Preparation of Monodisperse and Spherical Powders by Heating of Alcohol-Aqueous Salt Solutions

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Abstract. A method for the preparation of monodisperse and spherical powders from salt solution with a mixed solvent of alcohol and water is demonstrated. The volume ratio of alcohol to water (R/H ratio) in the alcohol-aqueous salt solutions greatly influenced the behavior of the precipitation and the morphology of the resulting particles. The precipitation, by heating an alcohol-aqueous salt solution, occurs by the decrease of dielectric constant of the solvent and thus a decrease in the salt solubility. The morphology and size variation of the resulting particles was explained by considering the parameters determining the colloidal stability in the DLVO theory; the zeta potential and the dielectric constant. During the preparation of the powders by heating of the alcohol-aqueous salt solution, the effect of heating methods on the characteristics of the resulting particles is also demonstrated. A microwave heating, as a uniform and rapid heating method, induced the uniform and rapid precipitation to produce monodisperse and spherical particles.

1. Introduction

Recently, significant research has been focused on the preparation of particles with controlled morphology, size, and size distribution. Fine and spherical particles with a narrow size distribution have been known to be desirable for producing advanced ceramics with enhanced reliability [1]. Thus, a large number of methods that satisfy these requirements have been developed.

Among these methods, a sol-gel process, using the alcoholic solution of metal alkoxides, and aqueous based methods, using the aqueous solution of metal salts, have been widely studied. The sol-gel process has shown many successful results and produced spherical particles with controlled size and size distribution, such as SiO_2 [2–4], Al_2O_3 [5, 6], Ta_2O_5 [7], TiO_2 [8–12], and ZrO_2 [13, 14]. However, characteristics of the particles prepared by the sol-gel process were changed very sensitively by experimental conditions and, in some case, were difficult to reproduce [9–11, 14]. In addition to this, metal alkoxides are relatively

expensive precursor materials. These have made the sol-gel process difficult to be more widely applied to industrial production.

On the other hand, several aqueous-based methods such as the forced hydrolysis method [15, 16] and the homogeneous precipitation method [17, 18] have been known to simply produce particles from relatively cheap metal salts. To control the characteristics of the resulting particles, the control of pH and the addition of electrolytes were generally used. However, due to the high reactivity of the metal salts, in the synthesis of the monodisperse and spherical particles, the concentration of reaction species has been found to be low and the reaction time very long [15–18].

Recently, the present authors have shown that monodisperse and spherical particles could be prepared at relatively high concentration of reaction species and short reaction time by heating alcohol-aqueous salt solutions [19–26]. These results could be achieved, in some part, by changing the aqueous medium, used in the conventional aqueous-based methods, to the mixed

solvent of alcohol and water. In the previous methods for synthesizing particles, different combinations of precursor materials and solvents, e.g., metal alkoxides and alcohols and metal salts and water have been used. Recently, these combinations of precursor materials and solvents have been changed in some cases, e.g., the preparation of monodisperse and spherical organo-silica particles by hydrolyzing organo-alkoxy silanes in water solution where no alcohol was added as a solvent [27].

In this paper, based on our previous results [19–26], a method for the preparation of monodisperse and spherical powders of ZrO_2, TiO_2, and $ZrTiO_4$ by heating of salt solution with mixed solvent of alcohol and water, is demonstrated. The precipitation behavior in the mixed solvent is discussed and the effects of the mixed solvent on the formation and morphology of particles are examined in view of colloidal stability. During the preparation of the powders by heating of the alcohol-aqueous salt solutions, the effect of heating methods on the characteristics of the resulting particles is also discussed.

2. Experimental Procedure

Figure 1 shows a flowchart of the process used in this work. As precursor materials, zirconyl chloride octahydrate (98% $ZrOCl_2 \cdot 8H_2O$, Aldrich Chemical, Milwaukee, WI), titanium disulfate (98% $Ti(SO_4)_2$, Wako Chemical Industries, Japan), and titanium tetrachloride (98% $TiCl_4$, Wako Chemical Industries, Japan) were dissolved in distilled and deionized water. These aqueous solutions were mixed with alcohols to adjust the volume ratios of alcohol to water (R/H ratio) at 4°C. Hydroxypropyl cellulose (HPC), if needed, was added to the starting solutions as a steric stabilizer. All reagents were used in the as-received form, with no further purification.

The starting solution was heated by an ordinary kitchen microwave oven (2.45 GHz, 650 W) or by being kept in an isothermal bath without stirring. When the starting solution was heated, it became supersaturated and precipitated at a certain temperature. After precipitation, mother liquor was neutralized by adding a $4NNH_4OH$ solution to remove the chloride ion. This neutralization prevented the formed precipitates from re-dissolution during cooling. The precipitates obtained from the above procedure were centrifuged repeatedly and washed in distilled water until no chloride ions could be detected in the supernatant solution.
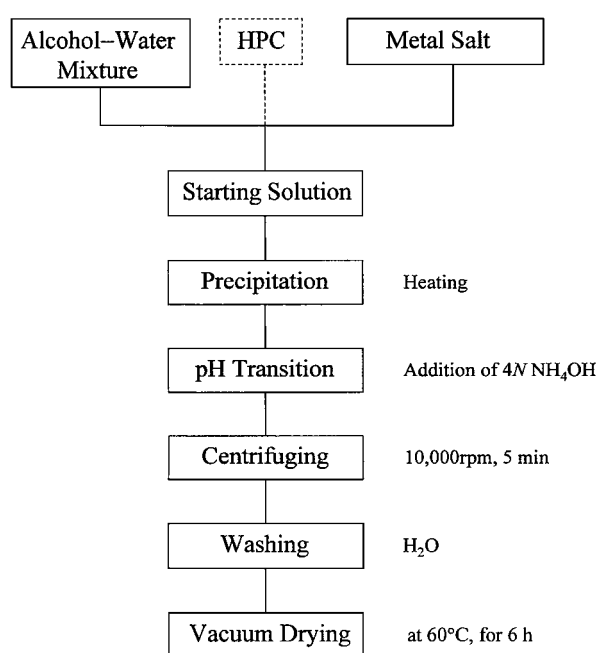

Figure 1. Flowchart of the process used for the preparation of particles by heating the alcohol-aqueous salt solution.

Resulting water-washed precipitates were dried in a vacuum oven.

To verify the effect of the mixed solvents of alcohol and water on the colloidal stability and thus the characteristics of resulting particles, zeta potential was measured by the use of an electrophoretic technique (Zetamaster, Malvern, UK). The morphology, size, and size distribution of the resulting particles were determined by scanning electron microscopy (SEM). More detailed experimental procedure and analysis methods are well documented in previous literature [19–26].

3. Results and Discussion

3.1. Precipitation in the Alcohol-Aqueous Salt Solution

When an adequate amount of alcohol is added to an aqueous salt solution, the salt solution becomes supersaturated and precipitation occurs. This phenomenon has been generally known and used for the extraction of salts from salt solutions in analytical chemistry or preparing ceramic or metal powders by the liquid drying method [28, 29]. The precipitation, induced by an addition of alcohol into the aqueous salt solution has

Table 1. Physical properties of water and several alcohols [20].

Solvent	Boiling point (°C)	Solubility of $ZrOCl_2 \cdot 8H_2O$	Dielectric constant at 20°C
Water	100	Soluble	80.37
Methanol	64.7	Soluble	32.35
Ethanol	78.3	Soluble	25.00
1-Propanol	97.2	Insoluble	20.81
2-Propanol	82.3	Insoluble	18.62
t-Butanol	82.5	Insoluble	8.44[a]
Glycerol	290	Insoluble	41.14

[a]Dielectric constant at 40°C.

Figure 2. Variation of dielectric constant (open mark) with temperature and precipitation point (closed circles) for each starting solution. The *R/H* ratio and the concentration of $ZrOCl_2 \cdot 8H_2O$ were 5 and 0.2M, respectively [15].

been known to occur because the alcohol of low dielectric constant decreases the solvation energy and thus the salt solubility of the mixed solvent [30, 31].

The dielectric constant of an alcohol-water mixed solvent decreases with an increase in temperature as well as an increase in the volume ratio of alcohol to water. The solubility of an inorganic salt decreases with a decrease in the dielectric constant of the solvent [32]. Thus, precipitation may occur by heating a salt solution with the mixed solvent of alcohol-water because the dielectric constant of the solution is decreased significantly with an increase in temperature. However, when aqueous salt solution is heated, precipitation does not generally occur. One of the reasons can be due to the fact, that a decrease in the dielectric constant of the aqueous solution with an increase in the temperature is not sufficient to induce precipitation, where water has much higher dielectric constant than alcohols, as shown in Table 1. Thus, precipitation can occur by adding alcohol to the aqueous salt solutions or heating the alcohol-aqueous salt solution. In the former method, uniform precipitation is not easy to occur because of the local composition inhomogeneity caused in adding the alcohol. Therefore, the authors prepared alcohol-aqueous salt solution by adding alcohol into the aqueous salt solution, where the solubility of the salt was decreased enough to induce precipitation by only heating, and then heating uniformly the alcohol-aqueous salt solutions to precipitate monodisperse and spherical particles.

Figure 2 shows the temperature dependencies of the dielectric constants of various alcohol-aqueous $ZrOCl_2 \cdot 8H_2O$ salt solutions. The precipitation temperature of each starting solution is represented by a closed circle. The precipitation temperature is very different for each starting solution, but the dielectric constants at the precipitation temperatures have simi-
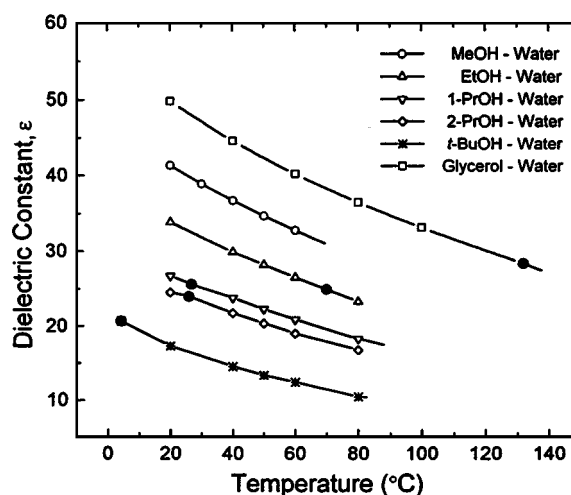
lar values (~25). This shows that the solubility of zirconium ion in an alcohol-water mixed solvent is related to the dielectric constant of the solvent and the precipitation can take place when the dielectric constant is decreased below a certain value by heating of the solution. From all kinds of alcohol-containing solutions except those containing MeOH, precipitation is observed during heating. The dielectric constant of the MeOH-aqueous $ZrOCl_2 \cdot 8H_2O$ solution can not be decreased enough to cause precipitation, because MeOH has a high dielectric constant and a low boiling point, as shown in Table 1.

Figure 3 shows the effect of the *R/H* ratio on the precipitation behavior. The precipitation temperature is decreased with an increase in the *R/H* ratio. The dielectric constants at each precipitation temperature, however, are about 25. This value is similar to the dielectric constants at the precipitation temperatures as shown in Fig. 2. This result also shows that the precipitation can take place when the dielectric constant is decreased below a certain value (~25) by heating of the solution. In the case of solutions with the *R/H* ratio of 6, precipitation occurs at about room temperature because the dielectric constant of the solution is sufficiently low. On the other hand, when the *R/H* ratio is below 1, precipitation cannot occur up to the boiling point of the 2-PrOH-containing solution because the dielectric constant of the solution is too high.

When precipitation occurs by heating the alcohol-aqueous salt solution, it can occur by the decrease of
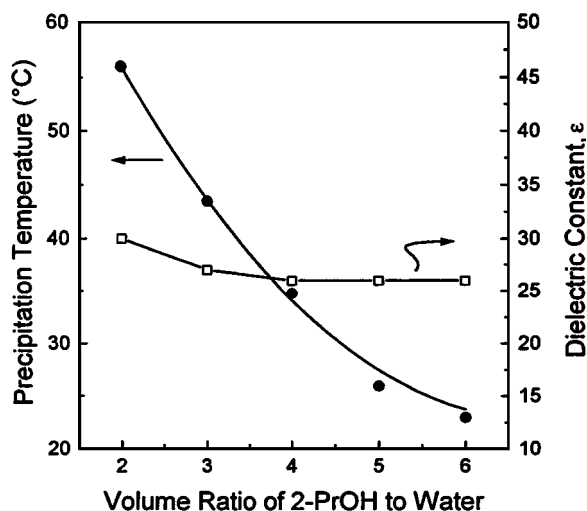
Figure 3.   Variation of precipitation temperature and dielectric constant at precipitation temperature with the *R/H* ratio. The concentration of $ZrOCl_2 \cdot 8H_2O$ was 0.2M [15].

salt solubility induced by the decrease of the dielectric constant or the chemical reaction such as the hydrolysis reaction of the salt ion. According to the above results (Figs. 2 and 3), precipitation takes places when the dielectric constant is decreased to about 25 regardless of the kinds of alcohol and the *R/H* ratios of the alcohol-aqueous salt solutions whereas the precipitation temperatures for each case are very different. These results strongly indicate that the precipitation was caused by the decrease of the dielectric constant of the solvent and thus the decrease of the salt solubility. This precipitation method can be used as another method to make uniform precipitation in systems where salt solubility is decreased by heating.

3.2.   Effect of Heating Methods on the Characteristics of the Resulting Particles

For the uniform precipitation by heating the alcohol-aqueous salt solution, the uniform heating of a reaction vessel is a necessary condition. If the alcohol-aqueous salt solution with the precipitation temperature of 40°C is heated slowly to 70°C, precipitation occurs continuously from 40 to 70°C during the increase of temperature. The precipitates formed at the different temperatures have different precipitation conditions and thus may have different characteristics. Thus, it is necessary to apply the rapid and uniform heating

method to get the uniform precipitation by heating the alcohol-aqueous salt solutions. However, the conventional heating apparatus, such as thermal bath, hot plate, and heating mentle, can not avoid the temperature gradient in the reaction vessel, because heat transfers from external to internal part in the reaction vessel. Furthermore, those heating methods are not suitable for a rapid heating. A microwave heating method can satisfy these requirements, i.e., uniform and rapid heating. Microwave heating, where material absorbs microwave and heats itself, has been known to provide the following properties [7]: (1) volumetric heating rather than the surface absorption and thermal diffusion afforded by conventional heating, (2) potentially uniform heat distribution, (3) rapid heating rate, and (4) the possibility of selectively heating desired materials. To date, the most common applications of microwave technology in ceramic processing include binder removal [34], drying [35], joining [36], and sintering [37, 38].

Figure 4(a) shows ZrO_2 particles obtained when the reaction vessel was heated rapidly (15°C/min) by abrupt immersion of the vessel into an isothermal bath at 80.3°C having a temperature gradient between the vessel wall and the inner part in the vessel, and Fig. 4(b) when the reaction vessel was deeply immersed in a bath whose temperature was increased to 80.3°C slowly (0.3°C/min) to avoid the temperature gradient. Figure 4(c) shows ZrO_2 particles obtained by microwave heating where the reaction vessel was heated very rapidly (120°C/min) with no temperature gradient in the vessel which is nearly impossible to obtain by the conventional heating methods. In the rapid heating with temperature gradient in the vessel (Fig. 4(a)), the particles were spherical but with a broad size distribution; the particles size and its geometric standard deviation were 0.29 μm and 1.25, respectively. Homogeneous precipitation could not occur because local supersaturation took place from the preferentially heated vessel wall. In the slow heating with no temperature gradient in the vessel (Fig. 4(b)), a large amount of precipitates settled to the bottom of the reaction vessel before the precipitation reaction was complete. Accordingly, subsequent precipitation resulted mainly in the growth of a neck between these particles. In the case of microwave heating, the obtained particles were monodisperse and spherical, with diameters of 0.28 μm and a geometric standard deviation of 1.12, indicating that a rapid and uniform heating by microwave is very effective to produce monodisperse and spherical particles in heating the alcohol-aqueous salt solution. Therefore,
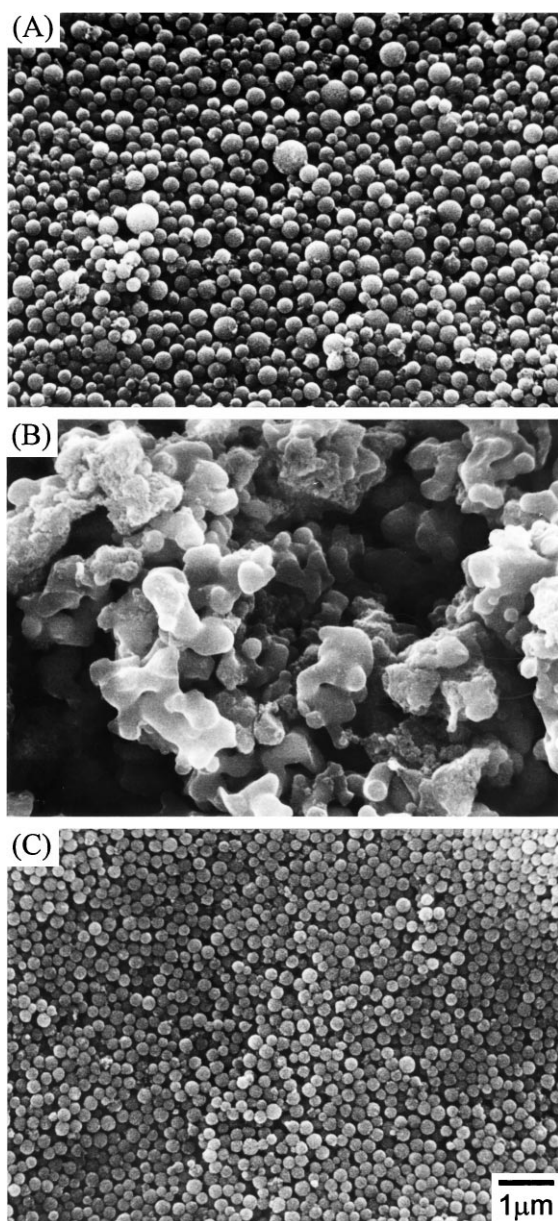
Figure 4. SEM micrographs of the ZrO_2 particles obtained when the reaction vessel was heated rapidly (15°C/min) by abrupt immersion of the vessel into a isothermal bath at 80.3°C (a), when the reaction vessel was deeply immersed in a water bath and slowly heated to 80.3°C with 0.3°C/min (b), and when the solution was rapidly heated to 80.3°C by microwave (c). The *R/H* of 2-PrOH to water was 5. The concentrations of $ZrOCl_2 \cdot 8H_2O$ and HPC were 0.2M and 1.5×10^{-3} g/cm³, respectively.

microwave heating can be applied to any other chemical synthesis, requiring a rapid heating without temperature gradient. Especially, for large reaction vessel, the microwave heating method will give more uniform and rapid heating than the conventional heating methods.

3.3. Effect of the Mixed Solvent of Alcohol and Water on the Characteristics of the Resulting Particles

As demonstrated in Section 3.1, the *R/H* ratio and the kind of the mixed solvent of water and alcohol influenced the precipitation behavior in the alcohol-aqueous salt solution. The change of the *R/H* ratio had an influence on the dielectric constant of the solvent and thus the salt solubility and precipitation temperature. The mixed solvent of water and alcohol may also have an effect on the colloidal stability of particles in solution to change the characteristics of the resulting particles. Li and Messing prepared spherical zirconia particles by adding 1-PrOH to a zirconia aqueous sol [39]. They argued that adding the 1-PrOH to the zirconia aqueous sol reduced the dielectric constant and thus energy barrier between particles, causing the sol particle to aggregate into the spherical particles. In solution, particles are influenced by various forces, such as van der Waals attractive forces, electrostatic repulsive forces, steric repulsion, and solvation energy.

The *R/H* ratio of the alcohol-aqueous salt solution, by changing the parameters of these forces determining colloidal stability, may influence the characteristics of the resulting particles.

According to DLVO theory, the energy barrier between two particles which inhibits agglomeration can be expressed as [40]

$$V = -\frac{Aka}{12} + 2\pi\varepsilon_0\varepsilon_r a\psi^2 \qquad (1)$$

Where A is the effective Hamaker constant, k the Debye-Huckel parameter, a the particle diameter, ε_r the relative dielectric constant of the liquid medium, ε_0 the dielectric constant of vacuum, and ψ the surface potential. The Debye-Huckel parameter is expressed as follows:

$$k = \left(\frac{2F^2Z^2N_0}{\varepsilon_0\varepsilon_r k_b T}\right)^{1/2} \qquad (2)$$

Where k_b is the Boltzmann constant, F the electrical charge (96,500 C), Z the ionic valence, and N_0 the concentration of the electrolyte. The effective Hamaker constant depends on the dispersion medium. The kind and composition of the solvent mixture may not greatly influence the effective Hamaker constant because the Hamaker constants of water and several aliphatic alcohols in free space have similar values, in the order of 10^{-20} J. The colloidal interaction potential depends
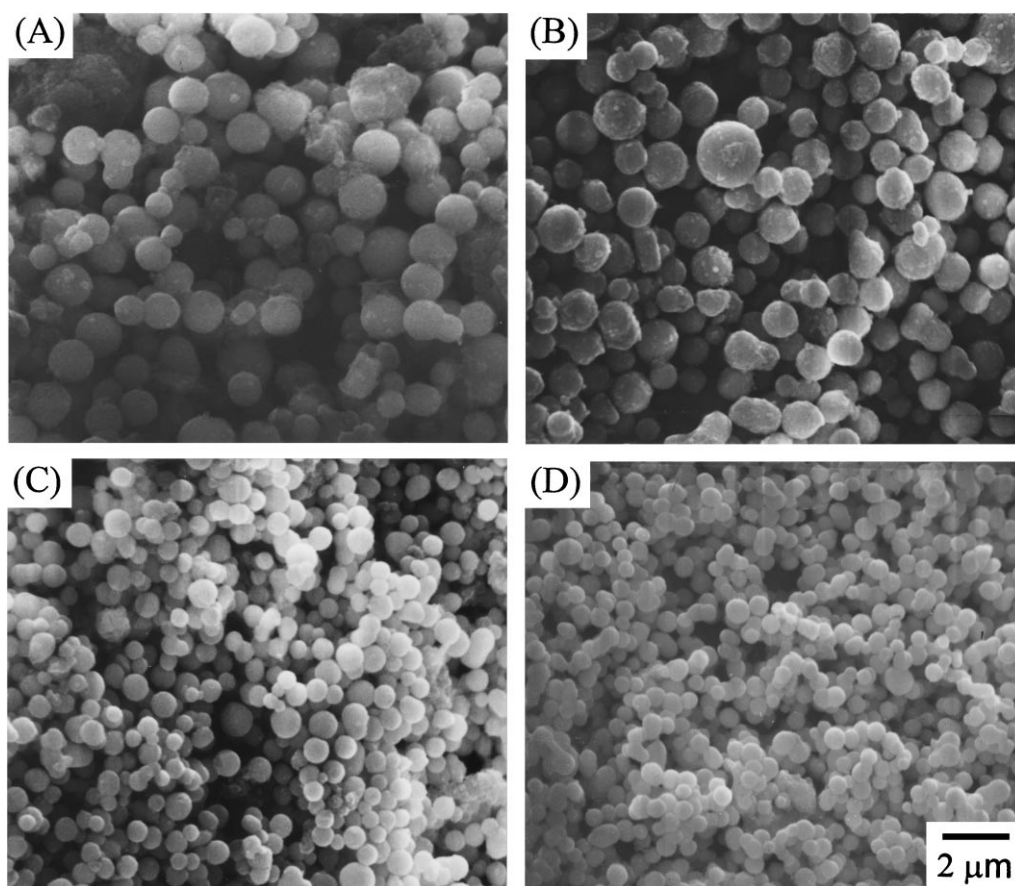
Figure 5.   SEM micrographs of the ZrO$_2$ particles obtained from the ZrOCl$_2$·8H$_2$O solutions with the various *R/H* ratios of 2-PrOH and water; (a) 2, (b) 3, (c) 4, and (d) 5. The concentration of ZrOCl$_2$·8H$_2$O was 0.2M.

on the electrolyte concentration, which determines the Debye-Huckel parameter. In the preparation of the starting alcohol-aqueous salt solutions, other electrolytes did not exist in the solutions, except for ions released from the starting salts. Under these conditions, when the *R/H* ratio of the starting solution is varied, the magnitude of the energy barrier between particles in the solutions can be compared mainly by the surface potential and the dielectric constant. Thus, considering of the surface potential and the dielectric constant may elucidate the characteristics of the resulting particles formed in the alcohol-aqueous salt solution.

Figure 5 shows the ZrO$_2$ particles obtained from ZrOCl$_2$·6H$_2$O solution with the solvent 2-PrOH and water with the different *R/H* ratios. The starting solutions were heated by an ordinary kitchen microwave oven (2.45 GHz, 650 W) to the boiling point

(about 80°C). The mean particle diameter of the resulting particles decreased with an increase of the *R/H* ratio. Table 2 shows the variation of the dielectric constant of the mixed solvents at the boiling point and the zeta potential of particles with the *R/H* ratios of the mixed solvents. The zeta potential is negatively increased and the dielectric constant of the solvent is

Table 2.   Dielectric constants of mixed solvents and zeta potentials of particles with the *R/H* ratios of the mixed solvents.

R/H ratio	Dielectric constant at boiling point [32]	Zeta potential (mV) at 20°C
2	25.29	−12.6
3	20.53	−25.9
4	18.52	−29.1
5	16.83	−37.4

decreased with the R/H ratio. According to Eq. (1), the magnitude of the energy barrier between particles is dependent more dominantly on the increase of the zeta potential than the decrease of the dielectric constant. Thus, the increase of the absolute zeta potential value increases the magnitude of the energy barrier. According to DLVO theory, under high energy barrier against aggregation between primary particles, the primary particles aggregate to form smaller particles than under low energy barrier. According to Li and Messing's results [39], primary zirconia sol aggregated to form large spherical ZrO_2 particles by an decrease of the energy barrier. Therefore, in this study, high R/H ratios with the high energy barrier produce smaller particles than low R/H ratios.

In Fig. 5, some particles are composed of agglomerates, fused with relatively uniform spherical particles. This means that the colloidal interaction potential operated by electrostatic force is not sufficiently repulsive to prevent the agglomerates. Jean and Ring suggested that a polymeric stabilizer, HPC, could be used to control the colloidal interaction potential [9, 10]. They 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 [9, 10]. They also reported the advantages of the HPC dispersant: (1) HPC provides thermodynamic stability, not kinetic stability as in electrostatic stabilization; (2) HPC physically adsorbed onto the particles prevents agglomeration during growth; (3) HPC molecules do not act as heterogeneous nucleation sites. In the present work, HPC, as a steric stabilizer, was also used to gives an additional repulsive force from the adsorption of macromolecules onto the particles, thus to prepare particles with more controlled morphology, size, and size distribution. Figure 6 shows the ZrO_2 particles when HPC is added as a steric stabilizer. Other experimental conditions were identical to those in the case of particles in Fig. 5. Compared with the particles formed without HPC (Fig. 5), the mean diameter of the particles decreased and the formation of doublet and/or multiplet also reduced. These results indicate that HPC, as a steric stabilizer, gave an additional repulsive force, producing smaller and well-dispersed particles. The mean diameter of the particles formed with the HPC, similar to the case without HPC, also decreased with an increase of the R/H ratio. This result can be also understood by considering the magnitude of the energy barrier between particles where just an additional

repulsive force by steric stabilizer, HPC, was added to the system shown in Fig. 5.

Figure 7 shows TiO_2 particles obtained at the R/H ratio of 0 and 3.5 from $TiCl_4$ solution with a solvent of 1-PrOH and water, where the concentration of $TiCl_4$ was 0.1M. The particles were precipitated by keeping the starting solutions in an isothermal bath of about 80°C without stirring. For an R/H ratio of 0, the precipitated particles were found to be very fine. In contrast, the particles formed at an R/H ratio of 3 were spherical and discrete, with some doublets fused together. These differences in morphologies indicate that the colloidal stability of the precipitated particles in the mixed solvent of 1-PrOH-water is different from that of water solvent. These results can be also understood by considering the parameters determining the colloidal stability. The dielectric constants, the zeta potential and the precipitate morphologies are summarized in Table 3. As the R/H ratio of solvent increases, the zeta potentials and the dielectric constants decrease rapidly. For the solvent with an R/H ratio of 0, the dielectric constant of the solvent and the zeta potential of the particles are very high whereas for the solvent with an R/H ratio of 3, the zeta potential and the dielectric constant are low. Considering the magnitudes of the potential energy barriers in Eq. (1), the potential energy barrier for R/H ratio of 0 and 3 is relatively high and low, respectively. Under high potentialn energy barrier, relatively small particles may be stable against the aggregation, the resulting particles appear to be fine as shown in Fig. 7(a). The large and discrete particles for an R/H ratio of 3, having a low potential energy barrier, should be formed by the aggregation of initially nucleated small particles. Formation of TiO_2 particles by the aggregation was well shown in our previous publication.

Figure 8 shows the TiO_2 particles obtained at various ratios of R/H ratio from $Ti(SO_4)_2$ solution with a solvent of 1-PrOH and water where the concentration of

Table 3. Dielectric constants of the mixed solvents and zeta potentials and morphologies of particles with the R/H ratios of the mixed solvents [22].

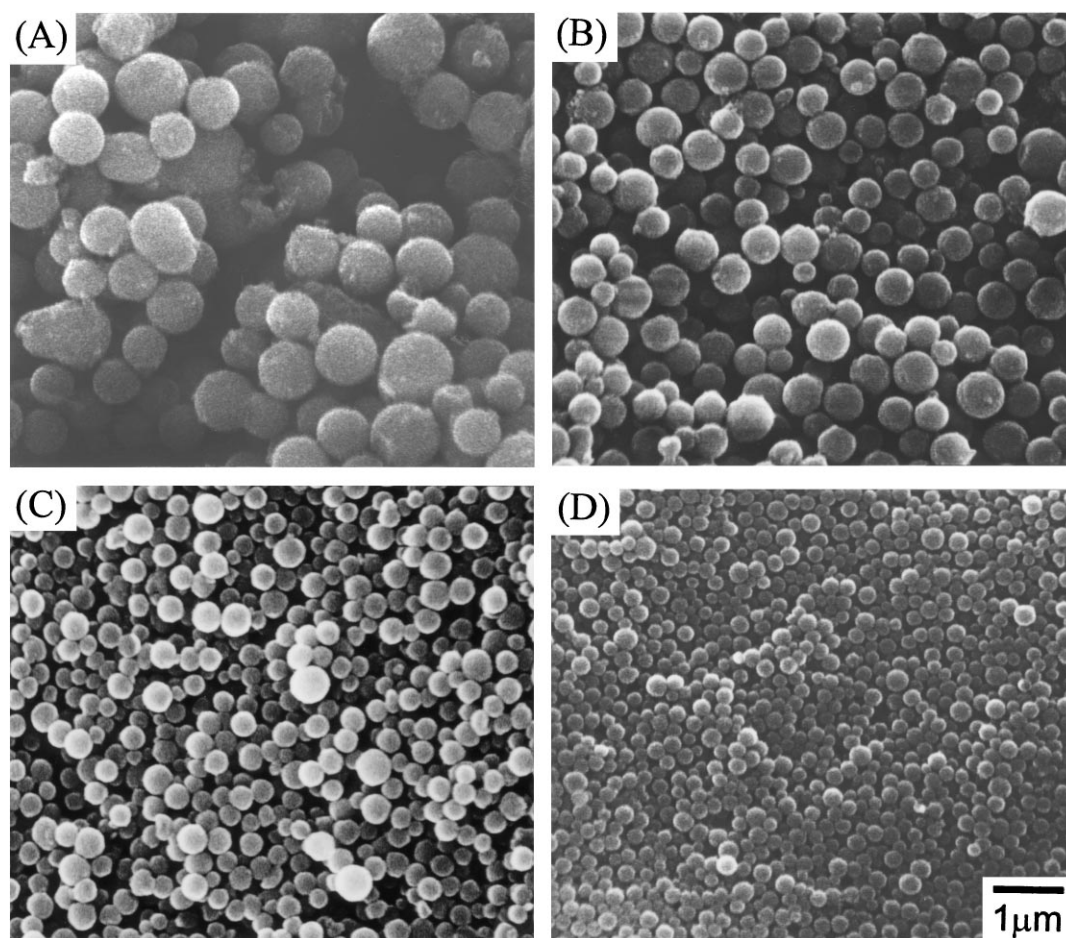| R/H ratio	Dielectric constant at boiling point [32]	Zeta potential (mV) at 20°C	Particle morphology
0	80	18.3	Fine, aggregated
1	48	11.4	Aggregated
2	36	6.7	Spherical, aggregated
3	32	4.5	Spherical, discrete

Figure 6.   Variations of mean particle size and geometrical standard deviation with the *R/H* ratios of 2-PrOH and water. The concentrations of ZrOCl$_2$·8H$_2$O and HPC were 0.2M and 1.5×10^{-3} g/cm^3, respectively.

Ti(SO$_4$)$_2$ was 0.12M. The particles were also precipitated by keeping the starting solutions in an isothermal bath of about 80°C without stirring. When the *R/H* ratio was 0, the powders were highly agglomerated. The particles obtained from the mixed solvent of 1-PrOH and water were more spherical with an increase of the *R/H* ratio. Especially at an *R/H* ratio of 1.0, the particles had spherical morphology. At an *R/H* ratio of 1.5, however, the particles appeared to be more agglomerated. Table 4 shows the zeta potentials, the dielectric constants, and the energy barriers with the variation of the *R/H* ratio. The zeta potentials of the powders were negatively increased and the dielectric constants of the solvent were decreased with the *R/H* ratios. Using $A = 2.5 K_b T$ ($T = 298$ K), $N_0 = 0.24$M (as determined by the concentration of SO$_4^{2-}$), and $a = 1 \mu$m, the energy barrier between the particles was determined

from Eq. (1). The barrier increased with the *R/H* ratios and the maximum energy barrier appeared at an *R/H* ratio of 1.0. At an *R/H* ratio of 1.5, the energy barrier decreased in spite of the negatively highest zeta potential. Thus, at an *R/H* ratio of 1.0 at the maximum

Table 4.   Dielectric constants of the mixed solvents, zeta potentials and energy barriers of particles with the *R/H* ratios of the mixed solvents [21].

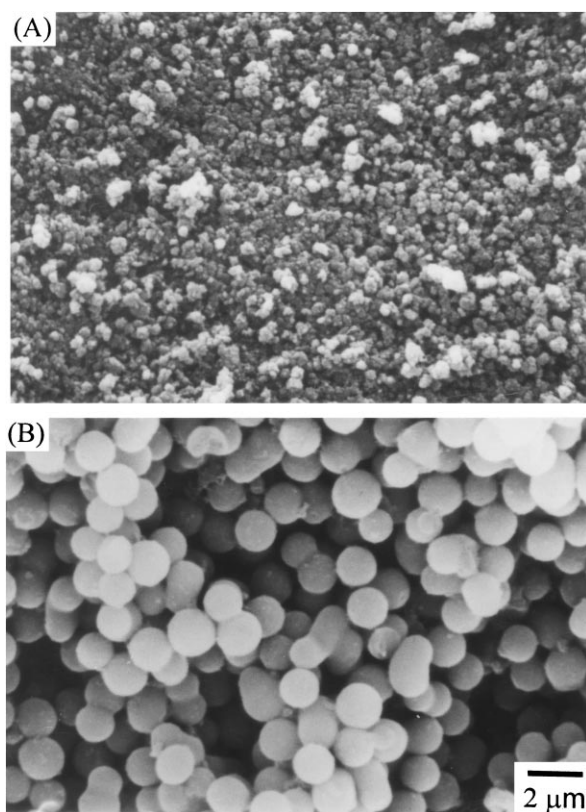| *R/H* ratio	Dielectric constant at boiling point [32]	Zeta potential (mV) at 20°C	Energy barrier, V_b (eV)
0	80.37	−20.6	11.90
0.5	59.21	−32.3	21.53
1.0	48.98	−38.5	25.30
1.5	40.09	−40.2	22.59

Figure 7. SEM micrographs of the TiO$_2$ particles obtained at the *R/H* ratio of 0 and 3.5 from TiCl$_4$ solution with a solvent of 1-PrOH and water. The concentration of TiCl$_4$ was 0.1M [22].

energy barrier, spherical particles were formed by sufficient repulsion force for the controlled aggregation of initially nucleated small particles whereas at other *R/H* ratios, irregular and highly agglomerated particles were formed by the uncontrolled aggregation of initially nucleated small particles because of low energy barrier.

Figure 9 shows the ZrTiO$_4$ particles obtained from ZrOCl$_2$·6H$_2$O and TiCl$_4$ solution with the solvent of 1-PrOH and water. Starting solutions were heated in ordinary kitchen microwave oven. It can be seen that monodisperse and spherical particles of the binary compound were successfully obtained by heating the alcohol-aqueous salt solution.

The above results show that the variation of the *R/H* ratio influences factors determining colloidal stability; the dielectric constant of solvents and the zeta potential of particles, to change the characteristics of the resulting particles.

4. Summary and Further Suggestion

From our results, it can be seen that monodisperse and spherical particles were successfully prepared by heating alcohol-aqueous salt solutions. This powder preparation method may be applied to many other systems as well as the systems mentioned in this paper.

In the heating of the alcohol-aqueous salt solution, precipitation occurred by the decrease of dielectric constant of the solvent and thus the decrease of salt solubility. The volume ratio of alcohol to water (*R/H* ratio) in the alcohol-aqueous salt solutions influenced the characteristics of the resulting particles as well as the precipitation behaviors. The morphology and size variation of the resulting particles could be explained in some part by considering the zeta potential and the dielectric constant, which are the parameters determining the colloidal stability in the DLVO theory.

In this study, we considered the alcohol as a solvent and not the possibility that alcohol could act as reaction element. According to our previous results [22], the chemical adsorption of 1-PrOH on growing TiO$_2$ particles decreased the zeta potential of the particles, which indicates that Ti–OR group could be formed in salt solution with a mixed solvent of alcohol and water. In the sol-gel process, silicon alkoxides are dissolved in alcoholic solution employing water as a reaction element for hydrolysis and mineral acid (HCl) or base (NH$_3$) as a catalyst. Under most conditions, a mutual solvent such as alcohol is used as a homogenizing agent because water and silicon alkoxides are immiscible. However, the alcohol as a mutual solvent takes part in the reaction as a reaction element through esterification (the reverse reaction of hydrolysis) and alcoholysis (the reverse reaction of the alcohol condensation). In the case of aqueous-based methods such as the forced hydrolysis method and the homogeneous precipitation method, metal salts are dissolved and reacted in water solution where water acts as a reaction element through the hydrolysis and condensation reaction as well as a solvent. Therefore, in the powder preparation from the alcohol-aqueous salt solution, the interactions between alcohol and particle surface and the hydrolysis reaction including the role of alcohol as a reaction element should be considered to elucidate the more detailed precipitation mechanism and the effect of the solution properties on the characteristics of resulting particles.
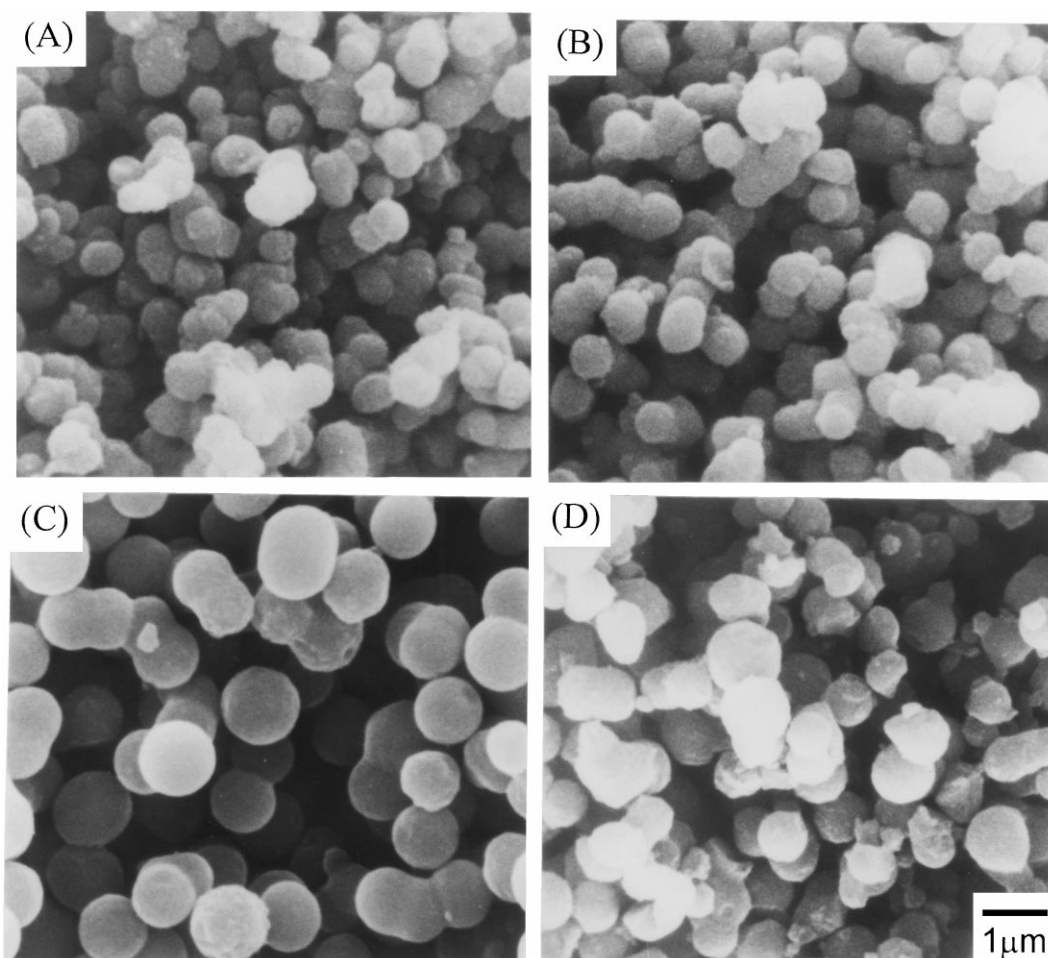
Figure 8. SEM micrographs of the TiO$_2$ particles obtained at various R/H ratios; (a) 0, (b) 0.5, (c) 1.0, and (d) 1.5. The concentration of Ti(SO$_4$)$_2$ was 0.12M [21].

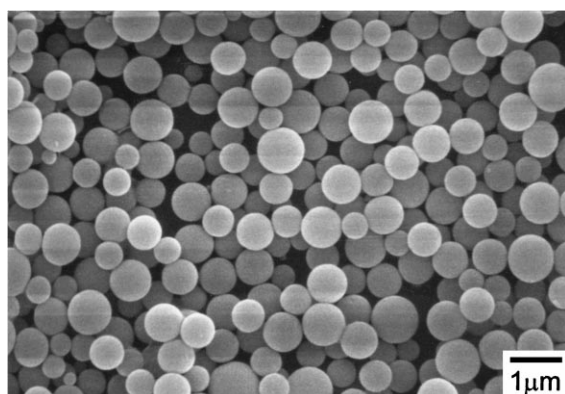*Figure 9.* SEM micrographs of the ZrTiO$_4$ particles obtained from ZrOCl$_2$·6H$_2$O and TiCl$_4$ solution with a solvent of 1-PrOH and water. The ratio of ZrOCl$_2$·6H$_2$O to TiCl$_4$ was 1 and the concentrations of the salts and HPC were 0.1M and 0.3×10^{-3} g/cm^3, respectively.

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