

Preparation of Titania Microballoons by Sol-Gel Process in Reverse Dispersion

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Abstract

Titania microballoons were prepared by sol-gel process of titanium tetra-2-propoxide in reverse dispersion. Hexane was used as continuous phase, in which sorbitan monooleate was dissolved as dispersion stabilizer. A buffer solution was used as dispersed phase, of which pH was adjusted from 5.0 to 7.0. These phases were mixed and stirred to prepare reverse dispersion. Titanium tetra-2-propoxide was added to the dispersion to start reaction, and stirring was kept for 24 h at 30°C. The crystalline phase of specimens calcined at 500°C was identified as anatase. Scanning electron microscopy showed that the products were hollow microspheres, or microballoons. The effects of preparation duration, dispersion stabilizer concentration, and pH on the yield and the mean diameter were investigated.

Keywords: A. organometallic compounds, A. oxides, B. sol-gel chemistry, C. electron microscopy

1. Introduction

Alkoxides of some metals are catalyzed by water to occur hydrolysis and subsequent dehydration-condensation, resulting in gel materials. This so-called sol-gel process is carried out generally in a homogeneous system with using alcohol as common solvent for alkoxide and water, because these two substances are immiscible each other. Now, sol-gel process is extensively used to produce materials in a variety of forms; e.g. massive bodies, thin films, thick coatings, fibers, fine particles, and so on [1–3].

The authors have been investigating the preparation of silica microspheres by sol-gel process of silicon alkoxide in a heterogeneous system [4]. In this technique, alkoxide and water are mixed and stirred without alcohol to prepare water-in-oil dispersion or reverse dispersion. The site at which sol-gel reaction proceeds is limited to the inside of the dispersed phase. Therefore, the products take the form of microspheres sustaining the morphology of the dispersed droplets, which can be easily controlled. Microcapsules containing some ingredients with silica matrix can be prepared by this approach [5]. Oil-in-water dispersion or normal dispersion is also usable to prepare silica microspheres [6]. Furthermore, it is possible to prepare particulate

titania/silica composites through sol-gel reaction of titanium alkoxide on the surface of silica wet gel microspheres [7].

Silica thin film is formed at the liquid-liquid interface at an earlier stage of this process [4]. However, a firm silica microballoon is not obtained. Final product becomes a solid microsphere, because hydrolyzed species can diffuse from the interface toward the center of the dispersed droplet and undergo dehydration-condensation throughout the droplet to form spherical gel. This result is due to the slowness of condensation of hydrolyzed species. If more reactive alkoxide is used instead of silicon alkoxide, condensation of hydrolyzed species should occur at the interface prior to their diffusing toward the inside. Consequently, it is expected that hollow microspheres or microballoons would be produced. This study was carried out with the aim of proving this expectation.

Inorganic microballoons are applicable to microcapsules with an inorganic wall material, which are more advantageous than those with a polymeric wall materials, regarding chemical durability, wear resistance, thermal resistance, etc. Several techniques for preparing inorganic microballoons have been reported [8–12].

In this study, sol-gel process of titanium tetra-2-propoxide ($\text{Ti}(\text{2-C}_3\text{H}_7\text{O})_4$, TTIP) in reverse dispersion was attempted to prepare titania microballoons. In order to discuss the formation process of the gel, the effects of pH of the dispersed phase and TTIP concentration on the diameter were investigated.

2. Experimental

2.1. Preparation

A preparation tank was a separable flask, inner diameter of 85 mm and capacity of 500 cm³. A disk turbine-type impeller with six blades of 50 mm in diameter was set at a third of the liquid depth from the bottom. Four baffles made of stainless steel were installed on an interior wall of the tank to inhibit the appearance of a vortex and air entrainment from the free surface of the dispersion.

Sorbitan monooleate (Span80, Wako Pure Chemical Industries Ltd.) of oil-soluble surfactant as dispersion stabilizer was dissolved in hexane (Wako Pure Chemical Industries Ltd.) to prepare continuous phase, so that the Span80 concentration became 10 mol/m³. McIlvaine buffer solution was used as dispersed phase, which was made from 0.1 mol/dm³ citric acid (Wako Pure Chemical Industries Ltd.) and 0.2 mol/dm³ disodium hydrogenphosphate (Na₂HPO₄, Wako Pure Chemical Industries Ltd.) in certain proportions to adjust the pH to 5.0 to 7.0. TTIP (Kanto Chemical Co., Inc.) was dissolved in 20 cm³ of the continuous phase to prepare a raw material TTIP solution. 380 cm³ of the continuous phase and 22 cm³ of the dispersed phase were mixed and stirred at 300 rpm to prepare reverse dispersion. After 30 min, 5 cm³ of the raw material TTIP solution was poured into the dispersion to begin the sol-gel reaction at 30°C. The raw material solution was added also at 6 h, 12 h, and 18 h by each 5 cm³. This procedure for adding TTIP separately is effective in depressing the production of fine gel particles in the continuous phase [7]. TTIP concentration was varied from 10 mol/m³ to 148 mol/m³ based on the total volume of hexane.

Wet gel particles produced was washed with hexane, acetone, and methanol in turn for 30 min each. Subsequently, they were dried in argon for 24 h at 30°C to dry gel particles, followed by calcining at 500°C in an air stream to obtain final product.

2.2. Characterization

The crystalline phase was identified by X-ray powder diffraction (XRD). The wet gel particles and final products were observed with an optical microscope and a scanning electron microscope (SEM). The yield Y was defined as a ratio of the total weight of the product after calcination to the theoretical weight of titania calculated from the amount of TTIP used. The diameter d_i was measured for spherical products on the micrographs, and the mean diameter D_p was evaluated as volume-area mean diameter, which is expressed by the following equation:

$$D_p = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2}$$

where n_i is the number of particles of d_i in diameter.

3. Results and discussion

3.1. Crystalline phase

Dry gel particles obtained under any condition had no diffraction line, showing that these were amorphous. All specimens after calcination revealed the same XRD pattern as illustrated in Figure 1. This result indicates that the product calcined comprises of single phase titania, of which crystalline phase is anatase.

3.2. Morphology

Figure 2 shows a SEM micrograph of the product obtained at a TTIP concentration $C_{\text{TTIP}} = 10 \text{ mol/m}^3$ and $\text{pH} = 7.0$ for preparation duration $t = 24 \text{ h}$ and calcined at 500°C . It is observed that the thickness is less than $1 \text{ }\mu\text{m}$, and the surface is smooth. Such a curved form appears a fragment of a hollow sphere. This is a piece of evidence that hydrolysis of TTIP and subsequent condensation occur at the liquid-liquid interface between the continuous phase and the dispersed phase. Under this condition, very small number of product keeping spherical shape was obtained. It is thought that most of gel produced like this has been fractured by shear stress under stirring.

Spherical particles were produced at a higher TTIP concentration $C_{\text{TTIP}} = 148 \text{ mol/m}^3$ as shown in Figure 3(a). It is regarded as a complete sphere without any crack or dimple. The external surface looks rough. Figure 3(b) was taken for the specimen crushed with a mortar and a pestle. This picture indicates that hollow microspheres or microballoons can be produced in this process.

Figure 3(c) is a higher magnification of Fig. 3(b). It is recognized that the wall has two-layer structure: dense inner layer of $1 \text{ }\mu\text{m}$ thick and porous outer layer of $3 \text{ }\mu\text{m}$ thick. Sol-gel reaction is initiated by hydrolysis when alkoxide molecules reach the interface to contact water as

catalyst. If the hydrolyzed species could condense prior to their diffusing toward the inside, rigid film would be constructed at the liquid-liquid interface. The inner layer is regarded as being formed in this manner.

On the other hand, the outer layer seems some sediment of fine particles of less than 1 μm in diameter. The formation mechanism of the outer layer is deduced as follows. As sol-gel reaction proceeds to form the inner layer, a by-product of 2-propanol is produced. It can dissolve in hexane to make the solubility of water in the continuous phase increase. Sol-gel reaction comes to occur in a later stage to produce fine particles by homogeneous nucleation even in the continuous phase. They deposit onto the inner layer having been formed, resulting in the outer layer.

It is known that such secondary production of fine particles can be avoided by decreasing alkoxide concentration below a certain limit over which the homogeneous nucleation occurs [7]. This was the reason for adding the raw material TTIP solution separately by four times. However, this attempt did not have sufficient effect against our expectation. Still finer control of TTIP concentration may be necessary.

3.3. Yield

Figure 4 shows the change in the yield Y with preparation duration t at a TTIP concentration $C_{\text{TTIP}} = 148 \text{ mol/m}^3$ and $\text{pH} = 7.0$. Y exceeded 80% for $t = 4 \text{ h}$ and reached 96% for $t = 24 \text{ h}$. This result means that the sol-gel reaction under this condition almost completes within 24 h.

Figure 5 shows the effects of TTIP concentration on the yield. At $C_{\text{TTIP}} = 10 \text{ mol/m}^3$, Y was so low as to be 36%. Most of this specimen has adhered to the impeller and the baffles, and it was hard to collect completely. The cause of this adhesion is thought that the products were easily fractured as shown in Fig. 2, and resulting fine fragments aggregated each other.

At TTIP concentrations higher than 20 mol/m^3 , Y reached to more than 90%. Discrete microballoons without any aggregation were produced under these conditions. They could be readily collected.

No significant effect of pH on Y was found.

3.4. Diameter

Figure 6 shows the change in the mean diameter D_p with preparation duration t at pH = 7.0. For experiments without TTIP, it was plotted with respect to the dispersed droplets. D_p was 105 μm at the beginning of the preparation and decreased steeply to 71 μm for 4 h. This implies that the dispersed droplets successively broke to finer ones also after the preliminary stirring for 30 min. After 4 h, it decreased gradually to 61 μm for 12 h and 56 μm for 24 h.

Also when TTIP was used at $C_{\text{TTIP}} = 10 \text{ mol/m}^3$, the size of the wet gel particles decreased with time but at a lower rate. D_p was 88 μm for 4 h, larger than that of the droplets. This may be due to some resistance to breakage of the dispersed phase, most likely caused by a thin film produced on the surface of a dispersed droplet. However, it was so weak as to be finally fractured under stirring. The fragments cannot grow further after fracturing, because they get separated from the aqueous phase of catalyst. Therefore, the resistance to breakage by the thin film is

almost steady, resulting in constant reduction in size. For 24 h, D_p decreased to 56 μm , close to 60 μm of the droplets.

Calcination brought about remarkable shrinkage, from 60 μm to 26 μm . This can be attributed to the small amount of solid included in a dispersed droplet.

In the case of increasing TTIP concentration to $C_{\text{TTIP}} = 148 \text{ mol/m}^3$, the extent of reduction in diameter was small; D_p was 95 μm for 24 h. It can be considered that, in addition to the effect of resistance to breakage, an escape of a by-product of 2-propanol from the dispersed phase to the continuous phase may contribute to this tendency. D_p after calcination was 76 μm , relatively large. This is due to the production of larger amount of titania gel.

Figure 7 shows the change in the mean diameter D_p with preparation duration t at $C_{\text{TTIP}} = 148 \text{ mol/m}^3$. D_p of wet gel particles produced for 24 h ranges from 82 to 95 μm by pH. Thus, it was found that pH does not affect significantly on the diameter either. D_p at pH = 5.0 and 6.0 were slightly lower than that at pH = 7.0. This result is attributed to the initial droplet size. The size after calcination was reduced with a similar tendency. That is, it can be concluded that it is unnecessary to use any pH-modifying reagent.

4. Conclusions

Sol-gel process of TTIP was attempted in reverse dispersion. The products were confirmed as titania microballoons of 76 μm in mean diameter and 4 μm in wall thickness without any crack or dimple. These characteristics are satisfactory for applying to certain

microcapsules. However, smooth surface should be preferable in practice. In order to actualize it, it is predicted that TTIP concentration in the continuous phase should be controlled to keep some level, below which fine particles are not formed by homogeneous nucleation.

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Figure Captions

Figure 1. XRD pattern of the product obtained at $C_{\text{TTIP}} = 148 \text{ mol/m}^3$ and $\text{pH} = 7.0$ for $t = 24 \text{ h}$ and calcined at $T = 500^\circ\text{C}$.

Figure 2. SEM micrograph of the product obtained at $C_{\text{TTIP}} = 10 \text{ mol/m}^3$ and $\text{pH} = 7.0$ for $t = 24 \text{ h}$ and calcined at $T = 500^\circ\text{C}$.

Figure 3. SEM micrographs of the product obtained at $C_{\text{TTIP}} = 148 \text{ mol/m}^3$ and $\text{pH} = 7.0$ for $t = 24 \text{ h}$ and calcined at $T = 500^\circ\text{C}$.

(a) As-calcined, (b) crushed, (c) higher magnification of a fragment shown in (b).

Figure 4. Change in the yield with preparation duration at $C_{\text{TTIP}} = 148 \text{ mol/m}^3$ and $\text{pH} = 7.0$.

Figure 5. Change in the yield with TTIP concentration at $\text{pH} = 7.0$ for $t = 24 \text{ h}$.

Figure 6. Change in mean diameter with preparation duration at $\text{pH} = 7.0$.

Open symbols designate the diameter of spherical products after calcination.

Figure 7. Change in mean diameter with preparation duration at $C_{\text{TTIP}} = 148 \text{ mol/m}^3$.

Open symbols designate the diameter of spherical products after calcination.

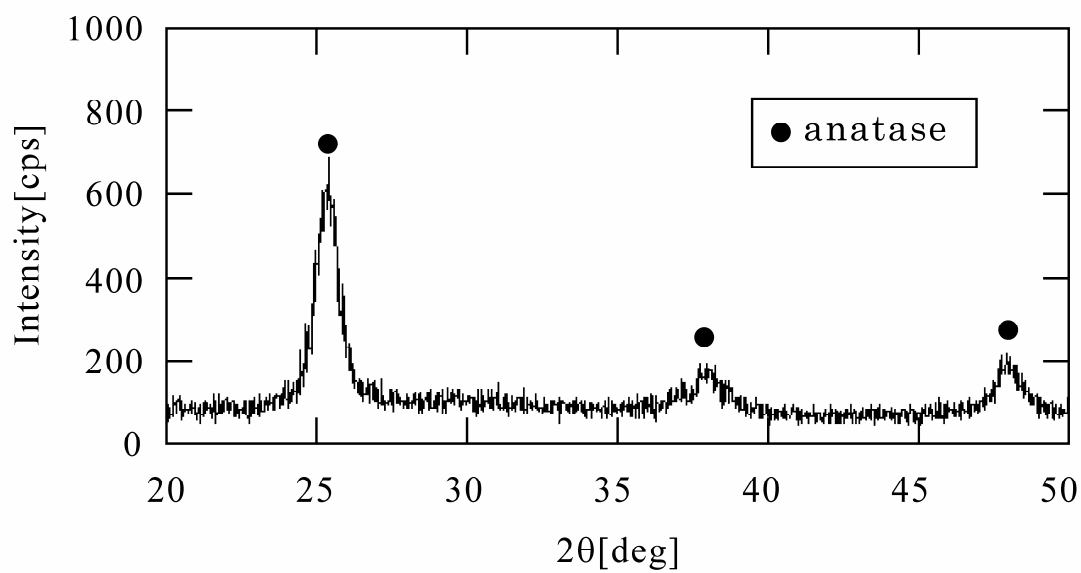


Figure 1. XRD pattern of the product obtained at $C_{\text{TIP}} = 148 \text{ mol/m}^3$ and $\text{pH} = 7.0$ for $t = 24 \text{ h}$ and calcined at $T = 500^\circ\text{C}$.

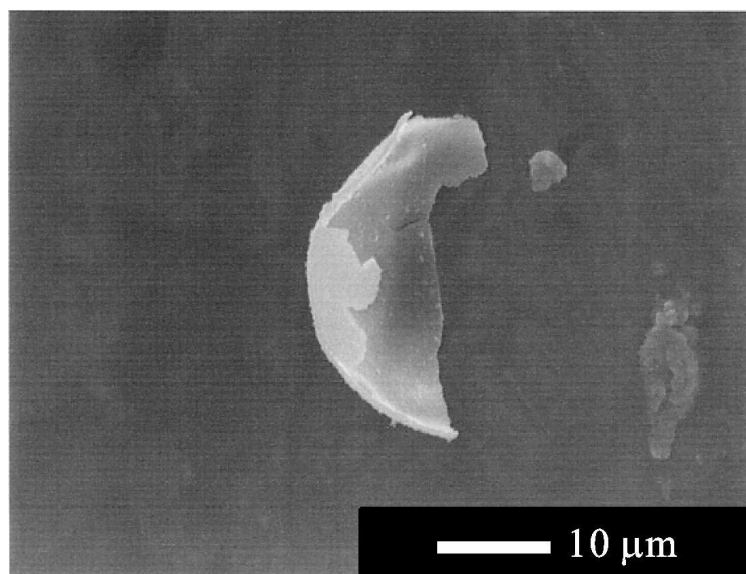


Figure 2. SEM micrograph of the product obtained at $C_{\text{TIP}} = 10 \text{ mol/m}^3$ and $\text{pH} = 7.0$ for $t = 24 \text{ h}$ and calcined at $T = 500^\circ\text{C}$.

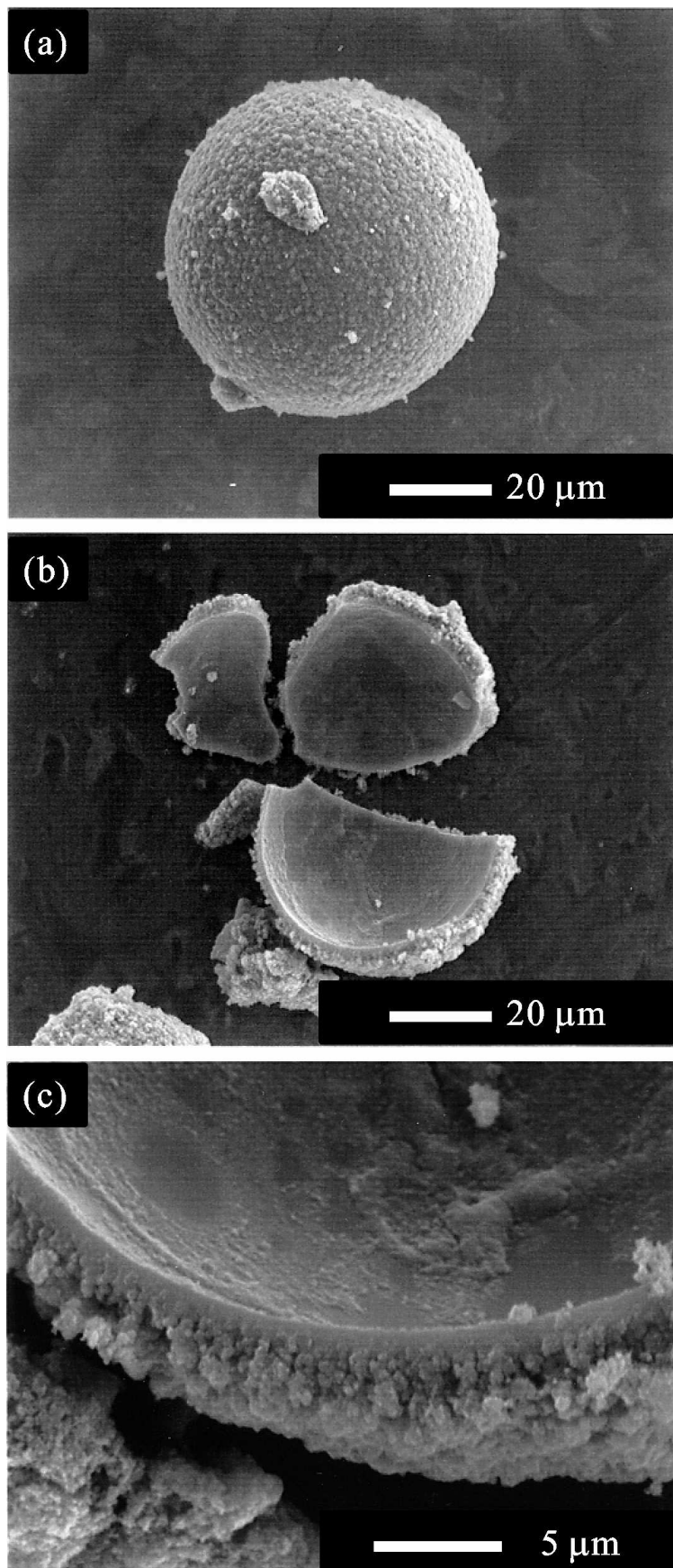


Figure 3. SEM micrographs of the product obtained at $C_{\text{TIP}} = 148 \text{ mol/m}^3$ and $\text{pH} = 7.0$ for $t = 24 \text{ h}$ and calcined at $T = 500^\circ\text{C}$.

(a) As-calcined, (b) crushed, (c) higher magnification of a fragment shown in (b).

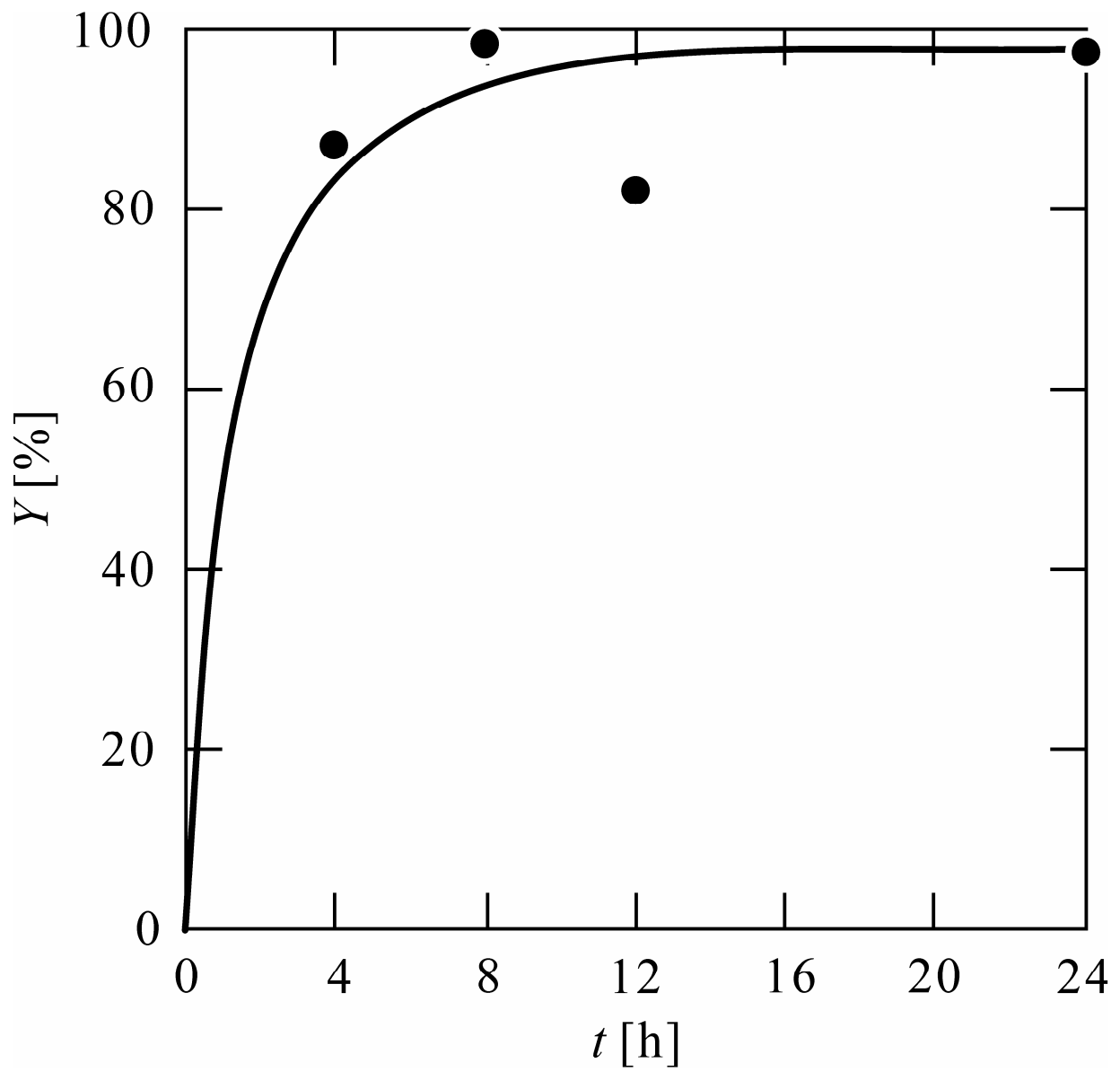


Figure 4. Change in the yield with preparation duration at $C_{\text{TIP}} = 148 \text{ mol/m}^3$ and $\text{pH} = 7.0$.

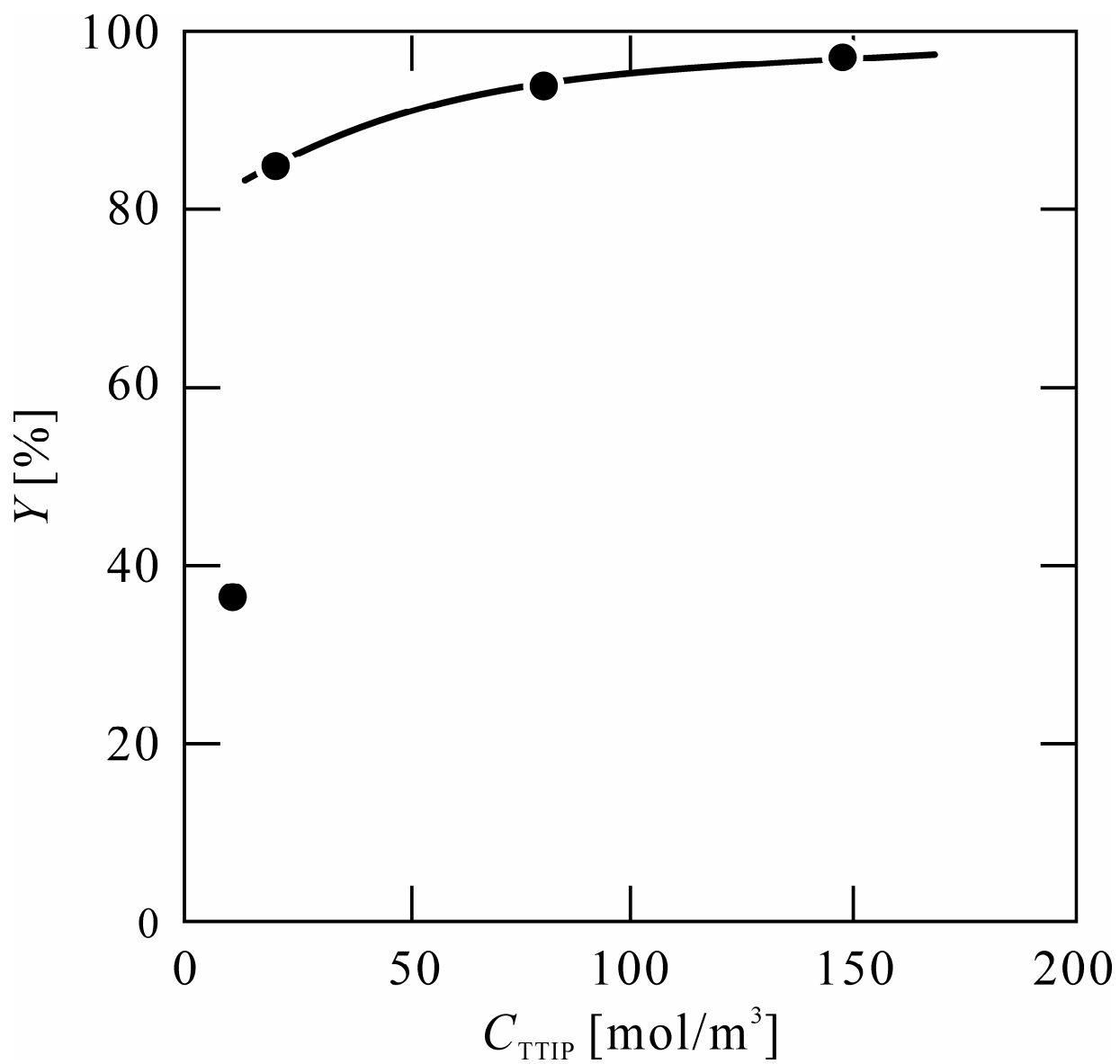


Figure 5. Change in the yield with TTIP concentration at $\text{pH} = 7.0$ for $t = 24$ h.

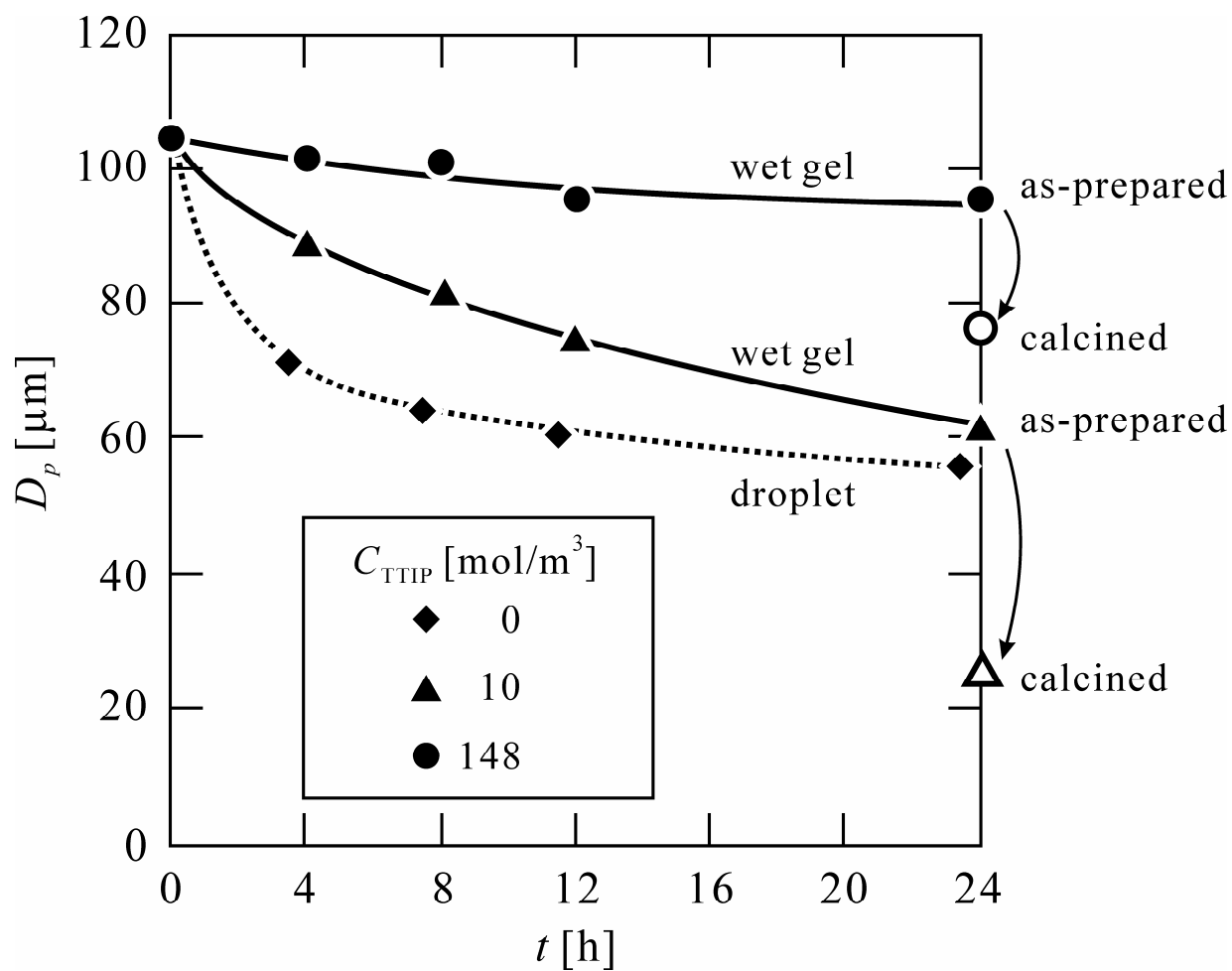


Figure 6. Change in mean diameter with preparation duration at pH = 7.0.
Open symbols designate the diameter of spherical products after calcination.

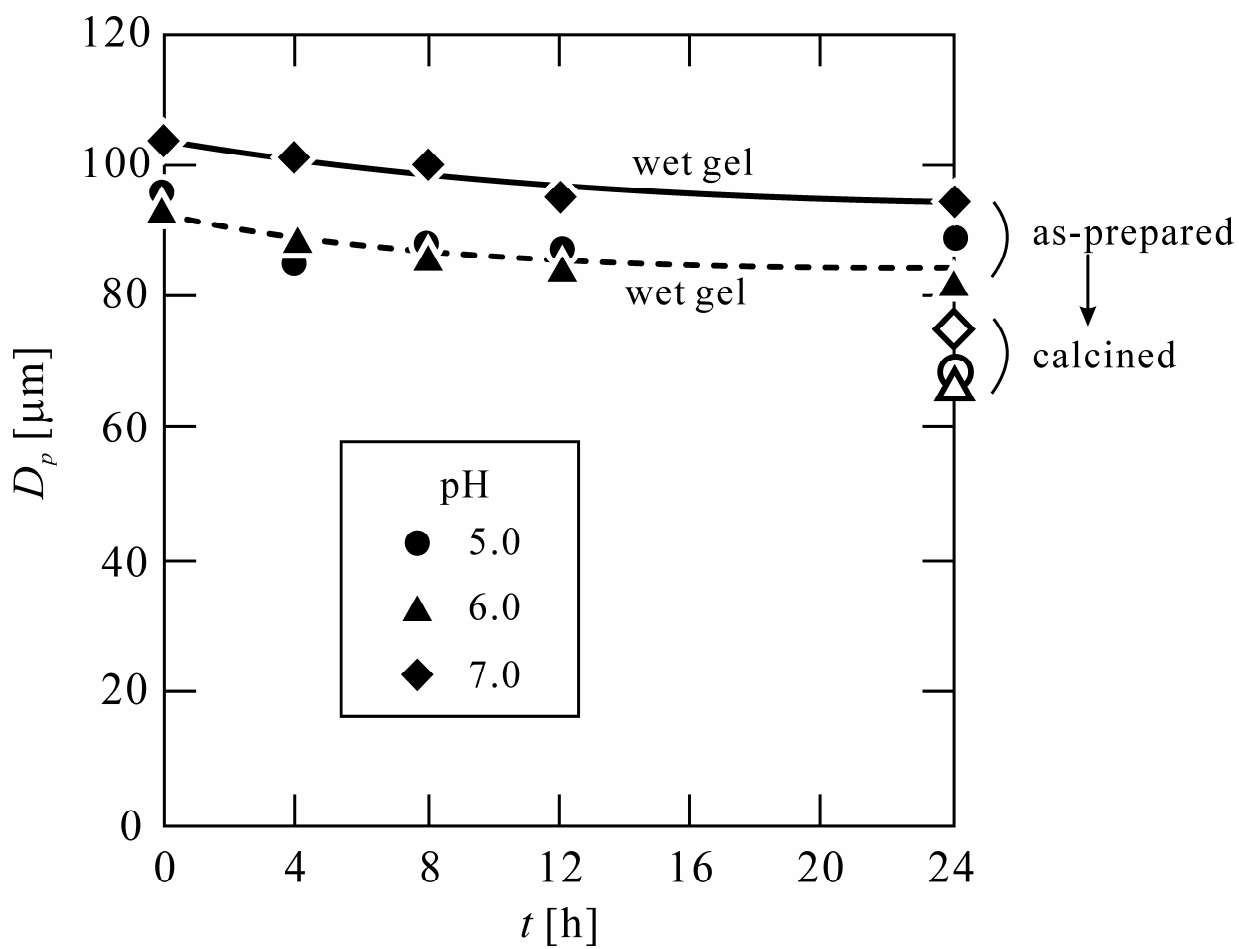


Figure 7. Change in mean diameter with preparation duration at $C_{\text{TIP}} = 148 \text{ mol/m}^3$. Open symbols designate the diameter of spherical products after calcination.