Formation of Monodisperse Spherical TiO₂ Powders by Thermal Hydrolysis of Ti(SO₄)₂

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I. Introduction

Titania powders have been prepared by the thermal hydrolysis of titanium sulfate at 80°C in a mixed solvent of n-propyl alcohol (n-PrOH) and water. The morphology of the powders was greatly influenced by the volume ratio in n-PrOH to water (RH ratio) of the solvent. An RH ratio of 1.0 was essential for the formation of spherical TiO₂ powders. When hydroxypropyl cellulose (HPC) was used as a steric dispersant, monodisperse spherical powders 0.7 μm in diameter were produced. As the RH ratio was increased, the zeta potential of the powders was negatively increased and the dielectric constant of the solvent was decreased. However, powders obtained at an RH ratio of 1.0 were observed to have the highest energy barrier. The colloidal stability of the powders in a mixed solvent of n-PrOH and water is discussed. As-precipitated powders were amorphous hydrates of titania and were crystallized by calcination into anatase (>600°C) and rutile (>800°C).

II. Experimental Procedure

Titanium diisulfate (98% Ti(SO₄)₂, Wako Chemical Industries, Ltd., Japan) was dissolved in distilled, deionized water at room temperature. This aqueous solution was mixed with n-PrOH (GR grade, Wako Chemical Industries, Ltd., Japan) and stirred for 12 h. The volume ratios of n-PrOH to water (RH ratio) of the solution were controlled to be 0, 0.5, 1.0, and 1.5 and the final concentration of Ti(SO₄)₂ was 0.12 mol/L. To give steric hindrance to the precipitating particles, hydroxypropyl cellulose (HPC) (molecular weight ~100 000, Aldrich Chemical Co., Milwaukee, WI) was used as a steric dispersant.

When the prepared solutions were kept in an isothermal water vessel of about 80°C without stirring, white products were precipitated after several tens of minutes. After evaporation for 25 min, the precipitates were centrifugally separated from the mother liquor. The obtained precipitates, washed twice with distilled water and finally with n-PrOH, were dried in a vacuum oven at 50°C for 24 h.

In order to measure the zeta potential of the precipitated powders, screw-cap covered test tubes containing a portion of the starting solutions were kept in the isothermal vessel at 80°C. Following a desired period of time, the tubes were allowed to cool, and then the supernatant solutions were centrifugally separated and decanted into other tubes. Small amounts of the precipitated powders were redispersed into the decanted supernatants to preserve the ionic strength of the solutions. These diluted suspensions were syringed into a zeta potentiometer (ZetaMaster, Malvern Instruments, England) at 20°C. Six measurements were taken for each sample. The zeta potentials were calculated from mobility measurements using the Smoluchowski equation.

The particle size and the morphology were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The samples for TEM analysis were prepared by drying small quantities of the suspensions for each reaction time on carbon sputtered, electron microscope grids. The phase transformation of the precursor powders was determined by X-ray diffractionmetry (XRD) after the heat treatments.
Heat treatment was performed at 400°, 600°, and 800°C for 2 h in air.

III. Results and Discussion

In the “sulfate process,” titania powders have been synthesized at an elevated temperature of about 90°C by the thermal hydrolysis of titanium(IV) sulfate. Figure 1 shows the morphology of the powders obtained from an aqueous solution of titanium sulfate at various reaction temperatures. The powders, in all cases, were found to be highly agglomerated. In the present system, the powders have nearly the same morphology irrespective of the reaction temperatures, indicating that powders with controlled morphology are not obtained in aqueous solution without addition of an external pH agent, such as HCl and NH₄OH, used to regulate the reaction rate.

It is generally accepted that the composition of the solvent affects the powder morphology. The variation of solvent composition may change the characteristics of the particle surface and the solvent, such as the surface potential of the powders, the dielectric constant of the solvent, and the Debye–Hückel constant. These factors are related to the powder interaction potentials in colloidal stability. Figure 2 shows the morphologies of the powders obtained at various RH ratios and HPC concentrations. The experimental conditions are shown in Table I. When the RH ratio was 0, the powders were highly agglomerated. The powders obtained from a mixed solvent of n-ProOH and water were more spherical with the RH ratio increasing. Especially, at an RH ratio of 1.0, the powders had spherical morphology. At an RH ratio of 1.5, however, the powders appeared to be more agglomerated. These results indicate that the composition of the solvent greatly influences the precipitate morphology. According to colloidal stability models, powders interacting with van der Waals attractive and electrostatic repulsive forces become more stable against aggregation when the surface potential of the powders is of sufficient magnitude and the ionic strength is low. The energy barrier (Vₖ), inhibiting the formation of particle aggregation, between the powders can be described as follows:

\[ Vₖ = \frac{A k \alpha}{12} + 2 \pi \varepsilon_0 \varepsilon_\alpha \alpha \psi^2 \]  

\[ k = \left( \frac{2F^2 Z^2 N_0}{\varepsilon_0 \varepsilon_\alpha \kappa_0 T} \right)^{1/2} \]

where A is the Hamaker constant, k the Debye–Hückel constant, \( k_0 \) the Boltzmann constant, \( \alpha \) the particle diameter, \( \varepsilon_\alpha \) the relative dielectric constant of the liquid medium, \( F \) the electrical charge (96 500 C), \( Z \) the ionic valence, \( N_0 \) the concentration of the electrolyte, \( \varepsilon_0 \) the dielectric constant of a vacuum, and \( \psi \) the surface potential. The effective Hamaker constant depends on the dispersion medium. The composition of the solvent, however, may not significantly influence the effective Hamaker constant because the Hamaker constants of water and aliphatic alcohols in free space have similar values, on the order of 10−20 J. If the Hamaker constant is regarded as a constant, it is seen from Eq. (1) that the energy barrier depends on the surface potential, the relative dielectric constant of the particle diameter, and the Debye–Hückel constant. Table II shows the zeta potentials, the dielectric constants, and the energy barriers with the variation of the RH ratio of the solvent. The ionic strength of the solution was determined by the Debye–Hückel constant of Eq. (2), which depended on the electrolyte concentration. In this work, other electrolytes did not exist in the solutions except for H₂SO₄ released from the starting salts. Under these conditions, the ionic strength of the solution is supposed to be constant. The zeta potentials of the powders were negatively increased and the dielectric constants of the solvents were decreased with the RH ratios. Using \( A = 2.5 K T \) (\( T = 298 \) K), \( N_0 = 0.24 M \) (as determined by the concentration of SO₄²⁻),

<table>
<thead>
<tr>
<th>Run</th>
<th>RH ratio</th>
<th>Reaction temp (°C)</th>
<th>HPC concentration (g/cm³)</th>
<th>Reaction time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>80</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>B</td>
<td>0.5</td>
<td>80</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>C</td>
<td>1.0</td>
<td>80</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>D</td>
<td>1.5</td>
<td>80</td>
<td>0.01</td>
<td>30</td>
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<tr>
<td>E</td>
<td>1.0</td>
<td>80</td>
<td>0.04</td>
<td>30</td>
</tr>
<tr>
<td>F</td>
<td>1.0</td>
<td>80</td>
<td>0.04</td>
<td>30</td>
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</table>

Table I. Reaction Conditions

1RH ratio, volume ratio of n-propyl alcohol to water. 2HPC: Hydroxypropyl cellulose.
and \( \alpha = 1 \mu m \), the energy barrier between the particles was determined by Eq. (1). The barrier was increased with the RH ratios and the maximum energy barrier appeared at an RH ratio of 1.0. At an RH ratio of 1.5, the energy barrier decreased in spite of a negatively highest zeta potential. These results show that the lower dielectric constant of the solvent at an RH ratio of 1.5 causes the energy barrier to decrease despite its higher surface potential. It is admitted, however, that the measuring temperature of the zeta potential does not correspond to the precipitating temperature. The zeta potential should be measured in situ over the course of the precipitation reaction in order

![Fig. 2. SEM micrographs of the powders derived for the various RH ratios of the solvent: (A) 0, (B) 0.5, (C) 1.0, (D) 1.5, (E) 1.0, and (F) 1.0. The HPC concentrations of (E) and (F) are 0.01 and 0.04 g/cm³, respectively.](image)

| Table II. Dielectric Constants, Zeta Potentials, and Energy Barriers of the Precipitated Powders in Their Mother Liquor |
|---|---|---|---|
| RH ratio \(^a\) | Dielectric constant (Ref. 19) | Zeta potential (mV) | Energy barrier, \( V_e^* \) (eV) |
| 0 | 80.37 | -20.6 | 11.91 |
| 0.5 | 59.21 | -32.3 | 21.53 |
| 1.0 | 48.98 | -38.5 | 25.30 |
| 1.5 | 40.09 | -40.2 | 22.59 |

\(^a\) RH ratio means the volume ratio of \( \alpha \)-propyl alcohol to water. \(^*\) Energy barrier was calculated by using Eq. (1).
Fig. 3. TEM and SEM micrographs of the powders for various reaction times at an RH ratio of 1.0. Reaction times: (A) 9, (B) 13, (C) 17, (D) 21, and (E) 30 min.
to explain the morphologies of the resulting powders more clearly. Based on these results, the spherical titania powders with narrow size distribution could be obtained by control of the composition of the solvent by using n-PrOH.

Hydroxypropyl cellulose (HPC) is widely used to prepare fine spherical powders in alcoholic solution of alkoxides. 3-5 Jean and Ring 5 demonstrated that the use of HPC as a steric stabilizer results in nonagglomerated particles with a narrow size distribution which are less sensitive to the reaction conditions of alkoxides. In the present work, when HPC was used as a dispersant, the particle size decreased to a size of about 0.7 μm. It seems that, besides the electrostatic repulsion, HPC gives an additional repulsive force by steric hindrance from the adsorption of macromolecules onto the particles, which has already been studied by other researchers. 3,5

Figure 3 shows TEM and SEM micrographs of the powders with the reaction time at an RH ratio of 1.0 and a temperature of 80°C. The precipitates after a reaction time of 9 min were found to be composed of agglomerated particles of about 30 nm. The shape of the precipitates was shown not to be spherical but highly agglomerated with smaller subunit particles. When the reaction time was 13 min, the precipitates grew as larger agglomerates. It was shown that as the size of the precipitates increased, the shape of the agglomerates became more spherical. When the reaction time reached 21 min, the precipitates became agglomerates of relatively uniform spherical particles that were fused together by well-formed necks. By further growth, the precipitates appeared to be spherical, as shown in Fig. 3(D). Generally, the smaller precipitates are coagulably unstable because of the low energy barriers for the same surface potential, as shown in Eq. (1). 17,18 Therefore, the initial unstable nuclei are rapidly agglomerated until the coagulable stability against further agglomeration is achieved.

Li and Messing 18 reported that spherical zirconia powders are obtained by mixing n-PrOH with zirconia aqueous sols, which is attributed to a lower potential energy barrier caused by the reduction of the dielectric constant of sols. It appears that the spherical morphology of agglomerates is the result of preferential aggregation of precipitating materials, having a low potential energy barrier at the neck. The neck formation of particles was extensively studied by Look and Zukoski. 12,13 They argued that the combination of electrostatic and short-range repulsion gives rise to a shallow secondary minimum which develops for certain particle sizes and results in the formation of doublets that can be fused together. Spherical and neck-formed powders are shown in Fig. 3(E).

Figure 4 shows the yield of powders obtained at RH ratios of 0 and 1.0 as a function of reaction time and temperature. The yield is determined by dividing the weight of powders dried at 100°C by the weight of product when n mol of titania is formed from n mol of titanium sulfate according to the following chemical reaction:

$$nTi(SO_4)\_2 + 2nH_2O = nTiO_2 + 2nH_2SO_4$$

As the reaction temperature increased, the yield rapidly increased with the reaction time. At 80°C and 90°C, the yield at a ratio of 1.0 increased more rapidly than that of an RH ratio of 0. It is thought that by reducing the dielectric constant of the solvent at higher reaction temperature, a mixed solvent of n-PrOH and water promotes the precipitation rate of titania powders, as shown by the results of Moon et al. 19,20 Similarly, a decrease of the dielectric constant with the RH ratio is believed to increase the yields of precipitates.

Figure 5 shows the X-ray patterns of powders calcined at various temperatures. It was found that the precursor powders were amorphous below around 400°C. A very broad and small peak of anatase phase appeared at 400°C. And as the calcination temperature increased up to 600°C, rutile phase peaks appeared. After calcination at 800°C for 2 h, anatase phase completely transformed into rutile phase. Figure 6 shows SEM micrographs for the precursor and the calcined powders at 800°C for 2 h. The calcined powders retained the morphology of the precursor powders, but their size decreased from approximately 0.9 to 0.7 μm. Crystalline titania powders of rutile phase with monodisperse spherical shape were obtained by calcination of the precursor powders at 800°C for 2 h in air.

IV. Conclusions

Titania powder morphology was affected by the composition of a mixed solvent in the thermal hydrolysis of titanium sulfate. The particle interaction potential varied with the solvent composition. When the RH ratio of the solvent was 1.0, the powders had spherical shape and nonagglomerated morphology. Considering the zeta potential of the powders and the dielectric constant of the solvent, the energy barrier was maximum at an RH ratio of 1.0. The shape of precipitating particles changed with reaction time. The initial nanoscale particles were found to be irregularly shaped. As the particle size increased, the shapes of the particles became more spherical by preferential aggregation at the neck. X-ray diffraction analysis showed that the precursor
Fig. 6. SEM micrographs of (A) the precursor powders and (B) the calcined powders at 800°C for 2 h.

powder was hydrated amorphous phase and that it transformed into rutile phase while retaining its shape after calcination.

References