiHap under UV irradiation.^{6)–9)} Although Hap is one of the metal phosphates, controlling the particle shape and size is very difficult because of its low solubility product. Since the hydrolysis of condensed phosphate ions, such as diphosphate (pyrophosphate, pp: $\text{P}_2\text{O}_7^{4-}$) and triphosphate (tripolyphosphate, tpp: $\text{P}_3\text{O}_{10}^{5-}$) ions, is endothermic process,^{10)–12)} the phosphate (orthophosphate: PO_4^{3-}) ions can be produced slowly by heating the solution, so called as a forced hydrolysis reaction. Therefore, it can be expected that the forced hydrolysis reaction of the mixed solution of Ca(II) and condensed phosphate ions can be applied for producing new calcium phosphate particles with unique shape and inner structure. As following this idea, the authors investigated in a previous study on the formation of calcium phosphate particles by using $\text{Ca}(\text{OH})_2$ -tpp mixed solution.¹³⁾ The authors disclosed that Hap particles with ellipsoidal shape (ca. 100–150 nm) composing by

aggregation of small primary particles with ca. 20 nm in length were prepared from this technique. Since the ellipsoidal secondary Hap particles were fabricated by the aggregation mechanism, these Hap particles exhibited a high specific surface area. We also succeeded the production of Ti(IV)-substituted calcium hydroxyapatite (TiHap) particles by using this forced hydrolysis reaction of aging $\text{Ca}(\text{OH})_2$ -tpp system.¹⁴⁾ By aging $\text{Ca}(\text{OH})_2$ and tpp mixed solution with various concentrations of TiCl_4 at 100°C for 18 h, the ellipsoidal secondary TiHap particles with ca. 100–150 nm in length were produced. The produced TiHap particles had a UV absorption property. However, since the degree of hydrolysis of tpp ions is low, the tpp ions did not give PO_4^{3-} ions in satisfactory yields for both the productions of Hap and TiHap. To improve this problem, it can be expected that pp ions is suitable for using the reaction, because pp ions condensed only two PO_4^{3-} ions and readily hydrolyze. In the present study, therefore, we attempted the productions of Hap and TiHap particles by forced hydrolysis reactions of $\text{Ca}(\text{OH})_2$ -pp and $\text{Ca}(\text{OH})_2$ -pp- TiCl_4 mixed solutions instead of $\text{Ca}(\text{OH})_2$ -tpp and $\text{Ca}(\text{OH})_2$ -tpp- TiCl_4 ones employed in the previous studies.^{13),14)} The produced particles were characterized by various physicochemical techniques. The knowledge in the present study obtained must contribute to develop new preparation method for Hap and TiHap particles with controlled morphology and high yields. To the best of our knowledge, except for our research group, no literature had been reported on the formation of Hap and TiHap particles by using the forced hydrolysis reaction of condensed phosphate ions. Hence, the development of this new method to be aspired.

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2. Experimental

2.1 Materials

Following the method reported by the authors in the previous paper,¹³⁾ we produced the calcium phosphate particles by aging a solution of $\text{Ca}(\text{OH})_2$ [1.0×10^{-3} – 1.0×10^{-2} mol/dm³] and Na_4pp [1.0×10^{-3} – 1.0×10^{-1} mol/dm³] in a 20-cm³ Teflon-lined screw-capped Polyethylene (PE) test tube. To facilitate the aging, the test tubes were allowed to stand for 18 h at 100°C in an air turbulent oven. We also fabricated Ti(IV) substituted Hap particles by aging $\text{Ca}(\text{OH})_2$ -pp mixed solution with various concentrations of TiCl_4 in a 20-cm³ Teflon-lined screw-capped Pyrex glass test tube. To enhance the incorporation of Ti(IV) ions in the crystal structure, the aging temperature was raised and fixed at 140°C in this procedure. The atomic ratio $\text{Ti}/(\text{Ti}+\text{Ca})$ (abbreviated as X_{Ti}) was ranged from 0 to 0.30. Since this high temperature, we employed Pyrex glass test tube in this experiment. The resulting particles were thoroughly washed by filtration with pure water and finally dried in air-oven at 70°C for 18 h. The solution pH before and after aging was monitored at room temperature. All the solutions were prepared by using pure water free from CO_2 . Pure waters from Elix (Millipore) had conductivities ca. 0.06 $\mu\text{S}/\text{cm}$. Guaranteed reagent grade chemicals from Wako Pure Chemical Co. Inc. (Osaka, Japan) were used without further purification.

2.2 Characterization

The resulting particles were characterized by transmission or scanning electron microscope (TEM; JEOL JEM-2100 or SEM; Hitachi High-Tech SU1510), thermogravimetric and differential thermal analysis (TG-DTA; SII-7200), powder X-ray diffraction measurement (XRD; Rigaku Rad-RC), adsorption experiments of N_2 . The adsorption isotherms of N_2 were measured at liquid N_2 temperature with an ordinary house built automatic volumetric flow method using a Baratron diaphragm-type manometer attaching a mass flow meter. The degree of confidence on specific surface area (SSA) measured by this apparatus was within 2%. Prior to these N_2 adsorption measurements, the samples were evacuated at 100°C for 2 h. Since only the sample F in Fig. 1 had small SSA, the SSA value of this sample was determined by BELSORP-miniIII from MirotacBEL corp. The IR spectra of the particles in vacuo were taken by a self-supporting disc method using a FTIR spectrometer (Nicolet, Protégé 460) with a sample cell capable of outgassing at various temperatures. The self-supporting disc in 1 cm in diameter was produced by pressing 50 mg particles at 30 MPa. The chemical composition of the precipitated particles (concentration of calcium, phosphorus and titanium) was determined by dissolving a few milligrams in

concentrated nitric or sulfuric acids. The solutions were diluted and the calcium, phosphorus and titanium concentrations were determined by an inductively coupled plasma atomic emission spectroscopy (ICP-AES; SII SPS3520UV-2). Diffuse reflection UV-vis spectra of TiHap particles were recorded by an UV-vis spectrometer (Shimadzu UV-3600) and an integrating sphere. For the measurement, 0.175 g of the samples were fully mixed with 3.325 g of BaSO_4 used as diluents.

3. Results and discussion

3.1 Preparation and characterization of Hap particles

Figure 1 displays (a) the solution pH and (b) morphology of the particles precipitated after aging the solution in the PE test tube for 18 h at 100°C. The solution pH of 12.09–12.54 was dropped 0.2–0.4 unit by the reaction, this is less than the tpp system (0.4–2.3 unit).¹³⁾ It has reported that the hydrolysis of pp and tpp ions is expressed as following two reactions (1) and (2).¹⁵⁾

Since the production of H^+ in the pp system is less than the tpp one, the pH drop in the pp system is small. Anyway, the pH drop observed in this experiment proves that the pp ions were hydrolyzed.

Figures 2 and 3 show the TEM or SEM pictures and XRD patterns of the typical particles precipitates at A–F points in Fig. 1 (displayed by grey circles). Clearly, no particles are produced at

Fig. 1. (a) The pH of mixed solutions of $\text{Ca}(\text{OH})_2$ and Na_4pp for aging at 100°C. Upper and lower numbers are solution pH before and after aging, respectively. (b) Particle shape of precipitates after aging. R; rod-like and EA; ellipsoidal aggregates. Bar in the circles indicate no precipitate after aging. Grey circles indicate the A–F samples investigated in this work.

Fig. 2. TEM pictures of typical samples A–F in Fig. 1. F' is a SEM picture of sample F.

higher concentration of pp ions. On the other hand, ellipsoidal aggregated (EA) and rod-like particles (R) are produced at other concentration domains. However, there was no large difference was observed among the particles produced at each same $\text{Ca}(\text{OH})_2$ concentration line. Hence we characterized typical A–F particles in the following section. It should be emphasized that Hap particles produced at A–E are the ellipsoidal particles with ca. 210–240 nm in the particle length which were composed by aggregation of much smaller particles with ca. 20–50 nm in length. It should be defined here that the large ellipsoidal and small particles are regarded, respectively, as secondary and primary particles. The particle sizes of secondary and primary particles were determined by counting over 300 particles in 10-fold enlarged TEM pictures for each system. Indeed, it has been reported that the aggregation of Hap nanoparticles in secondary unit is driven by dipolar forces between (001) faces.¹⁶⁾ This aggregation will be enhanced by the presence of pp molecules unhydrolyzed. These pp molecules will be adsorbed on the primary ellipsoidal particle surfaces and the aggregation of primary particles may be enhanced as well as the effects of tpp ones as the authors reported for the $\text{Ca}(\text{OH})_2$ -tpp system.¹³⁾ Clearly in Fig. 3, A–E particles with EA morphology exhibit characteristic peaks of Hap (JCPDS 9-432), though sample F shows $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (JCPDS 41-0488) along with small amounts of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (JCPDS 26-0306).

Figure 4 shows the average particle length and width of A–E Hap particles. These particles have 210–240 nm and 100–110 nm in length and width, respectively. The crystallite size from (002) face (D_{002}) from at $2\theta = 25.9^\circ$ was calculated by the Scherrer's equation and the results are plotted in Fig. 4 by filled circle. Since the D_{002} values are smaller than the average length of each parti-

cle, these A–E particles can be regarded as a polycrystalline. Moreover, the D_{002} value of 40–80 nm is identified with the size of primary particles. It can be concluded, therefore, the secondary EA particles of A–E are composed by the aggregation of single crystal primary particles.

The specific surface area (SSA) of the samples was calculated by applying the BET equation to the N_2 adsorption isotherms measured using a cross-sectional area of N_2 molecule of 0.162 nm.¹⁷⁾ The S_N values are also listed in **Table 1**. These values are ranged among 75.6–101.3 m²/g except for the sample F. The specific surface area with 20 nm in diameter is calculated to be 95 m²/g from Eq. (3).

$$S = 6/D\rho \quad (3)$$

where D and ρ are the diameter (20 nm) and density (3.16 g/cm³) of the primary particles by assuming they are rigid sphere. The specific surface areas of 75.6–101.3 m²/g measured are fairly agreed with the estimated value. This result indicates that the primary particles in the secondary particles are loosely aggregated.

The concentrations of calcium ([Ca]) and phosphorus ([P]) in the particles assayed are listed in Table 1 together with the Ca/P atomic ratios of the samples. The [Ca] values are less than the theoretical values of Hap (as shown in the bottom line), especially for samples D and E. On the contrary, [P] values are fairly coinciding with the theoretical one. Hence the Ca/P atomic ratios exhibit 1.63–1.47, those are less than the theoretical value of Hap (1.67), indicating that the A–E particles are calcium deficient. The yields of the precipitates produced in each tube are also listed in the last column of Table 1. The yield values of 9.4–25.6 mg/tube is extremely higher than those obtained for tpp systems (3–5 mg/tube) as reported in our previous paper.¹³⁾ This result implies that the degree of hydrolysis of pp ions is larger than tpp ones as we expected. It should be noted that the yields of precipitates are increased from A to F, coinciding with the decrease of $\text{Ca}(\text{OH})_2$ concentration. This result may indicates that the for-

Fig. 3. XRD patterns of samples A–F in Fig. 1.

Fig. 4. Particle length (□), width (○) and their crystallite size from Hap (002) face (●) of the Hap samples A–E in Fig. 1.

Table 1. Results of elemental analyses, SSA and yields for the A–F particles in Fig. 1

	Ca [mmol/g]	P [mmol/g]	Ca/P	Specific surface area (SSA) [m ² /g]	Yields* [mg/tube]
A	9.368	5.743	1.63	75.6	9.4
B	9.436	5.991	1.58	85.7	10.9
C	9.384	5.887	1.59	111.6	13.0
D	9.082	5.823	1.56	101.0	17.4
E	8.744	5.969	1.47	101.3	21.6
F	7.112	6.900	1.03	9.1	25.6
Theoretical values of Hap	9.954	5.972	1.667		

*The yields values represent the weight of precipitates per each Polyethylene test tube.

Fig. 5. (a) TG and (b) DTA curves of samples A–F in Fig. 1. Inset in TG is enlarged picture at 600–900°C.

Fig. 6. in-situ FTIR spectra of (a) samples A–F as shown in Fig. 1 and (b) TiHap particles produced at various X_{Ti} values.

mation of Hap particles are smoothly proceed under low $\text{Ca}(\text{OH})_2$ concentration because the production of PO_4^{3-} ions by hydrolysis reaction of pp ions is restricted and slowly progressed.

Figure 5 shows the TG–DTA curves of the A–F particles. The A–E particles of Hap possess a small TG weight loss at ca. 750–950°C as shown by an inset in Fig. 5. Berry¹⁸⁾ and Monma et al.¹⁹⁾ have reported for nonstoichiometric Hap that the large weight loss up to ca. 700°C is caused by the release of adsorbed and bound H_2O molecules and evolve a small amount of H_2O molecules by dehydration of HPO_4^{2-} ions while the smaller weight loss above 700°C resulted from a reaction of the $\text{P}_2\text{O}_7^{4-}$ ions formed by the reaction up to 700°C with OH^- ions. Applying the proposed mechanisms to the present materials with H_2O molecules in the lattice, the corresponding reactions can be expressed by Eqs. (4) and (5).

This result strongly supports that Hap particles are Ca(II)-deficient as is confirmed by the lower Ca/P atomic ratios as shown in Table 1. Indeed, the D and E samples with higher

Ca(II)-deficiency exhibit much more pronounced weight loss rather than the samples A–C. The large weight loss (ca. 13 wt %) as is observed for sample F at 200–400°C are due to the elimination of water of crystallization of $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. Certainly, the F sample has a sharp endothermic peak at 250–350°C in DTA curve. The TG loss value is in accord with the theoretical value of 12.4 wt %, suggesting that the principal crystal form of sample F is $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.

To characterize the surface and bulk structures of the precipitated A–F particles, in situ IR spectra were measured using the self-supporting method in vacuo. **Figure 6(a)** shows the spectra of A–F particles. All the particles exhibit a strong band at 3570 cm^{-1} that is assigned to the stretching vibrations of the bulk OH^- ions. These particle also exhibit sharp band at 3680 cm^{-1} and are assigned to the O–H stretching mode of surface P–OH groups, which are thought to be formed by protonation of the surface PO_4^{3-} ions to compensate the calcium deficiency of Hap.²⁰⁾ Ishikawa et al. reported that surface P–OH groups for the pure Ca deficient highly crystallized Hap particle will be appeared at 3659, 3673 and 3682 cm^{-1} .²⁰⁾ The single P–OH peak at 3680 cm^{-1} for A–E particles could be due to the low crystallinity with aggregated crystal structure of these particles. Similar result was observed on the Hap particles produced from

Fig. 7. TEM pictures of precipitates at various X_{Ti} values. The upper and lower values in the picture represent pH values before and after the reaction, respectively.

the $\text{Ca}(\text{OH})_2$ -tpp system as reported previously.¹³⁾ Of course, since the crystal structure of sample F is $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ with very small SSA value, this sample exhibits no such absorption band.

3.2 Preparation and characterization of Ti(IV)-substituted Hap particles

It was revealed in our previous work that Ti(IV) ions depress the extent of hydrolysis of pp ions.¹⁴⁾ Hence, to enhance the hydrolysis reaction of pp ions in the presence of Ti(IV) ions, the reaction temperature was raised from 100–160°C in 10°C intervals. In this experiment, Pyrex glass test tubes were used instead of PE ones, because PE test tubes do not stable at high temperature. The ellipsoidal aggregated secondary particles, which are consisting of smaller primary particles, were produced between 110–130°C. Similar ellipsoidal aggregated secondary particles were formed above 140°C, but the sizes of the primary ones are much larger than those produced between 110–130°C (see Fig. 7 $X_{Ti} = 0$). This result indicates that the formation of Hap particles is proceeded at high maturation temperature ($\geq 140^\circ\text{C}$). Therefore, we fabricated the TiHap particles at 140°C by changing the concentrations of TiCl_4 in a 20-cm³ Teflon-lined screw-capped Pyrex glass test tube under a condition for producing sample A. The atomic ratio $\text{Ti}/(\text{Ca}+\text{Ti})$ (abbreviated as X_{Ti}) was ranged from 0 to 0.3. To facilitate the aging, the test tubes were allowed to stand for 18 h at 140°C in an air turbulent oven.

Figure 7 displays TEM micrographs of the precipitates and the solution pH of the samples under various X_{Ti} values. The solution pH of 11.16–12.45 was dropped to 7.12–11.68 after the reaction for all samples, proving again that the pp ions were hydrolyzed. In the particles prepared without TiCl_4 ($X_{Ti} = 0$) at 140°C, the ellipsoidal secondary particles with ca. 240 nm in particle length were composed by aggregation of small primary particles with ca. 80 nm in length. Similar ellipsoidal aggregated particles are observed up to $X_{Ti} = 0.2$ while they are changed to aggregates of very fine particles with ca. 5–10 nm in diameter along with small amounts of large rod-like particles at $X_{Ti} = 0.3$. This result proves that Ti(IV) ions inhibit both the hydrolysis reaction of pp ions and crystallization of TiHap particles.

Figure 8 shows the change in the particle length (○) and width (□) of secondary particles fabricated at $X_{Ti} \leq 0.15$ where produced the TiHap particles exhibiting clear Hap crystal XRD patterns as will be shown in Fig. 9. These particle length and

Fig. 8. Particle length (○), width (□) and their crystallite size from Hap (002) (●) and (300) (■) faces of the TiHap samples produced at $X_{Ti} = 0$ –0.15.

Fig. 9. XRD patterns of precipitates produced at $X_{Ti} = 0$ –0.30.

Table 2. Results of elemental analyses and SSA for the particles produced at $X_{\text{Ti}} = 0\text{--}0.3$

X_{Ti}	Ca (mmol/g)	Ti (mmol/g)	P (mmol/g)	(Ca+Ti) /P	X_{Ti} in particle	Specific surface area (SSA) [m^2/g]
0	8.570	—	5.386	—	0	62.3
0.05	8.907	0.439	5.227	1.69	0.05	94.7
0.1	7.502	0.933	4.545	1.86	0.11	118.9
0.15	7.195	1.012	4.341	1.89	0.12	148.1
0.2	7.169	1.134	3.891	2.13	0.14	99.1
0.3	5.887	2.003	3.399	2.32	0.25	116.9
Theoretical values of Hap	9.954	—	5.972	1.67	—	—

width were also measured by counting over 300 secondary particles in each enlarged TEM picture as same as Hap system. Clearly, the length and width values are different for all the particles prepared at $X_{\text{Ti}} \leq 0.2$. This result suggests that all the TiHap particles produced in this region are ellipsoidal shape.

Figure 9 shows the XRD patterns of the particles as illustrated in Fig. 7. The particles precipitated at $X_{\text{Ti}} \leq 0.2$ exhibit the characteristic peaks of Hap (JCPDS 72-1243), though its intensity is extremely low for the particles precipitated at $X_{\text{Ti}} = 0.2$. It can be concluded from this result that highly crystallized pure TiHap particles can be produced at $X_{\text{Ti}} \leq 0.15$, but the Hap structure was almost disappear at $X_{\text{Ti}} = 0.2$. It can be regarded that the aggregated small primary particles produced at $X_{\text{Ti}} = 0.2$ are amorphous. On the contrary, the XRD pattern for the sample precipitated at $X_{\text{Ti}} = 0.3$ is very strong and sharp, though the precipitates are mainly composed by many tiny spherical particles with ca. 10 nm in diameter. The sharp XRD pattern for this sample may be attributed to the presence of a small number of large rod-like particles with highly crystallized Hap crystal structure.

The crystallite sizes of (002) and (300) faces of the TiHap particles precipitated at $X_{\text{Ti}} \leq 0.15$ were estimated by the Scherrer's equation and the evaluated values were plotted in Fig. 8. The crystallite sizes from (002) (●) and (300) (■) faces represent crystal size along with c - and a - or b -axes, respectively. These crystallite sizes are smaller than the particle length (○) and width (□) of secondary ellipsoidal particles in Fig. 8. This result indicates again that the secondary ellipsoidal particles are polycrystal as same as Hap particles produced in a previous section. It can be anticipated that the secondary ellipsoidal particles are fabricated by aggregation of single crystal primary particles.

The concentrations of calcium ([Ca]), titanium ([Ti]) and phosphorus ([P]) in the TiHap particles assayed are listed in Table 2 together with the (Ca+Ti)/P atomic ratios of these samples. All the particles produced at $X_{\text{Ti}} \leq 0.2$ have (Ca+Ti)/P molar ratio of 1.69–2.13. These values are larger than the theoretical value of 1.67, indicating phosphorus deficient. This result supports the fact that the pp molecules are hardly hydrolyze to orthophosphates in the presence of Ti(IV) ions as same as the results gained for the $\text{Ca}(\text{OH})_2\text{--tpp--TiCl}_4$ system.¹⁴⁾

Figure 6(b) displays the in situ IR spectra of the precipitated TiHap particles ($X_{\text{Ti}} \leq 0.2$). Almost the similar spectra for Hap particles as shown in Fig. 6(a) can be observed on TiHap ones. The new surface P–OH peak appeared at 3564 cm^{-1} though the 3680 cm^{-1} band was disappeared. This result suggests that the nature of surface P–OH groups was varied with substitution of Ti(IV) atoms in the particles. Similar result was reported for the highly crystallized TiHap particles fabricated by the coprecipitation method.²¹⁾ Furthermore, it should be mentioned here that the particles formed in this system have another weak band at 3736 cm^{-1} . Since the surface Si–OH groups reported silica gels

Fig. 10. Diffuse reflectance UV spectra of the TiHap particles produced at $X_{\text{Ti}} = 0\text{--}0.15$.

is 3740 cm^{-1} ,^{22),23)} this band can be due to the surface Si–OH groups. Hence, it seems reasonable to assign the 3740 cm^{-1} band to the Si–OH group produced from the silicate ions dissolved from the Pyrex glass vessel during the preparation under basic condition with $\text{pH} \geq 10$ (Fig. 7). The concentrations of silicate ions after the reaction in a PE tube assayed by ICP-AES measurement were very low, i.e., 10–20 ppm among all the systems for producing TiHap particles. Therefore, the effect of silicate ions on the formation of TiHap particles could be negligible. The silicate ions were only strongly adsorbed on the TiHap particles produced. Indeed, it was reported that the effect of silicate ions on the formation of Hap particles is weak.²⁴⁾ In other words, the particle morphology does not vary by silicate ions.

Figure 10 illustrates the diffuse reflectance UV spectra of the highly crystallized pure TiHap particles prepared at $X_{\text{Ti}} \leq 0.15$. Spectrum of Hap particle ($X_{\text{Ti}} = 0$) possesses no absorption peaks, proving that the Hap particle have no UV absorption property. For the TiHap particles, new peak due to charge transfer transition of $\text{O}^{2-} \rightarrow \text{Ti}^{4+}$ appears at 240–340 nm. This means that the synthetic TiHap particles have a UV absorption property. From the absorption edge, the band gap energy can be estimated as ca. 3.7–3.9 eV. It has been reported that Ti(IV)–doped MCM-41 has the band gap energy of tetrahedrally coordinated Ti(IV) is 3.9–4.2 eV.^{25)–27)} Similar result was reported for the micro-sized TiHap particles by Tanaka and Ohnishi.²⁸⁾ It can be concluded that Ti(IV) atoms in TiHap particles formed in this experiment exhibit the tetrahedral coordination.

The SSA values are also listed in Table 2. These SSA values are increased from 62.3 to $148.1\text{ m}^2/\text{g}$ by increase in the X_{Ti} values up to 0.2, though SSA one of the particle produced at

$X_{\text{Ti}} = 0.3$ is slightly decreased to $116.9 \text{ m}^2/\text{g}$. This depression of SSA value is due to the presence of large rod-like particles. Since the SSA values of highly crystallized TiHap particles ($0.05 \leq X_{\text{Ti}} \leq 0.15$) are large and they are ranged between $94.7\text{--}148.1 \text{ m}^2/\text{g}$, the enhancement of catalytic activity of TiHap produced in this study can be expected.

4. Summary

The degree of hydrolysis of pp ions is higher than tpp ones. Therefore, the yields of the precipitates by using the pp ions were remarkably increased rather than the tpp one. The ellipsoidal aggregated and rod-like particles are produced. The Hap produced are ellipsoidal secondary particles with ca. 210–240 nm in the particle length which are composed by aggregation of primary single crystal particles with ca. 20–50 nm in length. The TiHap facilitated at $X_{\text{Ti}} \leq 0.20$ are ellipsoidal secondary particles with ca. 240–380 nm in length composing by aggregation of small primary particles with ca. 30–100 nm in length. The highly crystallized pure TiHap particles produced at $0.05 \leq X_{\text{Ti}} \leq 0.15$ are phosphorus deficient but they exhibit a UV absorption property, especially fabricated at $X_{\text{Ti}} = 0.05$. Since these TiHap particles have large specific surface area, the enhancement of catalytic activity of TiHap is expected.

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