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Chemical Engineering Journal 101 (2004) 269–276

Chemical Engineering Journal

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Production of titania nanoparticles by using a new microreactor assembled with same axle dual pipe

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Abstract

The validity of utilizing microspace for nanoparticles production was investigated by using a newly proposed microdevice. The proposed reactor consists of same axle dual pipes, and this assembly gives a microspace by an annular laminar flow of two immiscible liquids. We tried to produce titania particles by supplying tetraisopropoxide (TTIP) solutes to the inner tube and isopropanol/water mixture to the outer tube. Mono-modal spherical particles of titania with narrow size distribution were successfully produced without precipitation of the particles at the wall. It was also found that the particle size was possible to control in the range from 40 to 150 nm only by changing the diameter of the inner tube at a low TTIP concentration. Thus, the proposed concept was confirmed to be valid for the production of nanoparticles.

Keywords: Titania nanoparticles; Microreactor; Axle dual pipe

1. Introduction

Nanoparticles are receiving interesting attention because of their distinct physical and chemical properties. It is expected that nanoparticles will be applied to many new and high-functional devices [1–3]. When the particle size decreases in single nanoscale, the quantum size effect appears and properties such as magnetic optical electronics greatly change by their size and shape [4–7]. Considering such an application of the nanoparticles, it is important to develop a manufacturing process for the nanoparticles with narrow size distribution. To date, various chemical methods have been applied for the production of the nanoparticles with narrow size distribution such as microemulsion method [8–10], hot soap method [11], and electrospray pyrolysis [12]. However, it is difficult to control the reaction precisely in a conventional macroreactor because of the non-uniformity of the residence time, mixing and so on. To overcome this, it is expected that microreactors can be applied to the production of nanoparticles with narrow size distribution, because microreactors provide a uniform reaction field in which the reaction condition is precisely controlled.

Generally, it is essential to design precise nuclei formation and aggregation processes for high quality particles. The way to form the nuclei is to keep a proper super-saturation state by controlling the gradient of temperature, concentration of reactant and so on. From this viewpoint, a microchannel is very attractive for easily forming the reaction conditions in continuous production. A few studies for the production of nanoparticles have been reported using chip-based microreactors and the advantages of microreactor for the nanoparticle production were claimed [13–15]. However, a chip-based reactor has an essential problem for particle handling. A way should be developed to prevent the clogging of tubes by adhesion of precipitated particles to wall surfaces.

In this study, a microdevice with the double-pipe structure shown in Fig. 1 was presented to control the condition for the nuclei formation and aggregation mentioned above. Two immiscible liquids were flowed in the inner and outer tubes, respectively, and maintained an annular and laminar flow of separated phase to create a microspace by the outer fluid wall. The radius of inner flow, which means a created microchannel, can be changed by the operation condition. On the basis of this concept, the reaction can be precisely controlled by the gradient of temperature and/or concentration of reactant in the outer fluid. In addition, the outer fluid plays the role of preventing precipitated particles from adhering to the tube wall. The device also has several advantages such as easy maintenance, cheap setting, etc. We tried to perform hydrolysis of titanium alkoxide as an example for a very fast reaction using the presented device, and clarified the validity of the concept by examining the possibility for production of uniform titania particles.

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doi:10.1016/j.cej.2003.11.011

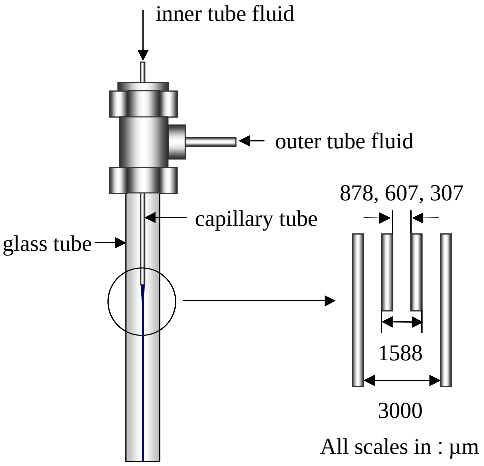

Fig. 1. Schematic of the microdevice presented.

2. Experimental method

2.1. Materials

Cyclohexane, 1-hexanol, 1-octanol, 1-decanol, and titanium tetraisopropoxide (TTIP) (Wako Pure Chemical Industries Ltd.) were used as materials.

2.2. Observation of flow pattern

Visual observations of two-phase flow patterns in the microdevice were carried out by changing the combination of average velocities of fluids in the inner and outer tubes. The 67 vol.% of isopropanol aqueous solution flowed in the outer tubes. To investigate the effect of the interfacial tension on two-phase flow pattern, cyclohexane and 1-octanol were supplied to the inner tube. Inner tubes of 307 and 877 μm i.d. were used to examine the effect of the diameter on the flow pattern.

2.3. Preparation titania particles

Titania particles were prepared by supplying TTIP solution to the inner tube and 67 vol.% of isopropanol aqueous solution to the outer tube, respectively, through two syringes. The flow velocities of the inner and outer tubes were adjusted to 0.372 and 0.075 $\mathrm{m\,s^{-1}}$, respectively. Since the length of reaction zone after encountering inner and outer fluids was 75 mm, the residence time of inner fluid was 0.2 s. In the microreactor, the TTIP in the solvent was reacted with the water in isopropanol at the interface between two immiscible liquids and titanium oxide was formed by the hydrolysis (1) and the condensation (2):

$$\mathrm{Ti(OC_3H_7)_4} + 4\mathrm{H_2O} \rightarrow \mathrm{Ti(OH)_4} + 4\mathrm{C_3H_7OH} \qquad (1)$$

$$\mathrm{Ti(OH)_4} \rightarrow \mathrm{TiO_2} \cdot x\mathrm{H_2O} + (2-x)\mathrm{H_2O} \qquad (2)$$

In order to investigate the effects of the various parameters on the particle size and shape, the titania particles were prepared under 1–8 vol.% of the TTIP concentration and four kinds of TTIP solutions with cyclohexane, 1-hexanol, 1-octanol and 1-decanol. Three internal diameters of the inner tubes, 307, 607, and 877 μm, were adopted. To terminate the reaction after flowing out the reactor, the product liquid was immediately diluted by a large amount of isopropanol in a recuperation vessel. We checked the effect of the amount of isopropanol in a recuperation vessel on the particle diameter, and confirmed that the amount of isopropanol used in the experiment was enough to terminate the hydrolysis reaction. Furthermore, in order to equalize the composition of the mixture, the solution with titania particles just after the reactor runoff was dispersed in an appropriate amount of the mixture of water, isopropanol and the solvent supplied in the inner tube.

2.4. Analysis of the product

Thus prepared particles were observed with a transmission electron microscope (TEM, JEOL JEM-1010) and a scanning electron microscope (SEM, JEOL JSM-6340F). To prepare SEM and TEM samples, a droplet of the colloidal suspension of the product was applied to a mica substrate or a copper mesh covered with carbon film and subsequently dried by a vacuum desiccator for 12 h at 30 °C. The particle size distribution was analyzed by the laser diffraction method (HORIBA Co. Ltd., LA-920). For the analysis of the particle structure, powder X-ray diffractometry with a Cu Kα ray (XRD, Shimadzu Co. Ltd., XRD-610) was conducted. To prepare the sample for the powder X-ray diffractometry, the colloidal suspension of the product was centrifuged in 4000 rpm for 30 min. To investigate the change of the X-ray diffraction spectrum with the thermal treatment, the colloidal suspension was directly ripened for 24 h at 80 °C in a water bath and then calcined for 2 h at 450 °C. For comparison, titania particles were also conventionally produced by a batch reactor under the same condition.

3. Results and discussion

3.1. Visual observation of two-phase flow patterns

First, we examined the operating conditions to achieve stable two-phase flow in the device presented. Since the two-phase flow was affected by the flow rates of inner and outer fluids and the properties of the fluids, we conducted the flow test under various conditions. Fig. 2 shows a flow pattern map obtained for two-phase flows in the microdevice. Stable annular flow was obtained when the difference in the velocity between the inner and the outer fluids was small. However, even if the relative speed difference was small, slug flow was formed when flow velocity was low. This was because the effect of the interfacial tension became

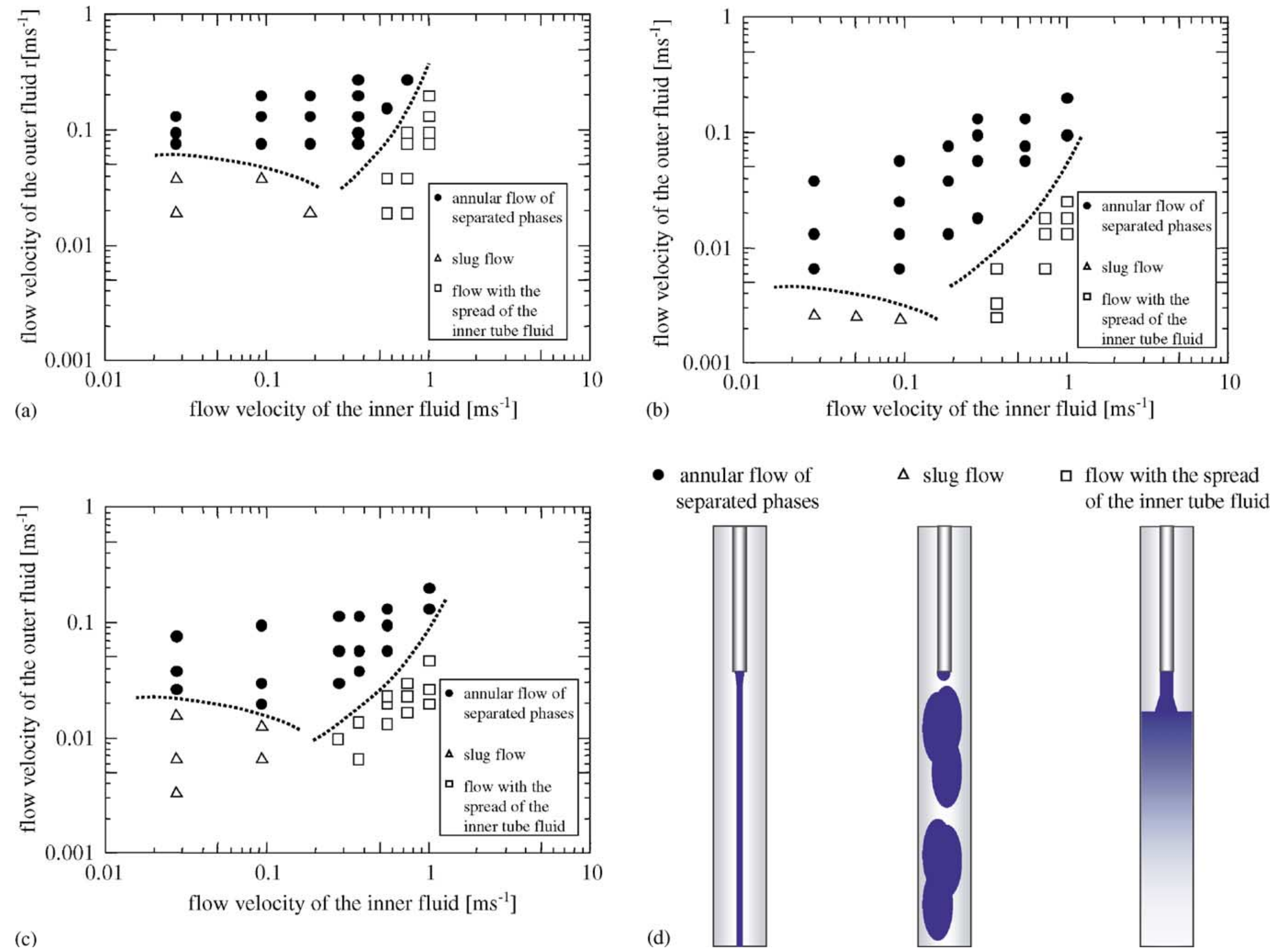

Fig. 2. Two-phase flow pattern transitions. The internal diameter of the capillary tube and the fluid in the inner tube were (a) 877 μm and cyclohexane; (b) 877 μm and 1-octanol and (c) 307 μm and 1-octanol.

dominant with decreasing the inertial force. Dispersive flow was formed when the velocity of the outer fluid was much higher than that of the inner fluid, since the resistance force caused by the relative speed difference increased. On the other hand, when the velocity of the inner fluid was much higher than that of the outer fluid, flow with the contraction of the inner fluid was formed. These results show that an optimal size of microspace is created by changing the flow rate. In short, the size of reaction zone can be controlled by the operating condition without microfabrication.

Next, we examined the effect of solvent type on the flow regime. When 1-octanol was used for the inner fluid, the flow rate range of which stable annular flow was formed became wide as compared with that for cyclohexane. The interfacial tension between 1-octanol and water is ca. six times smaller than that between cyclohexane and water. Similarly, 1-octanol seems also to have smaller interfacial tension against isopropanol aqueous solution. From this, the annular flow was obtained from the region of low velocities of outer fluid.

As compared with Fig. 2(b) and (c), the region formed by the annular flow was reduced with a decrease in the diameter of the inner tube. Since the surface area per unit volume of the inner fluid increases with the decrease in the radius of the microchannel, the effect of the interfacial tension comes out only after high velocity is attained. From these results it was confirmed that stable annular flow is formed under a large ratio of inertial force to the interfacial tension and small difference in the velocities between the inner and outer fluids. Thus, it was shown that a microspace could be created by the interface between immiscible two fluids without any microfabrication.

3.2. *Production of titania particles using the proposed microdevice*

3.2.1. *Comparison of the characteristics of TiO_2 particles produced by the microreactor and a conventional method*

Titania particles were produced and grown in an inner tube and no precipitation of particles was observed at the

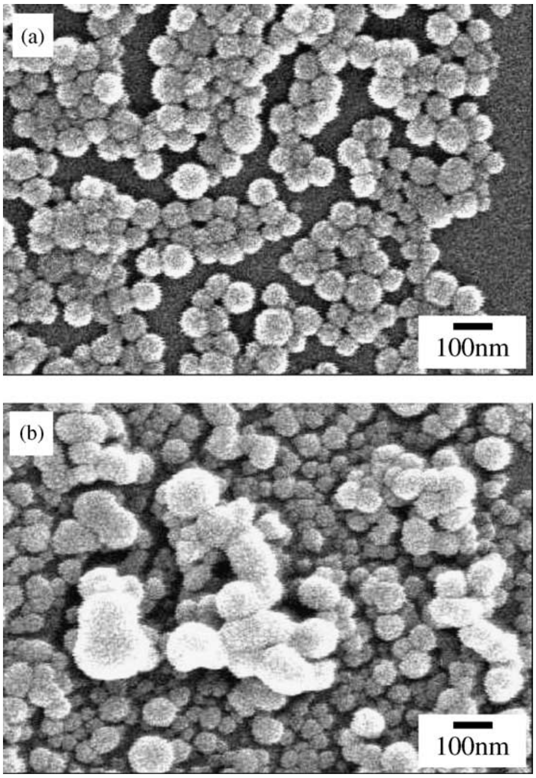

Fig. 3. SEM photographs of the titania particles (a) produced by the microreactor and (b) produced by a conventional method.

wall by an immiscible outer fluid. To confirm the validity of this concept, we also tried to produce $CaCO_3$ particles in the same manner and successfully obtained fine particles without precipitation. From these observations the proposed method was shown to have an advantage for production in a microchannel.

Fig. 3(a) shows the SEM photograph of the titania particles prepared by flowing the 1-hexanol solution including 1 vol.% of titanium tetraisopropoxide in an inner tube of 607 μm i.d. Fig. 3(b) also shows the SEM photograph of the titania particles produced by simple mixing under the same mixing ratio of the raw materials (66 ml of TTIP solution and 22.92 ml of isopropanol) in a 500 ml batch vessel. The particle size distribution measured from the photograph coincided well with that obtained from the laser diffraction method shown in Fig. 4. The size distribution of the titania particles made by microreactor had a sharp and narrow distribution whose peak was ca. 100 nm. From the SEM photograph of titania particles as shown in Fig. 3, the particles produced by the microreactor were clearly fine and mono-modal with a narrow particle size distribution. Fig. 5 shows the change in the X-ray diffraction spectra during the treatments of the titania particles. The titania particles just after reaction before the thermal treatment were amorphous. After ripening for 24 h at 80 °C and calcining for 2 h at 450 °C, the anatase structure appeared. The crystallites sizes calculated by Scherrer formula became to be 4.9 nm after ripening for 24 h at 80 °C and increased to 6.3 nm after calcining for 2 h at 450 °C, respectively. From X-ray diffraction spectra, there were no differences between the primary particles produced by the microreactor and a conventional method, while a distinct difference in the shape of particles was observed in Fig. 3. This indicates that the structure of the aggregate of the primary particle is greatly influenced by the reaction type. The particles prepared with the microreactor were mono-modal spherical particles around 100 nm

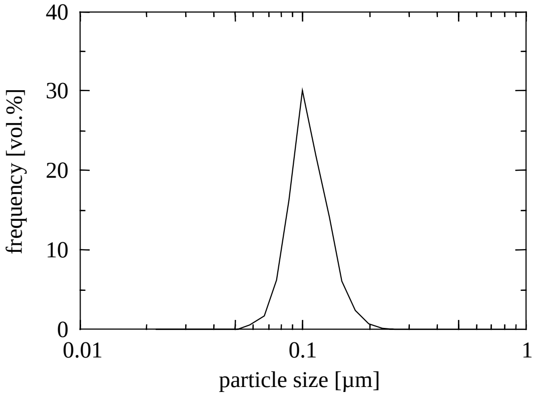

Fig. 4. Particle size distribution produced by the microreactor.

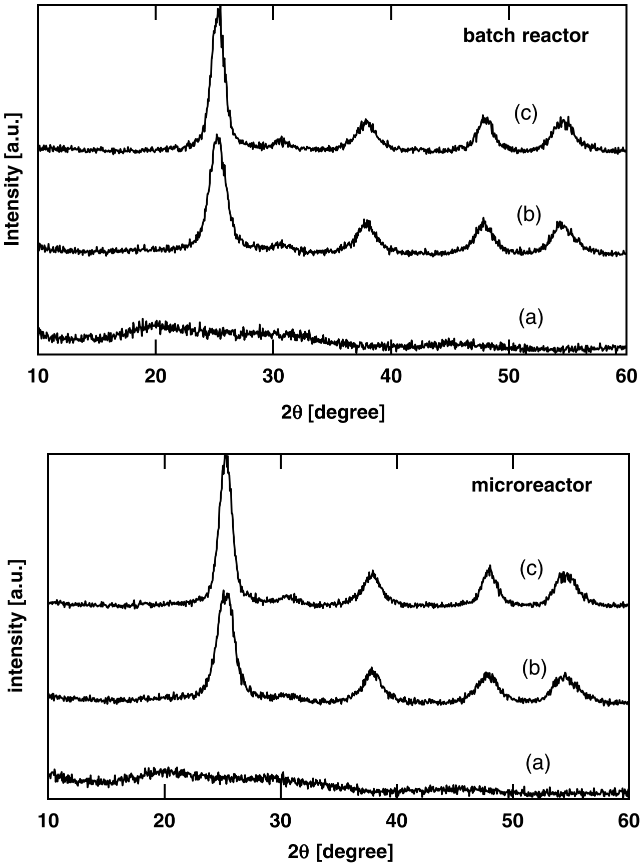

Fig. 5. XRD patterns of titania particles (a) after microreactor, (b) after ripening for 24 h at 80 °C and (c) after calcining for 2 h at 450 °C.

with a narrow particle size distribution. This result clearly shows that the grain of particles is uniformly grown near the interface between two liquids in the microreactor. On the other hand, the particles prepared with a conventional batch method had a random distribution of particle sizes. This was because the local concentration of the reactant was distributed according to the probability theory. Thus, the proposed device is valid for synthesis of a mono-modal nanoparticle with a narrow particle size distribution by controlling the aggregation processes.

3.2.2. *Effect of solvent type for the TTIP solution on the particle size and shape*

It was found that the proposed microreactor had the possibility of controlling the growth of nanoparticles. To clarify the validity of the microreactor, we examined the effect of solvent type on the particle properties. Fig. 6 shows the SEM photograph of the titania particles produced by flowing three types of solvents, cyclohexane 1-hexanol, 1-octanol or 1-decanol including 1 vol.% of TTIP in the inner tube of 307 μm i.d.

Size and shape of the particles significantly differed with the solvent type. Comparing three photographs, the size of the particles was spherical and mono-modal with a narrow size distribution for 1-hexanol and 1-octanol. The distribution of particle size in 1-hexanol was narrowest among these samples. However, the particles produced in cyclohexane or 1-decanol were large and randomly aggregated with no regularity. These results suggest that an optimum solvent type was present to produce the titania having mono-modal and narrow distribution.

Since it is well known that the hydrolysis of TTIP is rapid, the reaction via interface in the microreactor would be controlled by diffusion rate. The viscosities of these solvents increase in order of cyclohexane, 1-hexanol, 1-octanol, and 1-decanol. In a low-viscosity solvent such as cyclohexane, the diffusion rate of the solute is large, namely the number of the primary particles increased by the active primary nucleation and the concentration of unreacted TTIP became small. This increased the chance of the primary particle meeting each other and accelerated a random aggregation between them. Increasing the solvent viscosity, the amount of primary nucleation decreased and the concentration of unreacted TTIP was fairy large. In this situation, the flux of TTIP from the bulk to the primary particle was large and the aggregation by the secondary heterogeneous nucleation was dominant as compared with the aggregation between primary particles. This brought about a mono-modal particle with a narrow particle size distribution as the case of 1-hexanol and 1-octanol. For a more highly viscous solvent such as 1-decanol, the amount of primary nucleation decreased and the concentration of unreacted TTIP was large. However, the flux of TTIP decreased by low diffusion rate and the aggregation between primary particles was dominant, leading to random particles.

From these results, under diffusion control like the proposed microdevice, solvent properties such as viscosity and interfacial tension are the crucial factors for determining the particle size and shape. To obtain the uniform and small particles, a solvent of moderate viscosity and low interfacial tension should be selected to control the nucleation and the aggregation processes in a diffusion control regime.

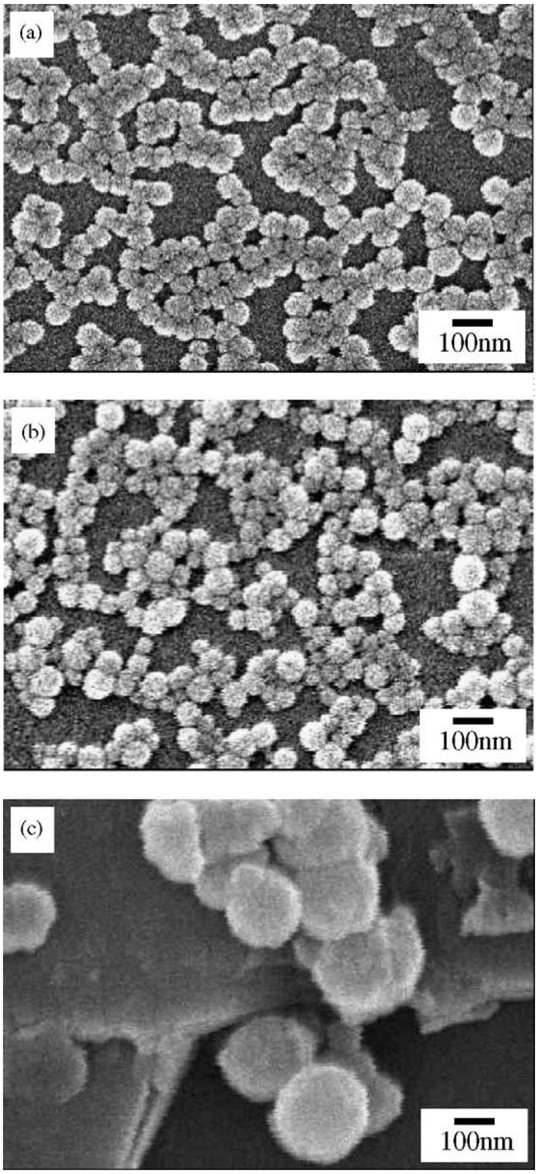

Fig. 6. SEM photographs of the titania particles prepared with different solvents: (a) 1-hexanol; (b) 1-octanol; (c) 1-decanol.

3.2.3. *Effect of the microchannel diameter on the particle size and shape*

Next, we examined the effect of the microchannel diameter on the particles properties. Fig. 7 shows the SEM photographs of the titania particles prepared by flowing the 1-octanol solution including 1 vol.% of titanium tetraisopropoxide in the capillary tube of 307, 607 or 877 μm i.d. The fluid for the outer tube was 66 vol.% of isopropanol aqueous solution. The larger the diameter of inner tube, the

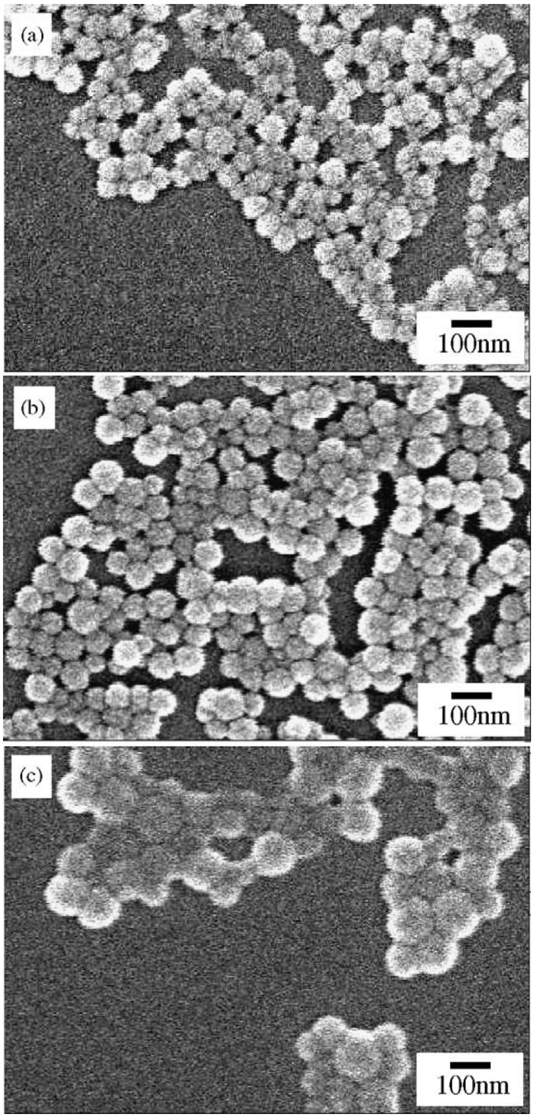

Fig. 7. SEM photographs of the titania particles with different inner tube diameters: (a) 307 μm i.d.; (b) 607 μm i.d.; (c) 877 μm i.d.

larger the particle size. The distribution of each particle was mono-modal with narrow size distribution. The mean particle size calculated from the data measured with a laser diffraction method was 45 nm for the tube of 307 μm, 84 nm for the tube of 607 μm and 121 nm for the tube of 877 μm, respectively. Similar results were obtained for other combinations of solvents. In the microreactor, the hydrolysis of TTIP occurred on the interface between two immiscible liquids, so it was speculated that TTIP located near the interface reacted immediately at the exit of inner tube (near the inlet of reactor zone) because the hydrolysis of titanium alkoxide was very fast. The primary particles near the interface by the fast reaction grew by the secondary heterogeneous nucleation by the unreacted TTIP in the inner flow. For small size of tube, the amount of TTIP has a limit by consuming TTIP to the primary nucleation on the interface. This caused the decrease in the flux of unreacted TTIP from the bulk, namely, secondary heterogeneous nucleation was restricted in the aggregation process. With the increase in the radius of the inner tube, the flux of TTIP from the bulk to the primary particles became large and the secondary heterogeneous nucleation accelerated. From this the particle size became large with a uniform state maintained.

3.2.4. Effect of the TTIP concentration on the particle size and shape

Finally, we prepared titania particles with different concentration of TTIP. Fig. 8 shows an SEM photograph of the titania particles prepared by flowing the 1-octanol solution including 1–8 vol.% of titanium tetraisopropoxide in the inner tube of 607 μm i.d. As the concentration of TTIP increased, the particles size increased and its distribution be-

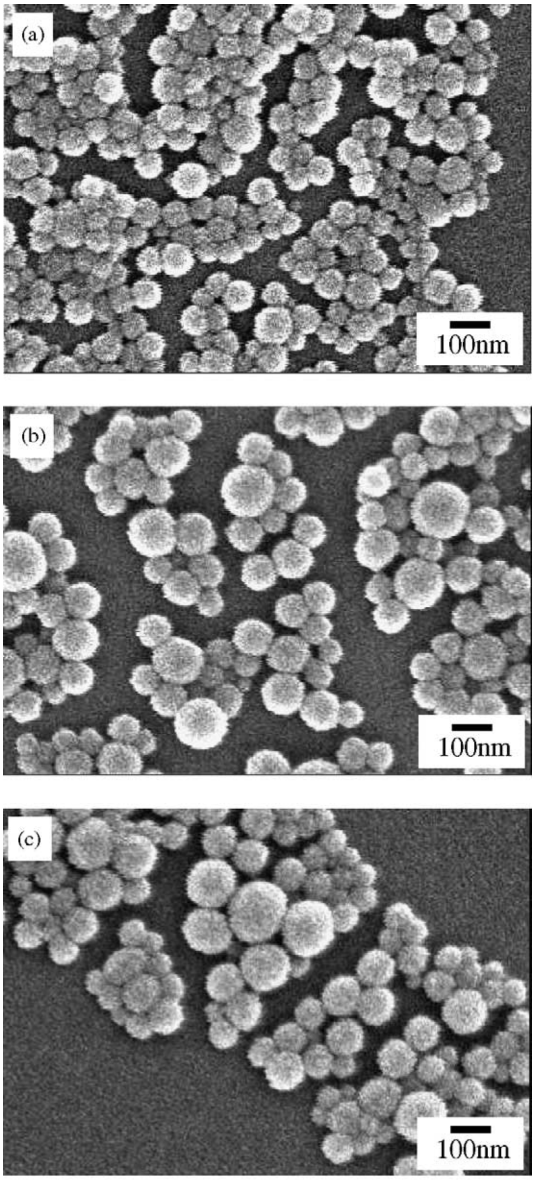

Fig. 8. SEM photographs of the titania particles with different concentrations of the TTIP solution: (a) 1 vol.%; (b) 5 vol.%; (c) 8 vol.%.

came broad. When the TTIP concentration was high, the number density of primary particles formed near the interface increased. In that condition, the particles grew by the aggregation between the primary particles as well as the secondary heterogeneous nucleation of the unreacted TTIP to the primary particles. In addition, the rapid aggregation of the primary particles increased the polydispersity of the nanoparticles product, resulting in an increase in the size of the particles and the broad distribution of particles. From this, it was found that the concentration of TTIP was the most important point for the production of uniform titania particles.

3.2.5. *Presumed mechanism of the formation of titania particles in the microreactor*

Summarizing the above discussion, the mechanism for the formation of titania particles in the microchannel was presumed as shown in Fig. 9. The formation of titania particles by hydrolysis in organic solvent consists of two processes: the formation of the primary particles via nucleation and the aggregation of the primary particles. When the number density of the primary particles was small, the secondary heterogeneous nucleation on the surface of the primary particles proceeded and then the spherical particles were formed as shown in Fig. 9(I). On the contrary, the number density

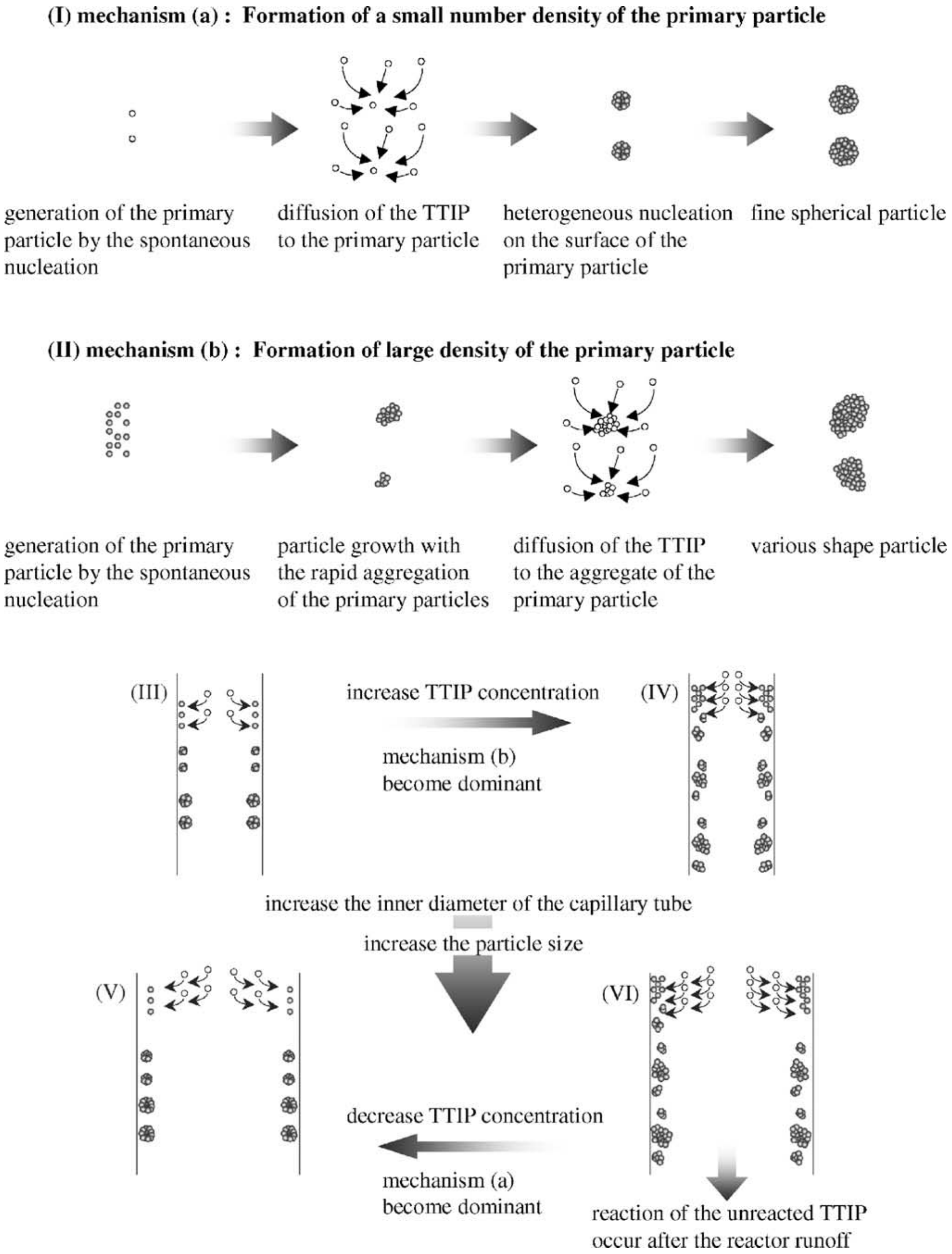

Fig. 9. Presumed mechanisms on the grain growth process in the microdevice.

of the primary particle was large, once aggregation between primary particles was rapidly occurring, the secondary heterogeneous nucleation to the various size of aggregates proceeded, resulting in the formation of the various shape particles as shown in Fig. 9(II).

In the microchannel, the formation of titania particles was governed by the balance of the rate of each process which changed by the dimensions of the microreactor and the operating conditions. Under low TTIP concentration and small diameter of inner tube shown in Fig. 9(III), fine and uniform titania particles were formed by following the mechanism (a). With the increase in TTIP concentration, the particles became large and of irregular shape because the number density of the primary particles was large, namely the mechanism (b) predominantly proceeded as shown in Fig. 9(IV). On the other hand, under low TTIP concentration and large inner tube diameter shown in Fig. 9(V), the number density of the primary particles was small. At that time, secondary heterogeneous nucleation to the primary particles was active by a high flux of unreacted TTIP from the bulk to the interface. Therefore, the particle sizes became large with a uniform state according to mechanism (a). By increasing the TTIP concentration in the inner tube of large diameter, mechanism (b) was dominant and the particle size and shape significantly became random.

Thus, the proposed microreactor had the potential to control the balance of primary nucleation and aggregation rates through adjusting the ratio of the reaction rate to the diffusion rate by changing the diameter of the inner tube, solvent type, and the concentration of the reactant. For the production of titania particles by hydrolysis, the TTIP concentration was a crucial factor in forming mono-modal particles and their particle size was controlled by the diameter of the inner tube and the length of the reaction zone.

4. Conclusion

A new microreactor design concept for particle production was presented. The idea lies in a realization of microspace by an annular laminar flow of two immiscible liquids to prevent the particle precipitation on the wall and to control particle formation. The proposed device was confirmed to be valid for the mono-modal and spherical particle formation, with the result that quite uniform spherical particles of titania were produced without precipitation of particles at the wall. The particle size and shape were varied with the solvent type of TTIP solution, the concentration of the TTIP and the diameter of the microchannel. It was found that the concentration of TTIP was a crucial factor for controlling the primary nucleation and the aggregation process. We successfully controlled the mono-modal particles from 40 to 150 nm by changing the diameter of the inner tube at a low TTIP concentration. From the investigation of the mechanism on the particle formation in the microchannel, it is suggested that the primary nucleation and aggregation by the secondary heterogeneous nucleation can be precisely controlled through adjusting the diffusion rate under the laminar flow in the inner tube. It is expected that a promising process for producing a valuable nanoparticle will be developed by a proper numbering-up device based on the proposed concept.

Acknowledgements

The research was conducted in the aid of the Micro-Chemical Plant Technology Union (MCPT) for the Project of Micro-Chemical Technology for Production, Analysis, and Measurement Systems financially supported by NEDO. We appreciate MCPT and NEDO for their assistance.

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