The agglomeration control of alkoxide derived TiO₂-SiO₂ hybrid nano-particle

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This paper describes the effects of the drying conditions of titania-silica (TiO₂-SiO₂) sol on the dispersibility of the hybrid particles. The hybrid sol of SiO₂ nano-particles coated with TiO₂ was prepared by a sol-gel process with controlled chemical modification (CCM). The effects of the initial pressure of supercritical drying (SCD) and the zeta potential in the sol on the dispersibility of the particles were investigated to obtain the well-dispersed TiO₂-SiO₂ hybrid particles. As a result, well-dispersed TiO₂-SiO₂ hybrid particles were successfully prepared by controlling the initial pressure of SCD and/or the zeta potential.

Key words: TiO₂-SiO₂, hybrid particles, supercritical drying, zeta-potential

1. INTRODUCTION

Recently, nano-particles have been widely studied in the various fields such as catalytic, optic and electric materials due to their unique physical and chemical properties. In general, the characteristics of particles do not change by the particle size and the shape. However, the physical properties dramatically change in the case of nano-particles. Haruta et al. reported that Au nano-particles have high catalytic activities for various reactions such as oxidation of CO, reduction of NO_x and so on [1]. In addition, Ohno et al. demonstrated that the dielectric property of barium titanate (BaTiO₃) increased with decreasing particle size [2]. Furthermore, Ishikawa et al. reported the surface relaxation model to explain the origin of the quantum size effect [3,4]. Although the quantum size effect has a possibility to improve the physical properties of materials, there is a difficulty in manipulation and handling of nano-sized particles, due to the adhesion and the coagulation of the primary particles. To solve this problem, we have proposed nano-coating of functional components on monodispersed SiO₂ particles [5,6].

In our previous studies, TiO₂-SiO₂ hybrid sol were prepared by a sol-gel process with CCM, and the hybrid particles were obtained by SCD of the sol to suppress the agglomeration during drying process. The obtained TiO₂-SiO₂ hybrid particles were in sub-micron size, but showed the blue shift of the band gap energy due to the quantum size effect [5]. This result indicated that the characteristic of particles was improved by hybridization. However, the agglomeration of the particles still appeared, even in the case of the SCD, indicating that the agglomeration force during drying process could not be completely suppressed in our previous drying conditions. This is likely to come from the contact to the vapor-liquid equilibrium line in SCD process

and/or coagulation of particles in the sol.

In this study, the effects of the initial pressure of SCD on the dispersibility of the particles were investigated to obtain the well-dispersed primary hybrid particles. In addition, relationship between the dispersibility of the sol and the agglomeration of the hybrid particles was also studied. The dispersibility of the sol was controlled by the zeta potential of particles in the sol.

2 EXPERIMENTAL PROCEDURE

2.1 Preparation of TiO₂-SiO₂ hybrid nano particle

TiO₂-SiO₂ hybrid sol were prepared by a sol-gel process with CCM technique. SiO₂ core particles were prepared by the Stöber method. The starting reagents were tetraethyl-orthosilicate (TEOS), ethanol, ammonia, and water. The particle diameter was controlled by changing the ratio of ammonia to TEOS ($R_{\text{NH}_3} = [\text{NH}_3] / [\text{TEOS}]$) [7]. In this paper, the particle diameter of SiO₂ was adjusted to be 100nm. The TiO₂ precursor solution for the nano-coating was prepared from titanium iso-propoxide, acetic acid, and 1-butanol. Acetic acid was used to control the hydrolysis rate of Ti alkoxide. The experimental details were described in elsewhere [5,6].

TiO₂-SiO₂ hybrid sol were prepared with $R_A ([\text{CH}_3\text{COOH}] / [\text{Ti}]) = 1.5$, $R_W ([\text{H}_2\text{O}] / [\text{Ti}]) = 1.5$, and $\text{Ti/Si} = 5$, followed by adjusting pH with hydrochloric acid to control the zeta potential of the hybrid particles in the sol. The obtained hybrid sol was dried by SCD process. The initial pressure was controlled by changing the amounts of N₂ gas charged.

2.2 Characterization

The crystalline structure and size were estimated by X-ray diffraction (XRD) (PANalytical, X'Pert PRO MPD). The specific surface area of the obtained particles was determined from the

adsorption isotherm of N_2 using the BET method. The surface morphology of the obtained particles was investigated by Transmission electron microscope (TEM) (Hitachi Co., H-9000NAR).

3 RESULT AND DISCUSSION

3.1 XRD analysis

Fig.1 shows the XRD profile of the obtained TiO_2 - SiO_2 hybrid particles. The obtained particles had the pure TiO_2 anatase phase. The crystalline size of TiO_2 was estimated to be 8nm from Scherrer's equation,

$$D = \frac{K\lambda}{\beta \sin \theta}$$

where $K(=0.9)$ is Scherrer's constant, λ is the wavelength of X-ray and β is the FWHM. Namely, TiO_2 with 8nm diameter were coated on the surface of SiO_2 particles.

Fig.1. XRD profile of the obtained TiO_2 - SiO_2 hybrid particles

3.2 Effect of the drying condition

Fig.2 shows the drying process and phase diagram. In the case of the conventional drying process, large capillary force acts among the primary particles, as the vapor-liquid equilibrium line is crossed during drying. In contrast, no capillary force appeared in SCD process, due to no crossing of the vapor-liquid equilibrium line. However, as shown in Fig.2, there is some possibility to cross the vapor-liquid equilibrium line even in the SCD, if the system is not pressurized sufficiently before heating. Hence, the effects of the initial pressure on the dispersibility of the hybrid particles were investigated to find out the suitable SCD condition. Fig.3 shows the change in the surface areas of SiO_2 and TiO_2 - SiO_2 hybrid nano-particles as a function of the initial pressure. The surface area of the both particles increased in keeping with the initial pressure. The largest surface area was obtained at the initial pressure of 1.0MPa. This result indicates that control of the initial pressure before SCD was important to obtain the well-dispersed particles. Fig.4 shows the TEM images of TiO_2 - SiO_2 hybrid particles

Fig.2. Drying process and Phase diagram

Fig.3. Change in the surface area of SiO_2 and TiO_2 - SiO_2 hybrid particles as a function of the initial pressure in supercritical drying

obtained by changing the initial pressure of SCD. At the low initial pressure, particles were agglomerated in SCD. In contrast, primary particles were retained after SCD when the initial pressure was raised to 1.0MPa. These TEM images were consistent with the results of surface area. From these results, we conclude the initial pressure of SCD was a key factor to control the agglomeration in SCD process. The surface area of TiO_2 - SiO_2 hybrid nano-particles was larger than that of SiO_2 in all cases. This can be accounted for by the model shown in Fig.5: TiO_2 nano particles were loaded on the surface of SiO_2 core particle. TEM image of primary TiO_2 - SiO_2 particles shown in Fig.4(c) supported this model.

3.3 Effect of the zeta potential in sol on the dispersibility of the hybrid particles

The dispersibility of the sol is also a very important factor to control the agglomeration of particles.

Fig.4. The surface morphology of the TiO₂-SiO₂ nano hybrid particles obtained by supercritical drying: (a) the initial pressure of 0.1MPa, (b) the initial pressure of 1.0MPa, (c) primary TiO₂-SiO₂ nano hybrid particle.

Fig.5. Model of SiO₂ coated with TiO₂ particles

In this study, the dispersibility of the sol was controlled by the zeta potential of particles. In general, zeta potential is calculated using equation 1.

$$\frac{1}{\kappa} = \left(\frac{\varepsilon_0 \varepsilon RT}{2F^2 CZ^2} \right)^{\frac{1}{2}} \cdots (1)$$

where $1/\kappa$ exhibits the thickness of electric double layer, ε_0 , ε show the dielectric permittivity in vacuum condition and the solvent, respectively, and F , C , Z shows the Faraday constant, the concentration of ion, and the atomic valence of ion, respectively. In this study, the zeta potential was varied with pH in the sol. In other word, the zeta potential was controlled by changing C in equation 1. An aqueous solution of hydrochloric acid was used to control pH in the sol.

Fig.6 shows the change in the surface area of TiO₂-SiO₂ hybrid particle as a function of pH in the sol. The particles obtained from the sol with pH of 0.6, 3.5 and 5.6 had large surface area, indicating that the particles were in well-dispersed form. In contrast, the surface area was low at pH of 2.0-2.5 and 4.5-5.0. The isoelectric points (IEP) of TiO₂ and SiO₂ were reported to be pH=2-3, and 5-6, respectively [8,9]. Thus, the low surface area is likely to result from coagulation of particles in the sol. This result indicates that the uncoated area remained in the hybrid particle. Fig.7 shows the TEM images of the hybrid particles obtained from the sol with different pH. From these TEM images, some secondary agglomerated hybrid particles were confirmed at IEP of TiO₂ and SiO₂ (Fig.7 (b) (d)).

Fig.6. Change in the surface area of TiO₂-SiO₂ particle as a function of pH in the sol.

In contrast, well-dispersed primary hybrid particles were obtained at pH of 3.5 and 5.4 (Fig.7 (a) (c)). These TEM images were consistent with the results show in Fig.6. The surface area of the hybrid particle at pH=0.6 and 5.4 was slightly larger than that at pH=3.5. At pH=3.5, TiO₂ and SiO₂ have the positive and negative zeta-potential, respectively. Therefore, there was a possibility of the hetero-coagulation by different zeta potential [10,11], leading to slightly lower surface area.

Suzuki et al. reported the relationship between the zeta potential of the sol and the surface area of mullite particles obtained from the sol by conventional drying process [12]. They controlled the zeta potential by change in the dielectric constant of the solvent. The surface area of mullite particles was reported to decrease with increasing the dielectric permittivity ε , indicating that well-dispersed particle in the sol were easily agglomerated in the drying process (Fig.8 (a)). However, in this study, the well-dispersed primary particles were obtained from well-dispersed particles in the sol (Fig.8 (b)). This difference can be explained by taking the capillary force into consideration. Particles are acted on by the capillary force in the conventional dry process, while no capillary forces appear in SCD process.

Fig.7. TEM images $\text{TiO}_2\text{-SiO}_2$ hybrid particles obtained from the sol with different pH: (a) pH=2.9, (b) pH=3.5, (c) pH=4.7, (d) pH=5.4.

Large zeta potential Small zeta potential

Fig.8 Agglomeration Models with different drying process

Therefore, dispersibility of the particles in the sol was kept after drying by SCD process. As a result, we confirmed the relationship between the zeta potential and the dispersibility of particles by SCD was different from that by conventional drying process, due to the different condition of capillary force.

4 CONCLUSION

$\text{TiO}_2\text{-SiO}_2$ hybrid sol was prepared by Chemical Solution Deposition (CSD) with CCM. The dispersibility of the hybrid particles obtained from the sol was dependent on the initial pressure of SCD and the dispersibility in the sol. The surface area of the hybrid particle increased with increasing initial pressure, and the largest surface area was obtained at a initial pressure of 1.0MPa. The surface area of the particles was also varied with pH in the sol. The surface area was low at the IEP of TiO_2 and SiO_2 , due to the agglomeration. In contrast, well-dispersed particles were obtained at pH away from IEP. In conclusion, we successfully controlled the agglomeration of the particles by the adjustment of the supercritical drying condition and by the control of the dispersibility in the sol.

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