Continuous Synthesis of Monodispersed Alumina Particles by the Hydrolysis of Metal Alkoxide Using a Taylor Vortex[†]

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Abstract

A continuous reactor was developed for industrial production of monodispersed alumina particles from metal alkoxide. Taylor vortex flows were used for solution mixing. Each of the Taylor vortices functioned as a batch reaction vessel. Monodispersed spherical alumina particles were prepared by hydrolyzing aluminum alkoxide in a mixture of octanol and acetonitrile. The particles were continuously produced for 5 h by using this reactor. Particle size and distribution were comparable to those obtained by batch processing. We investigated the effects of Taylor number (Ta) and residence time on the particle size, particle size distribution, yield, and particle number density of monodispersed alumina particles, which were obtained at Ta numbers from 50 to 150.

1. Introduction

Until now the usual way of synthesizing monodispersed oxide particles on an industrial scale has been to use reactors that hydrolyze metal alkoxide (the alkoxide route).^{1,3} As in the reactor developed by Ring^{4,5} and Fisher et al.,⁶ the principle of the system is as follows: when a hydrolyzed solution is put into a pipe under ideal plug-flow conditions, nucleation and growth occur continuously and form monodispersed particles. Consequently, it is difficult to maintain an ideal plug flow in a large pipe for a long time. We noted that using a Couette-Taylor vortex to prepare monodispersed particles keeps a large quantity of solution at the ideal plug flow for a long time. This vortex is generated by filling the space between the walls of two coaxial cylinders with a liquid, and generating a Couette flow with the viscous frictional force induced by rotating the inner cylinder. Increasing rotation speed causes a transition from a Couette flow to a doughnut-type Couette-Taylor vortex (C-T vortex) while spinning the inner cylinder (**Fig. 1**). The diameter of the C-T vortex is equal to the space between the inner and outer cylinders, and each vortex is independent.^{7,8} Each Taylor vortex generated

functions as a batch reaction vessel and brings about homogeneous mixing in the vortex. It is possible to improve non-homogeneous mixing in a large reaction vessel. C-T vortices have already been used for continuous seed emulsion polymerization in the preparation of monodispersed Latex particles.⁹ We created a trial version of a reaction apparatus which uses vortex flow, and used it to prepare monodispersed silica colloids.¹¹ We found that monodispersed silica colloids could be continuously prepared, while the hydrolysis and polymerization reaction of ethyl silicate (Stöber method¹⁰) was controlled, and the particle size distri-

Fig. 1 Schematic diagrams of Couette-Taylor vortex flow and reactor

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[†] This report was originally printed in J. Soc. Powder Technology, Japan. **37**, 722-727 (2000) in Japanese, before being translated into English by KONA Editorial Committee with the permission of the editorial committee of the Soc. Powder Technology, Japan.

bution of silica colloids obtained was the same as that yielded in batch processing.¹¹ This paper describes the continuous preparation of monodispersed alumina particles by applying this vortex flow to the hydrolysis of aluminum alkoxide, and relates our investigation on the effect of reaction conditions on particle formation. Especially in the synthesis of monodispersed particles^{12,13} from aluminum alkoxide, it is necessary to prepare the emulsion in a different kind of solvent mixture. Taking continuous reaction into account, it appears that using a C-T vortex is very effective because the size and size distribution of the emulsion are influenced by mixing uniformity and strength.

2. Materials and Methods

2.1 Starting solution

Al (sec-OC₄H₉)₃ (ASBD, Takefu Fine Chemical Co., Ltd.) was used as the starting material, which was prepared as described below. Water (Nacalai Inc.) was double distilled and deionized. Octanol (Nacalai Inc.) and acetonitrile (Nacalai Inc.) were used to prepare an emulsion as an organic solvent. Organic solvents were dehydrated using a molecular sieve (3A, 1/16) for 24 h. Hydroxy-propyl-cellulose (HPC, Wako Chemical Co., Ltd., MW 100,000) was used as the dispersant. For the preparation of monodispersed alumina particles, the starting solution was prepared according to concentration conditions for batch processing^{13,14} and the use of a continuous tube-type reactor.¹⁵ The concentration of HPC, which was dissolved in the octanol at R. T., was 0.2 g/cm³. ASBD was dissolved in the octanol at 50°C for 2 h under reflux, after which hydroxy-propyl-cellulose (0.2 g/dm³) was added to prepare a 0.05 mol/dm³ ASBD solution. Meanwhile, water was used to prepare a 0.05 mol/dm³ solution in octanol (60 vol %) and acetonitrile (40 vol %).

2.2 Preparation of alumina particles

The apparatus (Fig. 1) consisted of a starting solution tank, a feeder for supply to the mixer, a T-type mixer, a C-T vortex flow reactor, and collector.¹⁵ The reaction vessel consisted of a glass outer cylinder (50 mm diameter, 1500 mm length) and a stainless steel inner cylinder (38 mm diameter, 1500 mm length) with a common axis. The sum of the vortices developed in this reactor vessel was determined by dividing height (L) by inter-cylinder space width (b), which yielded a value of 125. The ASBD solution and aqueous solution were fed into the T-type mixer by

the feeder at the same rate (3×10^{-4} dm³/s). After mixing, they were put into the reaction vessel where the emulsion formed. Solution residence was controlled by pushing the mixture upward, and residence time is the interval starting when the mixed solutions enter the reactor vessel, and ending when the mixture exits. We set residence time to a maximum of 1 h in these experiments. For the sake of convenience, reaction temperature was 25°C because the experiments were carried out in a room kept at 25°C. The Taylor (Ta) number was defined as the determining flow condition factor in the C-T vortex, and it was determined by Equation (1).

$$Ta = \frac{\omega R_i b}{\nu} \cdot \left(\frac{b}{R_i} \right)^{0.5} \quad (1)$$

Where:

Ta is the Ta number,

ω is the angular speed of the inner cylinder (1/s),

R_i is the inner cylinder radius (mm),

b is the annular gap width (mm), and

ν is the fluid viscosity (m²/s).

The Ta number was controlled by the motor's rotational speed, and ranged between 30 and 200. Upon leaving the reaction vessel, the solution containing alumina particles was collected in a beaker, and the alumina particles were separated from the mother liquid using a centrifugal separator. After washing the alumina particles ultrasonically with ethanol for 10 min, an agglomerated chalk-like powder was obtained by drying at 100°C for 24 h.

2.3 Characterization of as-prepared particles

We used a scanning electron microscope (Hitachi Co., Ltd., S-800) to determine the as-prepared particles' average size, geometrical standard deviation, morphology, and state of agglomeration. SEM photomicrographs were analyzed to assess average size and geometrical standard deviation, and 200 particles were measured for each sample. Particle number density was calculated with Equation (2).

$$N = \frac{Y}{dV} \quad (2)$$

Where:

N is the particle number density ($\times 10^{26}$ /dm³),

Y is the yield (%),

d is the particle density (g/cm³), and

V is particle volume (cm³)

Particle volume was determined from average size,

C-T flow reactor

Batch reactor

Fig. 2 SEM photomicrographs of monodispersed alumina particles prepared with a C-T flow reactor and a batch reactor

assuming the particles are solid true spheres. The density of α -alumina (3.98 g/cm^3)¹⁶ was used as particle density. Hence, these values are not accurate, but they give us an idea of the relative tendency. Crystal phase was determined by powder X-ray diffraction (Macscience Co., Ltd., MXR-3V). Water and organic species contents of the particles were measured by a thermogravimetric and differential thermal analysis (Rigaku Co., Ltd., PTC-10).

3. Results and Discussion

3.1 Comparison of C-T vortex reactor and batch processing

Typical alumina particles shown in the SEM photomicrograph (**Fig. 2**) were made with a C-T vortex reactor. Their Ta number is 92 and residence time was 30 min. An SEM photograph of alumina particles obtained by batch processing¹⁷ is also shown in **Fig. 2** for comparison with monodispersed alumina particles obtained from the C-T vortex reactor. As-prepared alumina particles are spherical and unagglomerated. XRD showed that the crystal phase of as-prepared powders was amorphous. DTA-TG showed that the content of water, octanol, and unreacted ASBD was about 40 wt% (**Fig. 3**). The particle

size distributions of alumina particles prepared by the C-T vortex reactor and batch processing are shown in **Fig. 4 (a)** and **(b)**, respectively. The average size and geometrical standard deviation of alumina particles obtained from the C-T vortex reactor were $0.2 \mu\text{m}$ and 1.15, respectively. On the other hand, those of alumina particles obtained with batch processing were $0.17 \mu\text{m}$ and 1.16, respectively, showing that the size of alumina particles obtained by the C-T vortex reac-

Fig. 3 DTA-TG curves of monodispersed alumina powders

Fig. 4 Particle size distribution of monodispersed alumina particles prepared with a C-T flow reactor (a) and a batch reactor (b)

tor was comparable to that of particles made by batch processing.

3.2 Continuous preparation

It is apparent that this system is capable of preparing monodispersed alumina particles. We performed continuous production with this reactor for 5 h, during which time we collected 0.1 dm³ of solution at 30-min intervals and examined the change in average size (R), geometrical standard deviation (σ_g), yield (Y), and particle number density (N) of the monodispersed alumina particles obtained after centrifugal separation (**Fig. 5**). The Ta number was 92 and residence time was 30 min. There were no changes in the average size, geometrical standard deviation, yield, and particle number density of alumina particles during any one of the five hours. It was therefore evident that the ASBD hydrolysis reaction was controlled by this apparatus, which was able to maintain continuous production of alumina particles having uniform quality. One can presume that there is little ASBD diffusion from one vortex to another because if ASBD readily diffused among vortices, ASBD concentration differences among vortices might cause non-uniformity in both the droplet size distribution and emulsion number density. As a result, the average size, geometrical standard deviation, and particle number density of alumina particles obtained in each vortex would differ widely. However, as the variance in these values for alumina particles was slight in this experiment, the diffusion of ASBD is controlled among the vortices to an extent at which the particle size and

Fig. 5 Dependence of particle size, σ_g , yield, and particle number density on production time

yield of alumina particles are not influenced.

3.3 Effect of Ta number

We investigated the effect of Ta number on particle size, geometrical standard deviation, yield, and particle number density (**Fig. 6**). Residence time was 30 min. When the Ta number was less than 50, the apparatus produced polydispersed alumina particles with a

Fig. 6 Dependence of particle size, σ_g , yield and particle number density on Ta number. (a) Polydispersed region, (b) monodispersed region, (c) agglomerate region.

geometrical standard deviation of more than 1.2 and a broad particle size distribution. As a result, both the separation between vortices and the mixing in each vortex were incomplete because each vortex exists in

the boundary where the transition from a Couette flow to a Couette-Taylor vortex flow occurs. Monodispersed particles were obtained when the Ta number was more than 50. The particle size and geometrical standard deviation of alumina particles were constant in the Ta number range where monodispersed particles were formed.

On the other hand, the alumina particle yield increased as the Ta number increased, with 85% yield obtained at 150. Particle number density also increased as the Ta number increased. This is probably because the ASBD hydrolysis reaction was promoted by uniform mixing in the vortex when the Ta number grew larger. When the Ta number was greater than 150, the yield and particle number density further increased. However, unlike the alumina particles obtained at Ta 92, those formed at Ta 160 were agglomerated (**Fig. 7**), which indicated that the particles were agglomerated by the high collision frequency that occurred during particle formation by vigorous mixing. This showed that when preparing monodispersed particles using this apparatus, particle agglomeration occurs even in the range in which a Couette-Taylor vortex with plug flow is formed. Consequently, monodispersed alumina particles were produced in the range from 50 to 150.

Fig. 7 Effect of Ta number on the agglomeration of alumina particles

3.4 Effect of residence time

We investigated the relation among residence time, average size, geometrical standard deviation, yield, and particle number density (Fig. 8). The Ta number was 92. Residence time was controlled by allowing the feeder supply rate to change from 1.5×10^{-4} to 9×10^{-4} m³/s. Because the average size and geometrical standard deviation of alumina particles were always the same at a certain residence time, it was evident that these values were independent on residence time. On the other hand, yield rose to 86% at 1 h, and the particle number density also increased. Fig. 8 indicates that because the size of alumina particles did not change until the 1 h mark, the yield increase is not due to the growth of alumina particles, but to the increase in particle number density.

Fig. 8 Dependence of particle size, σ_g , yield, and particle number density on residence time

4. Conclusion

Monodispersed alumina particles were continuously prepared by the hydrolysis of aluminum alkoxide using a C-T vortex flow reactor. We reached the following conclusions:

- (1) Monodispersed alumina particles were amorphous, and the particle size and particle size distribution were comparable to those obtained by batch processing.

- (2) The average size, geometrical standard deviation, yield, and particle number density of monodispersed alumina particles were constant during continuous preparation, and reproducibility is possible.
- (3) The Ta number range in which monodispersed alumina particles were formed was from 50 to 150. Particle size and geometrical standard deviation were independent on the Ta number in this range, but the yield and particle number density increased as the Ta number increased. Alumina particles were also agglomerated when the Ta number was greater than 150.
- (4) The particle size and geometrical standard deviation of monodispersed alumina particles were independent on residence time, but yield increased with residence time. Yield increase is not due to the growth of alumina particles, but to the increase in particle number density.

Nomenclature

b	Annulus width	(mm)
d	Particle density	(g/cm ³)
F	Frequency	(%)
L	Length of cylinder	(mm)
N	Particle number density	($\times 10^{26} \cdot \text{dm}^{-3}$)
R	Average particle size	(μm)
R _i	Radius of inner cylinder	(mm)
Ta	Taylor number	
V	Particle volume	(cm ³)
Y	Yield	(%)
σ _g	Geometrical standard deviation of average size	
ν	Kinematic viscosity	(m ² /s)
ω	Angular velocity	

References

- (1) Ogihara, T., M. Ikeda, M. Kato and N. Mizutani. "Continuous Processing of Monodispersed TiO₂ Powders," *J. Am. Ceram. Soc.*, **72**, 1598-1601 (1989).
- (2) Ogihara, T., M. Iizuka, T. Yanagawa, N. Ogata and K. Yoshida. "Continuous Reactor System of Monosized Colloidal Particles," *J. Mater. Sci.*, **27**, 55-62 (1992).
- (3) Ogihara, T., M. Yabuuchi, T. Yanagawa, N. Ogata, K. Yoshida, N. Nagata, K. Ogawa and U. Maeda. "Preparation of Monodispersed, Spherical Ferric Oxide Particles by Hydrolysis of Metal Alkoxides Using a Continuous Tube-Type Reactor," *Advanced Powder Technol.*, **8**, 73-84 (1997).
- (4) Ring, T. A. "Continuous Precipitation of Monosized Particles with a Packed Bed Crystallizer," *Chem. Engng. Sci.*, **39**, 1731-34 (1984).
- (5) Jean, J. H., D. M. Goy and T. A. Ring. "Continuous Pro-

- duction of Narrow-Sized and Unagglomerated TiO_2 Powders," *Am. Ceram. Soc. Bull.*, **66**, 1517-20 (1987).
- 6) Kallay, N. and I. Fischer. "A Method for Continuous Preparation of Uniform Colloidal Hematite Particles," *Colloids & Surf.*, **13**, 145-9 (1985).
 - 7) Kataoka, K. and T. Takigawa. "Intermixing over Cell Boundary between Taylor Vortices," *A. I. Ch. E. J.*, **27**, 504-8 (1981).
 - 8) Mizushima, A., R. Itoh, K. Kataoka, Y. Nakajima and A. Fukuda. "Velocity Distribution of Taylor Vortex Flow in an Annulus between Rotating Coaxial Cylinders," *Kagaku Kougaku*, **35**, 1116-21 (1971).
 - 9) Imamura, T., K. Saito, S. Ishikura and M. Nomura. "A New Approach to Continuous Emulsion Polymerization," *Int. Symp. Poly. Microsphere*, Preprints, p. 151 (1991).
 - 10) Stöber, W., A. Fink and E. Bohn. "Controlled Growth of Monodispersed Silica Spheres in the Micron Size Range," *J. Colloid Interface Sci.*, **26**, 62-69 (1968).
 - 11) Ogihara, T., G. Matsuda, T. Yanagawa, N. Ogata, K. Fujita and M. Nomura. "Continuous Synthesis of Monodispersed Silica Particles by Using Couette-Taylor Vortex Flow," *J. Ceram. Soc. Jpn.*, **103**, 151-154 (1995).
 - 12) Lee, S. K., K. Shinozaki and N. Mizutani. "Influence of Mixed Solvent on the Formation of Monodispersed Al_2O_3 Powders by Hydrolysis of Aluminum sec-Butoxide," *J. Ceram. Soc. Jpn.*, **101**, 470-474 (1993).
 - 13) Ogihara, T., T. Yanagawa, N. Ogata and K. Yoshida. "Formation of Monodispersed Oxide Particles by Hydrolysis of Metal Alkoxide in Octanol/Acetonitrile Solutions," *J. Ceram. Soc. Jpn.*, **101**, 315-320 (1993).
 - 14) Mizutani, N., M. Ikeda, S. K. Lee, K. Shinozaki and M. Kato. "Preparation of Monodispersed Hydrous Aluminum Oxide Powders," *J. Ceram. Soc. Jpn.*, **99**, 183-186 (1991).
 - 15) Ogihara, T. and N. Mizutani. "Synthesis of Monodispersed Ceramic Particles from Emulsion Route," *Inorg. Mater.*, **3**, 177-187 (1996).
 - 16) JCPDS Card 10-173.
 - 17) Ogihara, T., H. Nakajima, T. Yanagawa, N. Ogata, K. Yoshida and N. Matsushita. "Preparation of Monodispersed, Spherical Alumina Powders from Alkoxides," *J. Am. Ceram. Soc.*, **74**, 2263-2269 (1991).

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