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# Effect of Solvent on Titania Particle Formation and Morphology in Thermal Hydrolysis of TiCl$_4$

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**Titania powders were synthesized by the thermal hydrolysis of titanium tetrachloride with the yield of above 85% in a mixed solvent of *n*-propanol and water. The morphology of the precipitates was controlled by adjusting the volume ratio of *n*-propanol to water (RH ratio) of the mixed solvent. Precipitates obtained with an RH ratio of 0 were fine, and highly agglomerated. In contrast, an RH ratio of 3 resulted in precipitates consisting of uniform and discrete particles. According to observations of the zeta potentials of precipitates and the dielectric constants of solvents, the discrete particles obtained with an RH ratio of 3 resulted from the low zeta potential and dielectric constant. The result of Fourier transform infrared (FTIR) spectroscopy showed the chemical interaction of particle surface with the solvent alcohol, which decreased the zeta potential of precipitates with an increase of RH ratio. Adding hydroxypropyl cellulose (HPC) as a steric dispersant made it possible to reduce the size of particles to the submicrometer range. Effects of the solvent on the formation and morphology of the resulting particles were investigated.**

## I. Introduction

I N RECENT years, significant research has been focused on the low-temperature sintering of ceramic devices. Improved sinterability has resulted from using particles with controlled morphology, size, and size distribution. Particles, such as Al$_2$O$_3$,[1–3] SiO$_2$,[4,5] Ta$_2$O$_5$,[6] TiO$_2$,[7–18] SiC,[19] ZrO$_2$,[20–26] and BaTiO$_3$[27,28] were prepared by the hydrolysis of metal alkoxides in a dilute alcohol solution and the thermal hydrolysis of metal salts in an aqueous solution.

Titania has been studied extensively because of its wide applications in pigments, photocatalysts, fillers, coatings, and photoconductors. Generally, titania is obtained either from its minerals or from a solution of titanium salts or alkoxides. Indeed, numerous studies on aqueous solutions of titanium salts have shown that titanium hydrolysis occurs even in highly acidic solutions (pH < 1) and that boiling the solutions accelerates hydrolysis and, consequently, titania precipitation.

Fine spherical particles with a narrow size distribution are desirable for producing advanced ceramics with enhanced reliability. Spherical titania particles have been prepared by chemical methods. Matijevic *et al.*[7] synthesized spherical titania particles of a narrow size distribution by aging a highly acidic solution of TiCl$_4$ at elevated temperatures for 6 to 47 days. Barringer and Bowen[8] obtained uniform titania particles from alcoholic solutions of titanium alkoxides. Several other research teams, however, found the above synthesis route difficult to reproduce.[9–12] Jean and Ring[9,10] showed that hydroxypropyl cellulose provided steric stabilization during the precipitation of titania from alcohol solution, resulting in uniform particles with lower sensitivity to reaction condition.

More research results had indicated that the powder morphology is influenced by the properties of the solvent. Look and Zukoski[13–16] demonstrated that particle interaction potentials play an important role in the development of precipitate morphology. They argued that the formation of agglomerates of discrete particles which have been fused together was due to a shallow secondary minimum through a combination of electrostatic and short-range repulsion. Harris and Byers[12] extensively studied the effect of solvent on the morphology of titania precipitates during homogeneous precipitation from an alcoholic aqueous solution of titanium ethoxide. They showed that particle growth was controlled by the surface phenomena of particles and that the type of precipitates formed was affected by the solvent. Seog and Kim[19] prepared monodispersed, spherical silicon carbide particles by the carbothermal reaction of spherical precursor particles and showed that particle morphology was controlled by changes in the surface potential of the particles. Li and Messing[21] prepared spherical zirconia particles by adding *n*-PrOH to a zirconia aqueous sol with zirconia concentration below 0.25 molal. Those workers reported that the role of *n*-PrOH during particle formation was to reduce the dielectric constant of sol. Recently, Moon *et al.*[25,26] synthesized monodispersed, spherical zirconia powders by the thermal hydrolysis of ZrOCl$_2$·8H$_2$O in a mixed solvent of iso-PrOH and water. In that study, amorphous zirconia particles were prepared by thermal hydrolysis without pH control of the mixed solvent. Their results also showed that the precipitation was caused by reduction of the dielectric constant of solvent. The effect of mixed solvent on precipitate morphology, however, was unclear.

The present paper describes the preparation of monodispersed, spherical titania particles by the thermal hydrolysis of TiCl$_4$ in a mixed solvent of *n*-PrOH and water. Effects of the solvent on the formation and morphology of particles are examined in view of colloidal stability.

## II. Experimental Procedure

### (1) Preparation of Starting Solution

Titanium tetrachloride (98% TiCl$_4$, Wako Chemical Industries, Japan) was used as a starting material. When TiCl$_4$ dissolved in water, the heat of the exothermic reaction explosively generated the formation of orthotitanic acid [Ti(OH)$_4$]. Because the formation of that species disturbed homogeneous precipitation, 5 mL (per 100 mL distilled, deionized water) of hydrochloric acid (35% HCl, Junsei Chemical Company, Japan) was added to prevent the formation of orthotitanic acid.

Titanium tetrachloride was dissolved in triple-distilled, deionized water. The concentration of titanium was adjusted to 1*M*. This aqueous solution was then mixed with *n*-PrOH (98%, Junsei) to adjust the volume ratio of *n*-PrOH to water (the RH
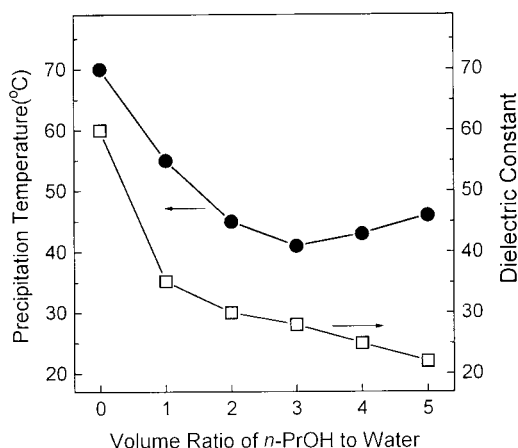
**Fig. 1.** Variation of the precipitation temperature and dielectric constant of the solvent with the RH ratio. The $TiCl_4$ concentration of the solution was 0.1 mol/L.



**Fig. 2.** Yield of precipitates formed at various reaction times as a function of RH. The reaction temperature was 70°C.

ratio) to 0, 1, 2, 3, 4, and 5. The final concentration of $TiCl_4$ in the mixed solution was 0.1 mol/L. A homogeneous solution was obtained by stirring for 6 h with a magnetic stirrer at 10°C. All of the reagents were used as received. A long-chained molecule, hydroxypropyl cellulose (HPC) (molecular weight ~100 000, Aldrich Chemical Company, Milwaukee, WI) was used as a steric dispersant.

#### *(2) Synthesis of Monodispersed Spherical Titania Powders*

When the starting solution was heated in an isothermal water bath of 70°C for a few minutes, it became supersaturated and precipitated. The solution was then aged further to precipitate growth. After precipitation, the mother liquors were neutralized with an $NH_4OH$–$n$-PrOH ($0.5M$ $NH_4OH$) solution to remove chloride ion. The precipitates next were separated from the mother liquor, by centrifuging at 10 000 rpm, then washed twice with distilled water and finally with $n$-PrOH. The washed precipitates were dried in a vacuum oven at 60°C for 24 h.

An experiment was carried out to reveal the effect of the dispersing solution of precipitates on the particle morphology. Titania precipitates were obtained by aging the $TiCl_4$ aqueous solution with titanium concentration of 0.5 mol/L at 80°C. The precipitates were separated centrifugally from the mother liquor and redispersed with distilled water, methanol, ethanol, and $n$-propanol, respectively. The dispersed suspensions were stirred for 3 h and separated into precipitates and supernatant. The precipitates were then dried by the same procedures.

#### *(3) Characterization of the Titania Particles*

The particle size and morphology were analyzed by scanning electron microscopy (SEM). The inner structures of the precipitates were observed by transmission electron microscopy (TEM). To study the inner structure of spherical particles, a small amount of powders, mixed homogeneously with epoxy (55 vol% LX-112 resin, 43 vol% NMA hardener, and 2 vol% DMT-30 catalyst, Ladd Research Industries, Burlington, Vermont), was cured at 80°C for 144 h. The specimen for TEM observation was then thinned by polishing, mechanical dimpling, and ion thinning.

The zeta potential of precipitates was measured by use of an electrophoretic technique (Zetamaster, Malvern, UK) at 20°C. The samples for measuring the zeta potentials of as-precipitates were prepared by the following route. Screw-cap covered test tubes containing a portion of the starting solutions were kept in an isothermal vessel. After a desired period of reaction time, the tubes were cooled and the supernatant solutions decanted into other tubes. A small amount of precipitates was redispersed in the decanted supernatant to preserve the ionic strength of the solution.

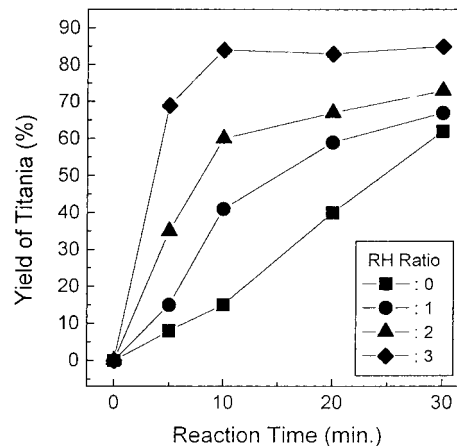Fourier transform infrared (FTIR) spectroscopy (Nicolet 800, Nicolet Instrument Company, Madison, WI) was used to determine the interaction between the solvent and the particle surface. Precipitate samples were mixed with dry KBr, and the FTIR cell was purged for 20 min prior to spectral collection. FTIR spectroscopy was used with a dry air purge. The yield of precipitates was determined by dividing the weight of product dried at 1000°C for 3 h by the weight of product when $n$ mol of titania was formed from $n$ mole of titanium tetrachloride.

### III. Results and Discussion

#### *(1) Precipitation Behavior in Mixed Solvent*

When the starting solution is heated at a rate of 10°C/min, it becomes turbid at a certain temperature, defined as the "precipitation temperature" of the solution. The precipitation temperature was determined by the usual observation, a turbidimeter (4700, Malvern, UK) on light scattering. Figure 1 shows the precipitation temperature as a function of the RH ratio of the solvent. The precipitation temperature decreases with an increase in the RH ratio, exhibiting a minimum at the RH ratio of 3. Further increases in the RH ratio cause the precipitation temperature to increase slightly. The dielectric constants of the starting solutions at the precipitation temperature are also shown in Fig. 1. The dielectric constant decreases as the RH ratio increases. According to previous studies,[29,30] precipitation can occur by heating a salt solution of alcohol–water, because the dielectric constant of the solution is decreased significantly with an increase in temperature. Similarly, it seems that a decrease in the dielectric constant of the mixed solvent promotes the precipitation of titania by reducing the solubility of the titania in the mixed solvent. For the RH ratio of $>5$, precipitates were not formed even at the temperature of 70°C, despite the lower dielectric constant of the solvent. When more water was added to the solvent at that temperature, precipitates formed abruptly. Apparently, no precipitation occurs, even at the lower dielectric constant of the higher-temperature solvent, because the amount of water required for the hydrolysis of $TiCl_4$ becomes deficient at an RH ratio above 4.

Figure 2 shows the yield of precipitates formed at various reaction times at 70°C as a function of the RH ratio. As the RH

**Table I.    Dielectric Constants of Mixed Solvents and Zeta Potentials and Morphologies of Precipitates with the RH Ratios of Mixed Solvents**

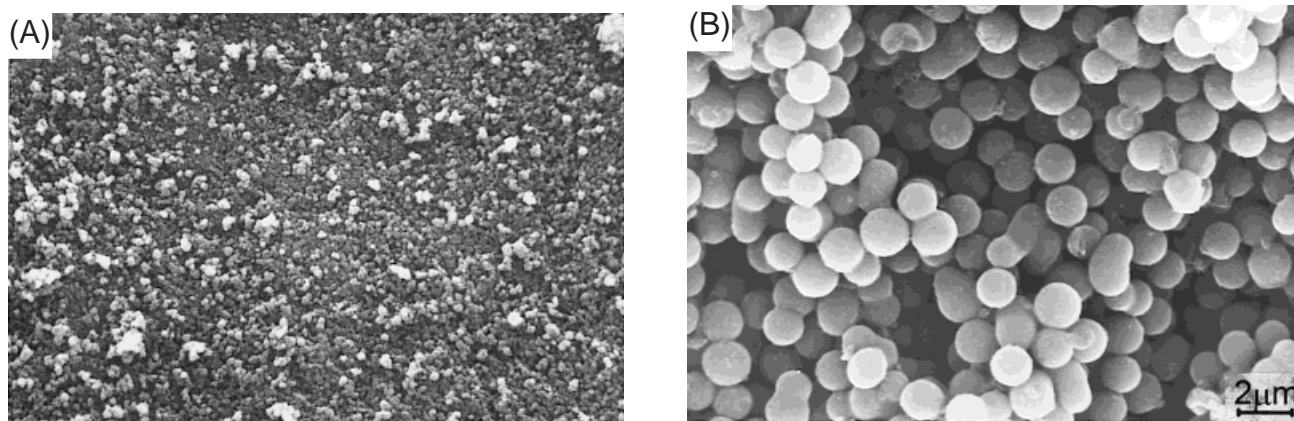| RH ratio | Dielectric constant of solvent at 20°C | Zeta potential at 20°C | Particle morphology |
|---|---|---|---|
| 0 | 80 | 18.3 | Fine, aggregated |
| 1 | 48 | 11.4 | Aggregated |
| 2 | 36 | 6.7 | Spherical, aggregated |
| 3 | 32 | 4.5 | Spherical, discrete |

**Fig. 3.**  SEM micrographs of the precursor particles obtained at RH ratios of (A) 0 and (B) 3.

ratio increases, the yield of precipitates increases at the same reaction time. While the yield of the precipitates obtained in the solvent with an RH ratio of 0 is ~58% after a reaction time of 20 min, the RH ratio of 3 gives a yield of 85%. These results seem to indicate that the reduced dielectric constant of a mixed solvent promotes the supersaturation of titania in the solvent.

### (2)   Effect of Mixed Solvents on Particle Morphology

The composition of mixed solvents also affects the morphology of the resulting particles. Figure 3 shows the particles obtained at the RH ratios of 0 and 3. For an RH ratio of 0, the precipitated particles are found to be very fine and highly agglomerated. In contrast, the particles formed at an RH ratio of 3 are spherical and discrete particles, with some doublets fused together. These differences in morphologies indicate that the colloidal stability of the precipitated particles in the mixed solvent of $n$-PrOH–water is different from that of water solvent. These results can be understood by considering the parameters determining the colloidal stability.[19,26,31] Typically, the maximum repulsive force can be estimated from the equation of $2\pi\varepsilon_0\varepsilon_r\kappa\alpha\Psi^2$ for electrostatically stabilized particles, where $\varepsilon_0$ is the permittivity in free space, $\varepsilon_r$ the dielectric constant of the continuous phase, $\kappa$ the Debye–Huckel parameter, $\alpha$ the particle diameter, and $\Psi$ the particle surface potential.[13–15] Under the constant ionic strength of the solvent, the maximum repulsive force depends on the particle surface potential, the dielectric constant, and the particle size. According to Derjaquin–Landau–Verwey–Overbeek (DLVO) theory,[31] the energy barrier between two particles which inhibit agglomeration can be also expressed as

$$V_b = -\frac{A\kappa\alpha}{12} + 2\pi\varepsilon_0\varepsilon_r\alpha\Psi^2 \tag{1}$$

where $A$ is the effective Hamaker constant. The effective Hamaker constant depends on the dispersion medium. The Hamaker constants of water and several aliphatic alcohols in free space are reported to have similar values, on the order of $10^{-20}$ J.[31,32] Considering that the mixed solvent is composed of alcohol and water, the mixed solvent may not greatly influence the effective Hamaker constant.[31,32] Additionally, there were no electrolytes in the mixed solvents in the present work, except for HCl added to inhibit the precipitation of orthotitanic acid during dissolving the TiCl₄ in water. Therefore, the ionic strength is supposed to be constant in the solvent. Under these conditions, the magnitude of the energy barrier and maximum repulsive force is determined mainly by the surface potential, the dielectric constant, and the particle size.

The dielectric constants, the zeta potentials and the precipitate morphologies are summarized in Table I. As the RH ratio of solvent increases, the zeta potentials and the dielectric constants rapidly decrease. For the solvent with an RH ratio of 0, the dielectric constant of the solvent and the zeta potential of the

precipitates are very high. According to Eq. (1), the potential energy barrier is relatively high. Under this condition, relatively small particles may be stable against the aggregation, and the resulting particles appear to be fine as shown in Fig. 3(A). In the case of the solvent with an RH ratio of 3, the zeta potential and the dielectric constant are low. The precipitates have a low potential energy barrier and maximum repulsive force. Therefore, the colloidal stability of the precipitates increases with the particle size increase, because the potential energy barrier and the maximum repulsive force increase with the particle size. Consequently, the resulting precipitates, shown in Fig. 3(B), are composed of large and discrete particles. These results show that the composition of the mixed solvent affects the particle size and morphology through the change of the zeta potential of precipitates and the dielectric constant of the mixed solvent.
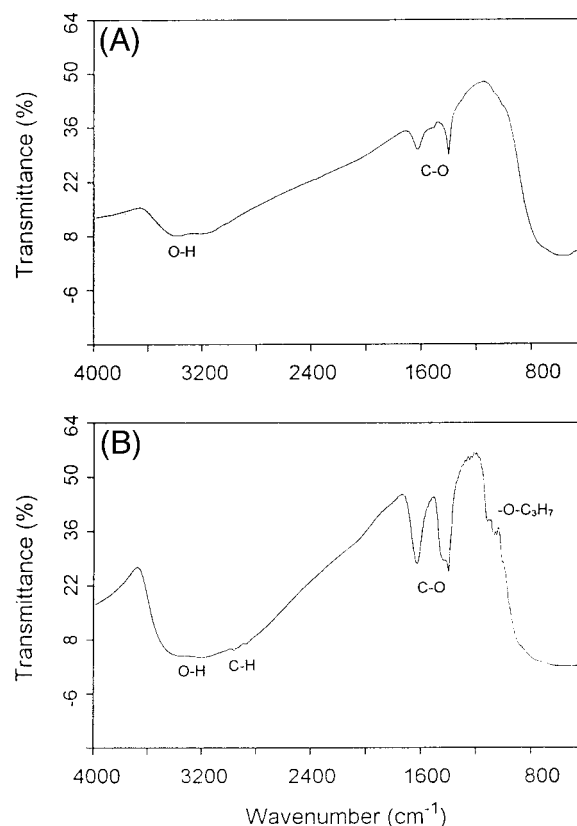


**Fig. 4.**  FTIR spectra of the precipitates formed with an RH ratio of (A) 0 and (B) 3.

**Table II.  Carbon Analysis of the Particles Prepared from the Different Processes**

| Sample name | Dispersing solution | Carbon content (wt%) |
|---|---|---|
| Sample A* | $H_2O$ | 0 |
| Sample B* | *n*-propanol | 2.04 |
| Sample C‡ | *n*-propanol | 8.5 |

*Precipitated in the RH ratio of 0. ‡Precipitated in the RH ratio of 3.

### (3)  Interaction of Mixed Solvents with Particles

Figure 4 shows the FTIR spectra of titania precipitates, obtained at the RH ratios of 0 and 3, after drying. In both spectra, the broad absorption bands corresponding to an O–H stretch appear from ~3600 to ~3000 cm$^{-1}$, and the two peaks centered approximately at 1620 and 1350 cm$^{-1}$ correspond to $CO_2$ adsorbed on the surface of the particle.[24,33,34] The spectrum of the precipitate obtained with an RH ratio of 3 reveals new absorption bands (Fig. 4(B)). The absorption bands at 3000 and 2900 cm$^{-1}$ are due to C–H stretching. The small peaks at 1160 and 1063 cm$^{-1}$ correspond to the C–O stretching in terminal titanium alkoxide.[33,34] Absorptions due to C–O stretching in excess propanol are not observed, which may be due to the overlap with water and carbon dioxide. Considering that the starting solutions are composed of $TiCl_4$, *n*-PrOH, and water, the formation of terminal titanium alkoxide is due to the bonding between the oxygen of $Ti(OH)_4$ and the carbon of R ($C_3H_7$).

According to the stabilization of colloids by electrostatic interaction, the surface potential of oxide particles is determined by the charges of potential determining ions. For hydrous oxides, the charge-determining ions are $H_3O^+$ and $OH^-$ below and above the point of zero charge, respectively.[35] The concentration of potential determining ions is determined mainly by the pH of the solution under constant ionic strength. In this work, as shown in Table I, the zeta potential of particles decreases with the increase of the RH ratio of the solvent without the pH control of the solvent. These results indicate that the potential-determining ions ($H_3O^+$) on the particle surface decrease under the constant pH of the solvent. Considering the FTIR, the low zeta potential of the precipitates in the mixed solvent (with RH ratio of 3) is attributed to the chemical adsorption of alcohol on the particle surface. Table II shows the result of carbon analysis performed on precipitates prepared by different processes. The carbon contents of sample A obtained from $TiCl_4$ aqueous solution is 0 wt%. When sample A is redispersed in *n*-PrOH (sample B), it contained 2.05 wt% of carbon. In contrast, in the case that precipitates are obtained in the solvent with an RH ratio of 3 (sample C), the carbon content is 8.5 wt%. It is believed that these results also support the interaction between titania precipitate and *n*-PrOH in the mixed solvent of *n*-PrOH and water.

### (4)  Effect of Alcohol on Particle Growth

Generally, the primary particles nucleated from solutions are known to grow by molecular addition or aggregation with small subunits.[14–16] The particle growth after nucleation can be also affected by the kinds of solvents, because the particle interaction potential is different in each solvent. Figure 5 shows the morphologies of precipitates, prepared from $TiCl_4$ aqueous solution, redispersed in distilled water and various alcohols. The precipitates redispersed in distilled water consist of fine and subunit particles. The precipitate size is about 0.05 μm. In contrast, the precipitates redispersed in alcohols are found to
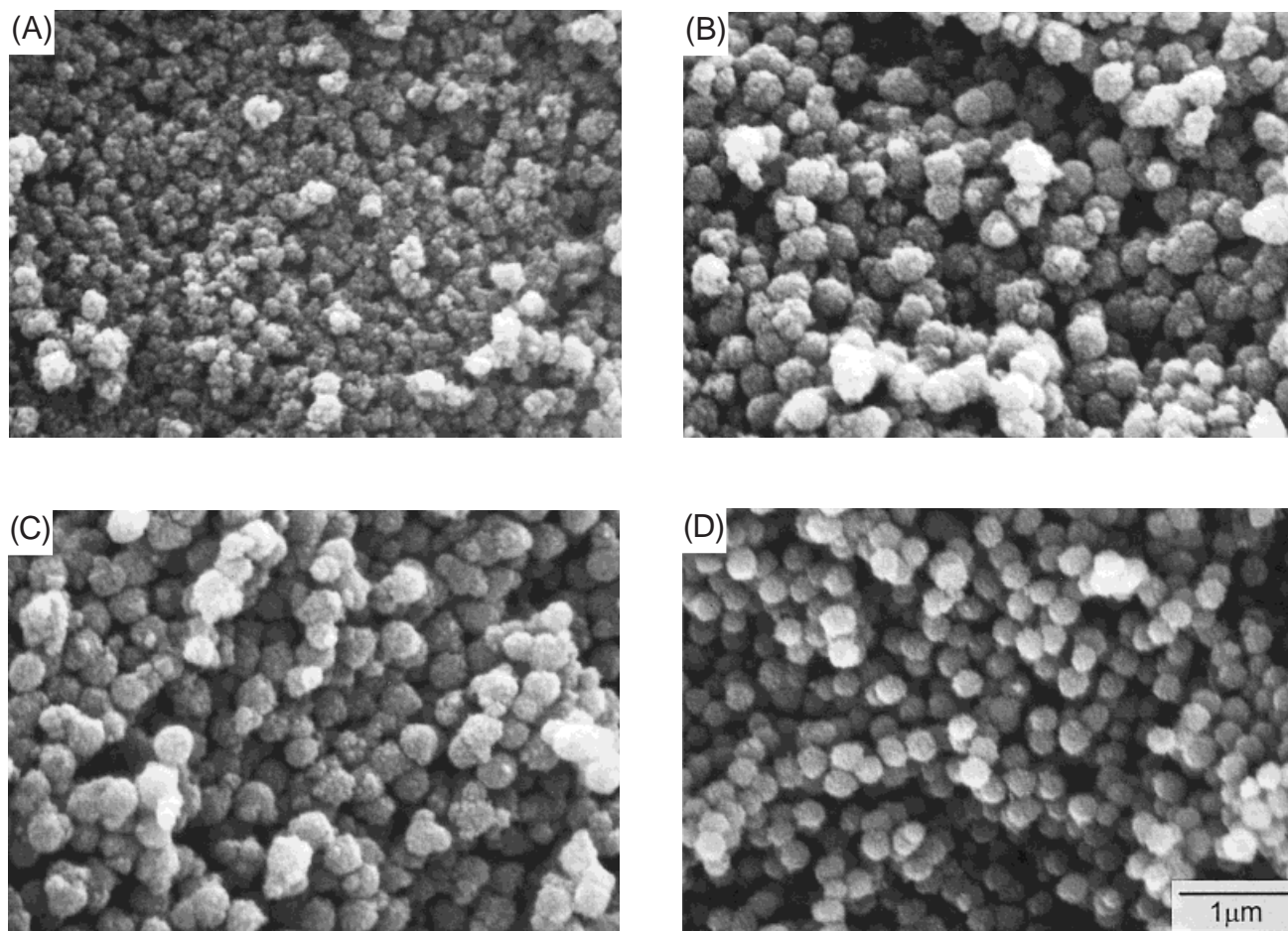
**Fig. 5.**  SEM micrographs of the precipitates redispersed in distilled water and various alcohols for 3 h. The dispersing solutions of (A), (B), (C), and (D) are distilled water, methanol, ethanol, and *n*-propanol, respectively.
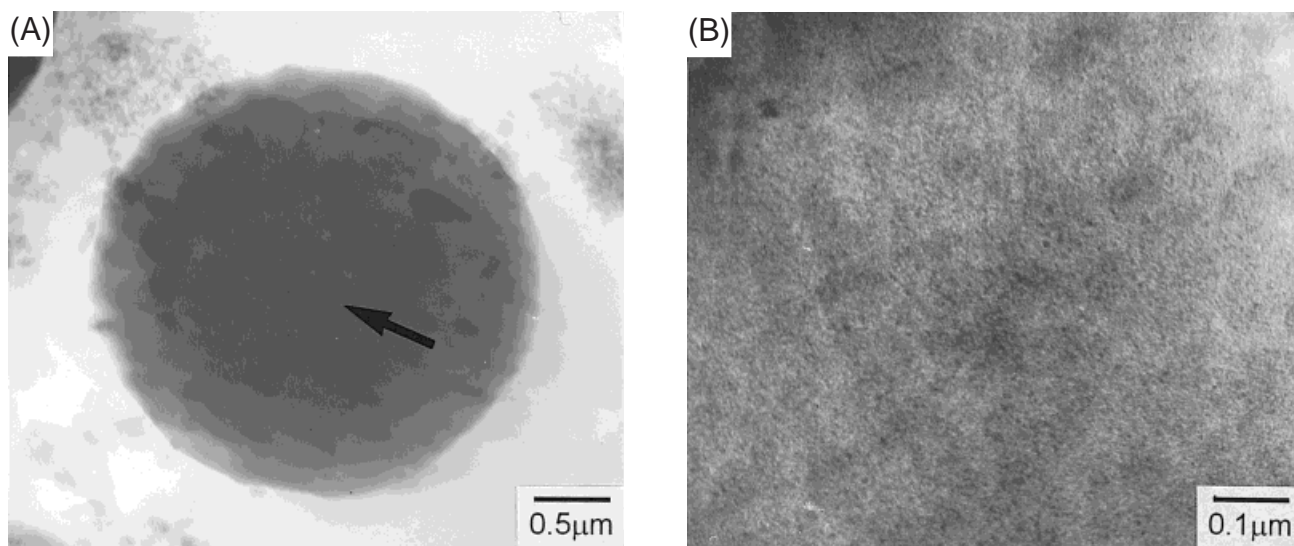
**Fig. 6.** TEM micrographs of the inner structure of the precursor particle obtained at the RH ratio of 3.

be composed of spherical secondary particles, as shown in Fig. 5(B, C, and D). The size of the secondary agglomerates decreases as the number of carbons in the alcohol increases. In case of the precipitates redispersed in *n*-PrOH, secondary agglomerates measuring ~0.2 μm, and with a narrow size distribution resulted. The titania precipitates obtained from TiCl$_4$ aqueous solution are not soluble in alcohol.[30] Therefore, the secondary particles are apparently formed by the aggregation of the fine and subunit particles. Figure 6 shows the inner structure of a particle precipitated at an RH ratio of 3. The particle is composed of smaller particles of nanometer scale. The precipitates obtained in a mixed solvent of *n*-PrOH and water are found to be also spherical secondary agglomerates. From these results, it is thought that the particle is grown by the aggregation of fine primary particle in mixed solvents.

Table III shows the zeta potentials of the precipitates, obtained from TiCl$_4$ aqueous solution, redispersed in distilled water and various alcohols. The precipitates dispersed in water show a relatively high zeta potential. In alcohol solutions, however, the zeta potentials of the precipitates are relatively low. Furthermore, the precipitates redispersed in alcohols possess nearly the same zeta potentials, whatever the kinds of alcohol used. Consequently, it seems that the low zeta potentials of particles, as well as the low dielectric constant of the dispersing solution, promotes the aggregation of the fine precipitates in alcohol solutions.

Figure 7 shows the schematic diagram of particle growth in an *n*-PrOH–water solution. In a solvent with a high dielectric constant, precipitates with high surface potentials are stable for relatively small particle sizes. If the solvent for the precipitates is changed, the surface potential of the precipitates and the dielectric constant of the solvent are also changed. Subsequently, the precipitate morphology will be changed as in path 4 of Fig. 7. The fine precipitates with low surface potential will be colloidally unstable in the solvent with low dielectric

constant. Those precipitates show rapid aggregative growth as in path 3. The precipitates are found to be relatively large in size. The formation of doublets in the *n*-PrOH–water solvent, however, is not explained in the present work. Look and Zukoski[13–16] extensively studied doublet formation in the preparation of titania particles from an aqueous ethanol solution of tetraethyl orthotitanate. Apparently, the formation of some doublets at an RH ratio of 3 results from the solvation force caused by the low surface potential of the particles and the dielectric constant of the solvent, as shown in those previous studies.[13–16]

### (5) Effect of HPC as a Dispersant

Steric interaction basically is caused by the adsorption of polymer molecules onto the surface of particles. Hydroxypropyl cellulose (HPC) has been known to provide steric stabilization during the precipitation of TiO$_2$ from an alcohol solution.[9,10] Figure 8 shows the morphology of precipitates formed in *n*-PrOH–water solution with and without HPC as a dispersant. In the absence of HPC, the precipitates consist of agglomerates of discrete particles which have been fused together. When a small concentration of HPC (i.e., $0.64 \times 10^{-3}$ g/cm$^3$) is added to the starting solution, agglomerate formation is greatly reduced, giving fine, spherical, and well-dispersed particles. Figure 9 shows the effects of HPC concentration on the size and size distribution of the particles. As the HPC concentration increases, the particle size decreases. Above $0.64 \times 10^{-3}$ g/cm$^3$ of HPC concentration, the average particle size slightly decreases and the size distribution rapidly increases with an increase in the HPC concentration. At high concentration of HPC, several large particles of 20 μm were found in submicron-scaled particles, which kept the average particle size constant. It seems that the excess HPC have acted as a nucleation site for precipitation. At an HPC concentration of $0.64 \times 10^{-3}$ g/cm$^3$, fine, spherical titania particles with a narrow size distribution were produced in the mixed solvent of *n*-PrOH and water, as shown in Fig. 9(B).

### IV. Conclusions

Monodispersed, spherical titania particles were synthesized by the thermal hydrolysis of titanium tetrachloride in a mixed solvent of *n*-propanol and water. The morphology of the titania particles was controlled by the volume ratio of *n*-PrOH to water (RH ratio) in the mixed solvent. As the RH ratio increased, the particle size increased and the particle morphology became more uniform and discrete. These discrete particles were agglomerates of the fine, nanometer-scaled particles and formed by
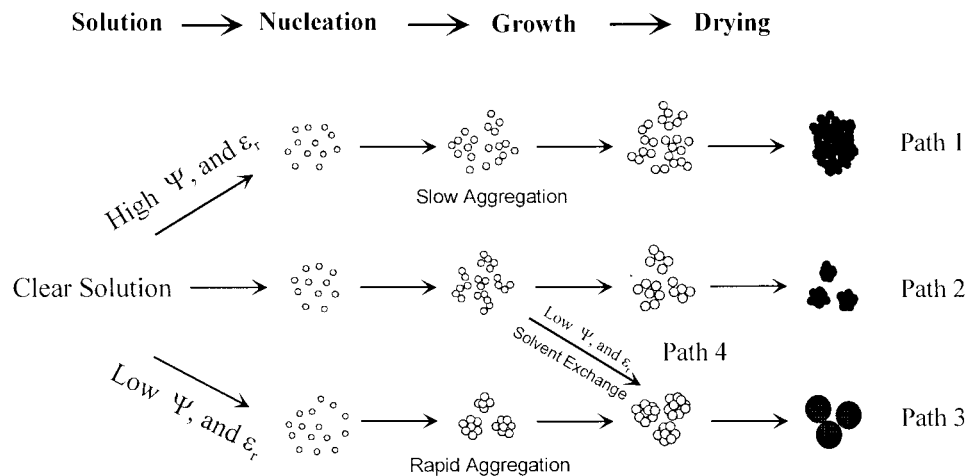
**Table III. Variation of Particle Zeta Potential with Dispersing Solutions**

| Dispersing solution | Dielectric constant* (20°C) | Viscosity (20°C)* (centi-poise) | Zeta potential (mV) |
|---|---|---|---|
| Water | 80.37 | 1.002 | 16.8 |
| Methanol | 32.80 | 0.593 | 8.90 |
| Ethanol | 24.60 | 1.410 | 8.20 |
| *n*-propanol | 19.50 | 2.256 | 9.10 |

*Reference 29.

**Fig. 7.** Schematics of particle growth in the mixed solvent of alcohol and water.
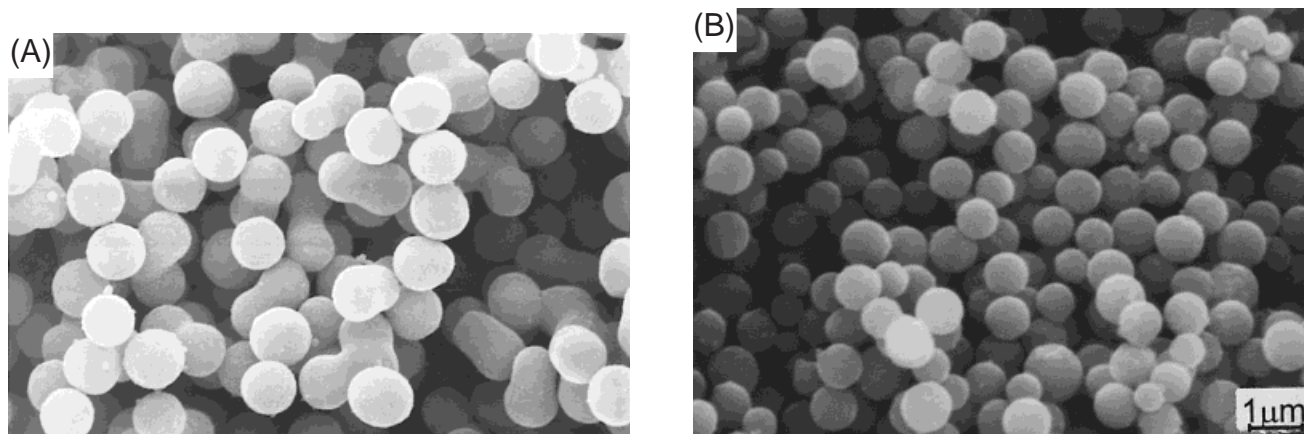


**Fig. 8.** SEM micrographs of the precursor particles obtained from the solution (A) without HPC and (B) with HPC. The RH ratio of the solution is 3.
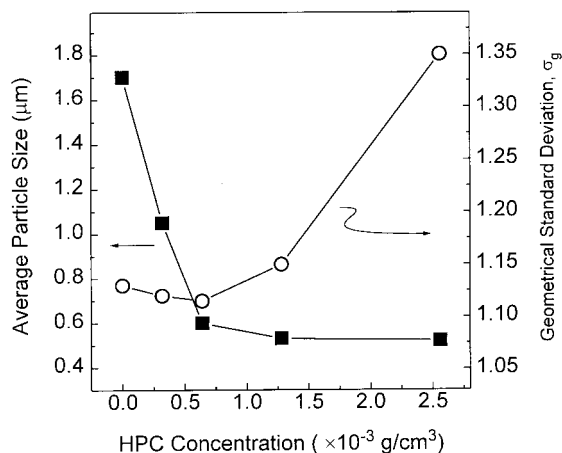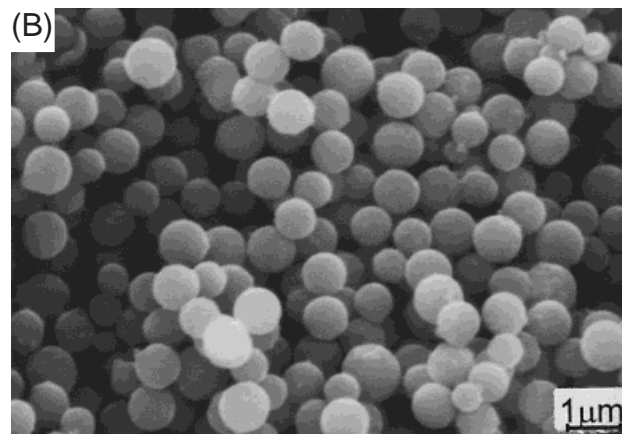


**Fig. 9.** Variation of average particle size and geometrical standard deviation with the HPC concentration.

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aggregative growth of the fine particles. The formation of uniform and discrete titania particles was attributed to the low surface potential of the particles and the low dielectric constant of the mixed solvent. The particle size decreased to the submicron range when hydroxypropyl cellulose (HPC) was used as a steric dispersant. Particles with a narrow size distribution were obtained at an HPC concentration of $0.64 \times 10^{-3}$ g/cm³.

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