

EFFECT OF REACTION CONDITIONS ON SIZE AND MORPHOLOGY OF SiO_2 POWDER IN A SOL-GEL PROCESS

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(Received 10 May 1996 • accepted 22 August 1996)

Abstract – We have investigated effects of the reaction conditions such as mixing of solution, reactant concentration, feeding time and molecular weight of alcohol solvents on the size and morphology of silicon oxide in a sol-gel process in Rushton type reactor. To describe the intensity of mixing of solution the power input, which means the energy dissipated in the solution, was used. The particle nucleation and growth processes of silicon oxide were varied with all the reaction conditions. However, the particle morphology of silicon oxide depended mostly on the reactant concentration and molecular weight of alcohol solvents under various reaction conditions. If the supersaturation level of silicon oxide in the solution was promoted by variation of reaction conditions, the particle nucleation and growth processes were facilitated and it resulted in reduction of relative induction time and in increase of mean particle size of silicon oxide. To explain the principal mechanism of particle growth process of silicon oxide the two-step growth model was applied.

Key words: Silicon Oxide, Particle Nucleation, Particle Growth, Relative Induction Time, Two-Step Growth

INTRODUCTION

Since the sol-gel process has advantages on the control of the purity and size of particles in the synthesis of fine powders, this process is one of the most popular ways to produce the fine powder for engineering ceramics.

Since Stober et al. [1968] studied on the synthesis of silicon oxide powder with silicon alkoxide by sol-gel process, a lot of investigations on synthetic powder processes has been carried out [Bell and Matijevic, 1974; Barringer and Bowen, 1982; Ogihara et al., 1988; Jean and Ring, 1986; Okamura et al., 1986]. Most their studies focused on synthesis of spherical ceramic powders by sol-gel process and observed variations of particle size and morphology of powder with varying experimental conditions such as reactant concentration and reaction temperature. However, they did not suggest any engineering model to describe the influence of experimental conditions on particle formation and particle growth in the sol-gel process.

To describe growth mechanism of the particle in the sol-gel process Nakanishi and Takamiya [1988] used a chronomal analysis which was derived to predict the crystal growth in crystallization processes [Nielson, 1964]. In the sol-gel process silicon oxide is supersaturated by hydrolysis and condensation of silicon alkoxide, as in the reaction crystallization, and it results in formation and growth of silicon oxide particles, which is called a sol, because silicon oxide has very low solubility in the solution. According to a chronomal analysis of Nakanishi and Takamiya [1988], the particle growth process of the silicon oxide in the sol-gel process was described by two-dimensional polynuclear growth model [Ohara and Reid, 1973], which was derived on the basis of assumptions of polynucleation on the particle surface and no lateral growth rate of nuclei. In this growth model the particle growth rate of silicon oxide was as-

sumed to be controlled by polynucleation rate on the particle surface, which is frequently called as "surface reaction". However, this growth model did not consider an influence of hydrodynamic condition of the solution, such as turbulent mixing of reactants and solution, on the particle growth process and did not include a particle formation process in the solution.

In general, it is sure that the particle growth process in a solution is mostly dependent on the supersaturated concentration of solute and the hydrodynamic condition of solution. In the crystallization of barium sulfate Leung and Nancollas [1978a, 1978b] and Liu and Nancollas [1973, 1975] observed that at low supersaturation level of barium sulfate the particle growth rate were controlled by supersaturated concentration of barium sulfate rather than by hydrodynamic condition of solution. Silmilar dependency of particle growth process on the supersaturated concentration of calcium sulfate at low supersaturation level was also measured by McCartney and Alexander [1958]. From those experimental data they insisted that the particle growth process of barium sulfate and calcium sulfate be determined by the surface reaction rate.

However, Kim and Tarbell [1991, 1996] showed that at high supersaturation level of barium sulfate the hydrodynamic condition of solution such as turbulent mixing became important to the particle growth process in barium sulfate crystallization. According to Kim and Tarbell, the particle growth rate increased with increase of agitation speed of solution and it was predicted by the micromixing model which was based on the two-step growth model [Karpinski, 1985] and 3-E closure model [Dutta and Tarbell, 1989; Mehta and Tarbell, 1987].

In this study we studied the effects of reaction conditions of the solution, such as hydrodynamic condition of solution, reactant concentration, feeding time and molecular structure of alcohol solvents, on the silica particle formation and particle growth in the sol-gel process. Since these reaction conditions are suspicious to be related with production of supersaturation

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level of silicon oxide in the sol-gel process, it is expected that they may give a clue to understanding a basic mechanism of particle growth process.

The two-step growth theory suggested by Karpinski [1985] was used to describe the particle growth mechanism of silicon oxide in the sol-gel processes.

BASIC MECHANISM FOR PARTICLE SYNTHESIS

In the sol-gel process the silicon oxide is produced by the consecutive reactions of hydrolysis and condensation of silicon alkoxide as follows;



where R indicates alkyl group. In the sol-gel process of silicon alkoxide, generally, since the reaction rate of hydrolysis is slow, an acidic or alkalic homogeneous catalyst is used to facilitate the hydrolysis reaction. In present study ammonia solution is used as a catalyst to promote the reaction of hydrolysis of tetra ethyl ortho silicate (TEOS). It should be noted that in general the condensation reaction of silicon hydroxide is much faster than the hydrolysis reaction of silicon alkoxide.

The synthetic processes of silicon oxide powder by sol-gel method may be schematically expressed as shown in Fig. 1. In an alcohol solvent the silicon alkoxide has high solubility while the silicon oxide produced by the consecutive reactions of hydrolysis and condensation of the silicon alkoxide is almost insoluble. Therefore, the solution is supersaturated with the silicon oxide and it results in formation of tiny solid particles of silicon oxide, which are called as nuclei, and in growth of the particles in the supersaturated solution of silicon oxide.

To describe the particle growth process in the supersaturated solution the two-step growth model which was suggested by Karpinski [1985] is frequently used. In this model the particle growth process is composed of two steps; one is mass transfer step and the other is surface reaction step. Mass transfer step is to describe the molecular transport of silicon oxide from the bulk to the particle interface and surface reaction step is to

predict the integration of silicon oxide into particle surface. If we assume a spherical morphology for all particle sizes, the two-step growth model can be expressed as,

$$C - C_s = \rho G/k_m + (\rho G/k_r)^{1/r} \quad (3)$$

where C is the silicon oxide concentration at the bulk solution, C_s is the silicon oxide concentration at the equilibrium (that is, solubility), k_m is the mass transfer coefficient, k_r is the surface reaction rate constant, r is the surface reaction order, ρ is the particle density and G is the linear growth rate of particle defined as dR/dt, where R is the radius of the spherical particle. In Eq. (3) if the mass transfer rate is dominant to the surface reaction rate, the particle growth is controlled by the surface reaction step and if vice versa, the mass transfer step determines the particle growth rate. It is interesting that the mass transfer rate is sensitive to the hydrodynamic condition around the particle while the surface reaction rate is independent of the hydrodynamic condition.

EXPERIMENT

To produce the silicon oxide powder by the sol-gel method TEOS (Fluka, ACS Grade) was used as a reactant. The reactant solution was prepared by dissolving TEOS into 50 ml of alcohol solvent and then was fed into a reactor having a 150 ml of the homogeneous catalyst solution of which is prepared by a mixture of 25 ml of pure ammonia solution (Showa, ACS Grade) with 125 ml of alcohol solvent (Junsei, ACS Grade). TEOS concentration of the reactant solution was modified from 0.35 to 3.0 mol/l. To change the reaction conditions in the sol-gel process the feeding time was varied from 10 min to 60 min. In this study the feeding time is defined as a period which is required to completely feed the reactant solution into the reactor.

To investigate the effect of impeller speed on silicon oxide particles a standard Rushton-type reactor, as displayed in Fig. 2, was used. This reactor had a 0.5 liter of working volume and was made of pyrex glass. The six blade turbine type impeller was used to agitate the solution. The impeller speed was changed from 400 to 1500 rpm. Four baffles were installed for effective mixing of solution in the reactor.

To observe the influence of molecular structure of alcohol solvents on the synthesis of silicon oxide powder methanol, ethanol, n-propanol and n-butanol were used as solvents in the sol-gel process.

The particle size of powder was measured by particle size analyzer (Malvern Mastersizer E, U.K.) and the morphology of the powder was observed by SEM (Leica 400, Germany).

POWER DISSIPATION BY IMPELLER AGITATION

To quantitatively describe the influence of agitation of solution on the sol-gel process we convert impeller speed into a power input which means a energy dissipated per unit mass of solution for mixing and agitation. The relationship between impeller speed and power dissipation in a solution can be expressed with power number which is defined as [McCabe and Smith, 1976],

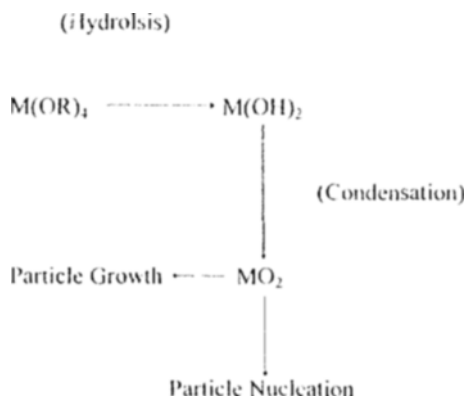


Fig. 1. Schematic diagram for powder synthesis mechanism in sol-gel processes.

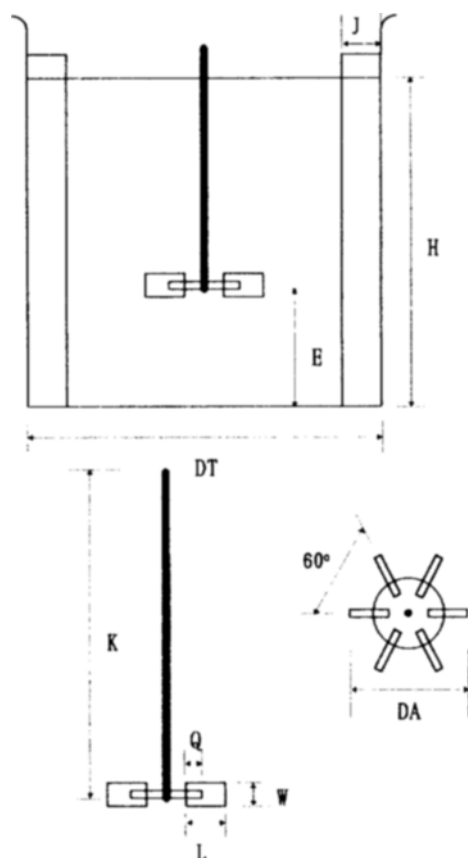


Fig. 2. Schematic designs of Rushton type reactor and six-paddle turbine impeller.

(DT=H=8.3 cm, DA=E=3.3 cm, J=0.7 cm, Q=0.42 cm, L=0.825 cm, K=50 cm, W=0.55 cm)

$$N_p = Pg_c / n^3 D_a^5 \rho_s \quad (4)$$

where P is the power dissipated into the solution, n is the impeller speed (revolution per second), D_a is the diameter of impeller and ρ_s is the density of solution.

The power number is dependent on the configuration of vessel, such as types of impeller and baffle, and Reynolds number which is defined for the mixing in the vessel as,

$$N_{Re} = n D_a^2 \rho_s / \mu \quad (5)$$

where μ is the viscosity of solution.

In Eq. (5) the Reynolds number is expressed in terms of characteristic parameters of mixing in the reactor. Therefore, if the dependency of power number on Reynolds number is obtained in the Rushton type reactor, the power dissipation in the solution can be calculated with Eq. (4). The power input per unit mass of the solution is simply calculated by dividing the power dissipation with the mass of solution in the reactor.

RESULTS AND DISCUSSION

In general, the intensity of mixing is quantitatively expressed in terms of power input into solution. In this study since the impeller speed was varied from 400-1500 rpm, which was

Table 1. Prediction of power input in Rushton type reactor

Impeller speed (RPM)	Reynolds no.	Power no.	Power input (m^2/s^3)
400	6019	6	0.185
700	10511	6	0.4625
900	13476	6	0.9028
1200	17968	6	3.05
1500	22460	6	5.81

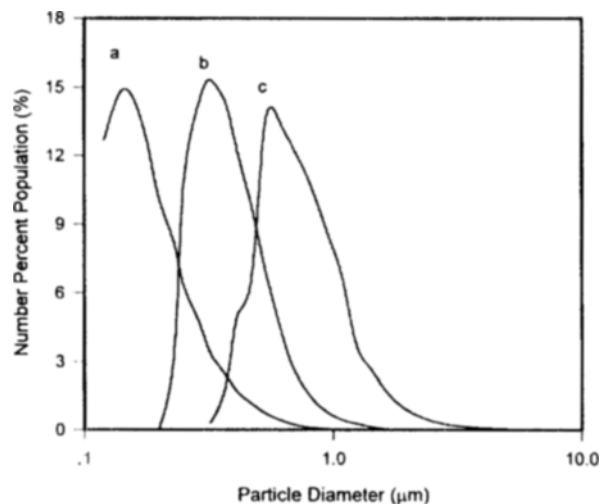


Fig. 3. Influence of power input and TEOS on the SiO_2 particle size distribution.

(a) 1 mol/L TEOS and $0.4625 \text{ m}^2/\text{s}^3$ of power input, (b) 1.5 mol/L TEOS and $0.9028 \text{ m}^2/\text{s}^3$ of power input and (c) 2 mol/L TEOS and $3.05 \text{ m}^2/\text{s}^3$ of power input.

equivalent to 6019-22460 of Reynolds number, the power number for the Rushton type reactor could be assumed almost constant as six [McCabe and Smith, 1976]. Then, the power dissipation per unit mass of solution in the reactor was calculated by Eq. (4) as shown in Table 1. The power input increased exponentially with increase of impeller speed.

In Fig. 3, typical size distributions of the silicon oxide particles produced by the sol-gel process were displayed. The particle size distribution of silicon oxide was greatly affected by the reaction conditions and was shifted in right with increase of power input and reactant concentration. However, the mode of particle size distributions was kept constant as monomodal.

The mean particle size of silicon oxide powder was calculated with the size distribution and as shown in Fig. 4, it was markedly influenced by the power input and reactant concentration. Below 1.0 mol/l of the reactant concentration the mean particle size of silicon oxide was insensitive to the power input. However, when the reactant concentration is greater than 1.0 mol/l, the mean particle size of silicon oxide became sensitive to the power input and then increased with increase of power input.

This trend of experimental data may be explained by the two-step growth model [Karpinski, 1985]. Since the supersaturation level of silicon oxide generated below 1.0 mol/l of reactant concentration were expected to be low, the mass transfer rate of sil-

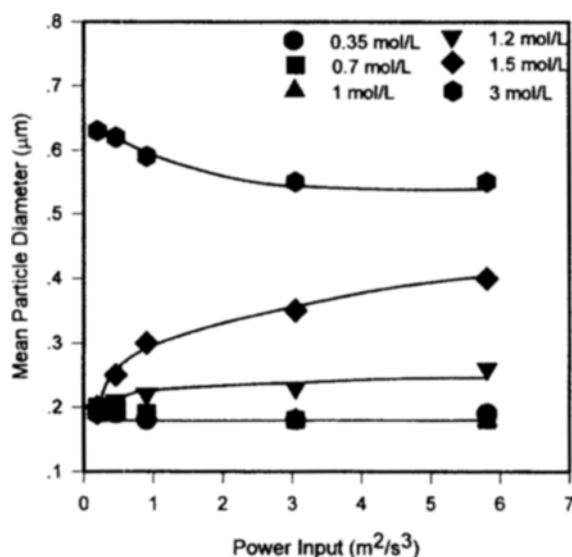


Fig. 4. Influence of power input and TEOS concentration on the mean particle diameter of SiO₂ at 30 min of feeding time in methanol solvent.

icon oxide from the bulk to the particle interface could be assumed dominant to the surface reaction rate on the particle surface, as mentioned in the model previously. Thus, the particle growth process of silicon oxide was determined by the surface reaction step and became independent of the power input. This result was consistent with the experimental data of Leung and Nancollas [1978a, 1978b] and Liu and Nancollas [1973, 1975] in barium sulfate crystallization. However, as the concentration of TEOS increased, the supersaturated concentration of silicon oxide in the solution increased and then the surface reaction rate was assumed to surpass the mass transfer rate in the particle growth process of silicon oxide. The particle growth rate of silicon oxide was controlled by the mass transfer step and became sensitive to hydrodynamic condition of the solution. Consequently, at TEOS concentration greater than 1.0 mol/l the mean particle size of silicon oxide increased with increase of the power input. Our experimental result for the dependency of mean particle size on the power input at high reactant concentration was also consistent with the experimental data of Fitchett and Tarbell [1990] and Kim and Tarbell [1991].

It should be noted that at 3.0 mol/l of TEOS each particle was much deviated from a spherical shape and was seriously aggregated together. Thus, it was obvious that the mean particle size measured by particle size analyzer did not represent the size of a single particle but the size of aggregate of particles. This experimental results will be confirmed by microscopic figures in later.

As shown in Fig. 5, even if the feeding time was widely changed, the mean particle diameter of silicon oxide produced at 1.0 mol/l of reactant concentration was almost insensitive to power input. This experimental data indicated that at low reactant concentrations the surface reaction step may dominantly influence on the particle growth process.

To observe the influence of the power input and feeding time on the particle nucleation process the relative induction

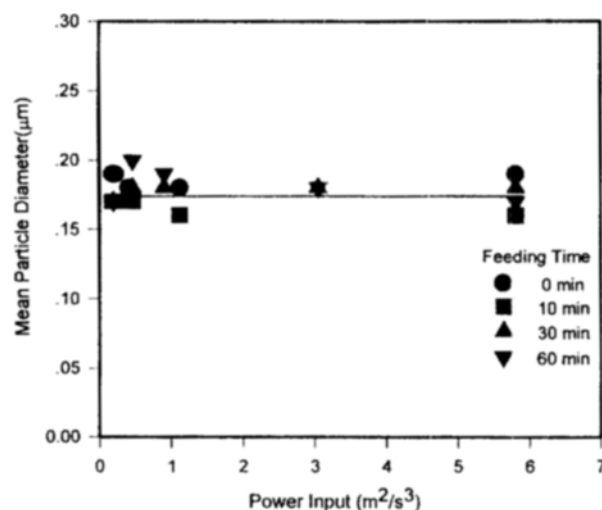


Fig. 5. Influence of power input and feeding time on the mean particle diameter of SiO₂ at 1.0 mol/L of TEOS in methanol solvent.

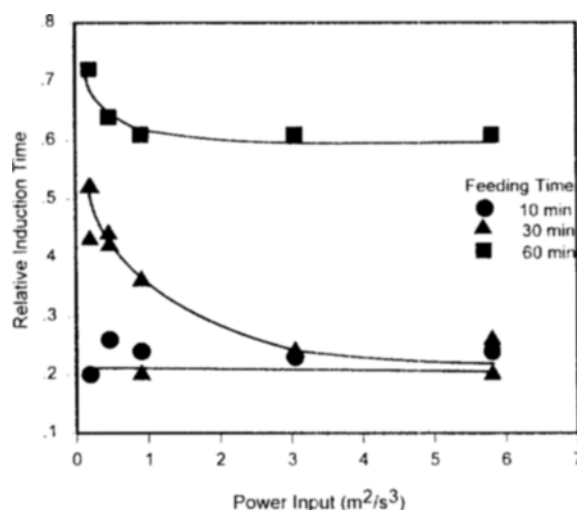


Fig. 6. Influence of power input and feeding time on the relative induction time of SiO₂ at 1.0 mol/L of TEOS in methanol solvent.

time was measured, as shown in Figs. 6 and 7. In this study the relative induction time was defined as the ratio of the induction time to the feeding time, where the induction time represented the time interval between beginning of reactant feeding and the first formation of particle nuclei in the solution.

Even at the low reactant concentration of TEOS, in contrast to the mean particle diameter, the relative induction time was markedly influenced by the reaction conditions of power input and feeding time (Fig. 6). In general, the particle nucleation of silicon oxide occurred by supersaturated concentration of the silicon oxide and its rate depended on supersaturation level of solution. Since the silicon oxide was produced by the hydrolysis and condensation of TEOS, the supersaturation level of silicon oxide in the solution might be directly influenced by micromixing of reactant solution, as described previously. The higher power input into solution might improve the actual rates of hydrolysis and condensation of TEOS and result in gen-

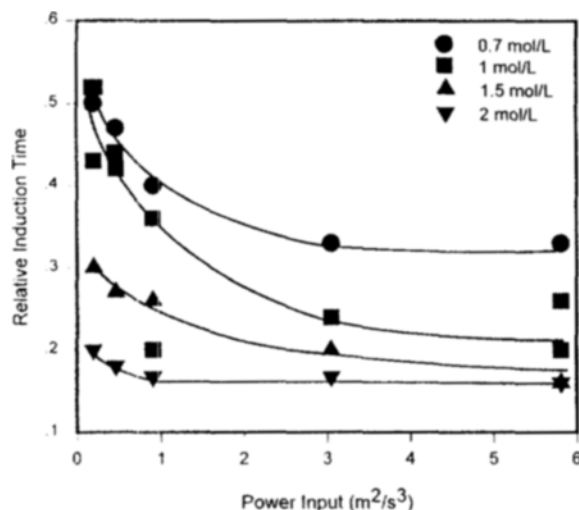


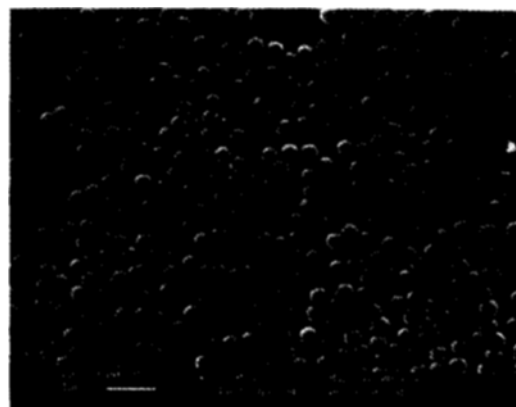
Fig. 7. Influence of power input and TEOS concentration on the relative induction time of SiO_2 at 30 min of feeding time in methanol solvent.

erating higher supersaturation level of the silicon oxide in the solution and facilitating the particle nucleation process. In addition, the shorter feeding time which means the higher flow rate of TEOS solution into the reactor might cause rapid increase the supersaturated concentration of the silicon oxide in the solution. Therefore, the relative induction time was reduced with increasing power input and feed flow rate.

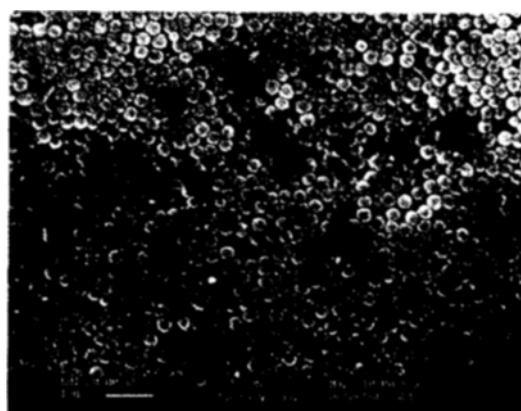
At high reactant concentration of TEOS the dependency of relative induction time on the power input and feeding time was similar to that at the low reactant concentration. As displayed in Fig. 7, the relative induction time was reduced with increase of the power input and reactant concentration due to the increase of supersaturation level of silicon oxide in the solution.

The effects of the reaction conditions of power input, reactant concentration and feeding time on the morphology of the silicon oxide particles were observed, as shown in Fig. 8. Below 2.0 mol/l of reactant concentration a spherical particle of the silicon oxide was produced. However, the morphology of the silicon oxide particle which was synthesized at 3.0 mol/l of TEOS concentration was much deviated from a spherical shape and the particles were seriously agglomerated.

Even though stoichiometric molar ratio of TEOS to water in the hydrolysis reaction is four, Brinker and Scherer [1990] recommended that the molar ratio of TEOS to water be the greater than 20 to obtain a single spherical particle of silicon oxide in sol-gel process. In our study a spherical particle of silicon oxide was successfully obtained until the molar ratio of TEOS to water was 11, which was equivalent to 2.0 mol/l of TEOS concentration at a fixed amount of water. However, the shape of silicon oxide particle becomes irregular at 7 of molar ratio of TEOS to water, which corresponded to 3.0 mol/l of TEOS concentration, due to too much reduction of the molar ratio from the value suggested by Brinker and Scherer [1990]. It is interesting that the morphology of silicon oxide was not affected by variation of power input and feeding time in the range carried out in our experiment.



(a)



(b)



(c)

Fig. 8. Influence of power input and TEOS on the morphology of silicon oxide particles produced in methanol solvent at 30 min of feeding time.

(a) 1 mol/L of TEOS and $0.9028 \text{ m}^2/\text{s}^3$ of power input, (b) 2 mol/L of TEOS and $3.05 \text{ m}^2/\text{s}^3$ of power input and (c) 3 mol/L of TEOS and $3.05 \text{ m}^2/\text{s}^3$ of power input.

Since the alcohol is generally used as a solvent in the sol-gel process, the structure of solvent may play an important role in the production of silicon oxide particles. In Figs. 9-11, we observed the influence of solvent structure on the particle nucleation, particle growth and particle morphology of silicon oxide. As shown in Fig. 9, the relative induction time for silicon oxide nucleation was reduced with increase of molecular weight

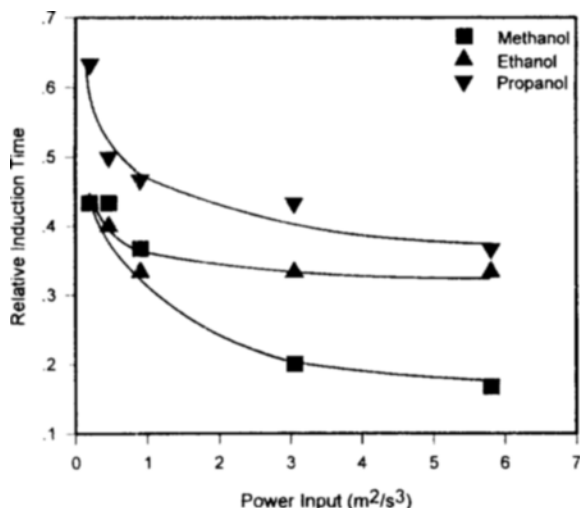


Fig. 9. Influence of alcohol solvents and power input on the relative induction time of SiO₂ at 1.0 mol/L of TEOS and 30 min of feeding time.

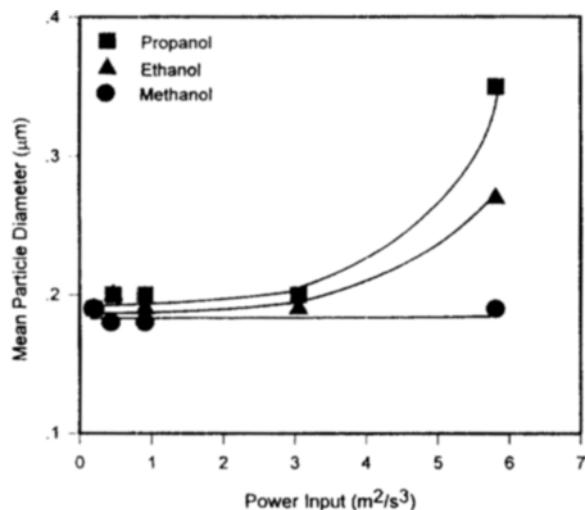


Fig. 10. Influence of alcohol solvents and power input on the mean particle diameter of SiO₂ at 1.0 mol/L of TEOS and 30 min of feeding time.

of alcohol solvent. This result implied that the supersaturated concentration of silicon oxide increased and the particle nucleation process was facilitated. According to Stober et al. [1968], the structure of alcohol solvent gave an influence mainly on the reaction rates of hydrolysis and condensation of silicon alkoxide, and the reaction rates were reduced with increase of molecular weight of the alcohol solvent due to the structural inhibition of alcohol solvents on the reactions. Thus, since in the methanol solvent the production rate of the silicon oxide was relatively faster than in the ethanol and n-propanol solvents, the supersaturation of silicon oxide in the methanol solvent increased to the higher level and it resulted in the shorter relative induction time.

Since the lower molecular weight solvent exerted the less inhibition on the production of silicon oxide, it could cause the



Fig. 11. Morphological change of silicon oxide particles produced by sol-gel process under n-butanol alcohol solvents at 3.05 m²/s² of power input and 1.0 mol/L of TEOS and 30 min of feeding time.

higher particle nucleation of silicon oxide by the higher supersaturation level in the solution and could result in the more population of small size of particles. Therefore, the mean particle size was reduced with decrease of the molecular weight of solvents as shown in Fig. 10. The influence of the alcohol solvents on the particle size of silicon oxide became clearly exhibited as the power input was increased.

The morphology of the silicon oxide particles were significantly affected by the solvent structures of alcohols. In the solvents of methanol, ethanol and n-propanol the shapes of particles were kept in a sphere. However, as shown in Fig. 11, the silicon oxide powder produced in the n-butanol solvent exhibited a serious flocculation of irregularly shaped particles. This morphological change solvent was due to promoting flocculation of particles by n-butanol solvent and was agreed with experimental results Stober et al. [1968], Lee et al. [1991] and Lee et al. [1992].

CONCLUSION

In semi-batch Rushton type reactor the effects of reaction conditions such as power input, TEOS concentration, feeding time and molecular structure of alcohol solvents on the particle synthesis of silicon oxide in the sol-gel process were observed. The particle nucleation and growth of silicon oxide in the sol-gel process were affected by power input and TEOS concentration because the production rate of silicon oxide in the solution and the mass transfer and surface reaction rates in the particle growth process were changed. The mean particle size of silicon oxide increased and the relative induction time was reduced with increase of power input in the reactor. This trend was clearly exhibited at high reactant concentration of TEOS rather than at low reactant concentration and was coincident with that of crystal growth in the reaction crystallization. Thus, it may be possible to apply the two step growth model [Karpinski, 1985] to properly describe the principal mechanism of the particle growth of the silicon oxide in sol-gel process.

The particle morphology of the silicon oxide was changed

with variation of the TEOS concentration and molecular weight of alcohol solvents. To produce the spherical shape of particle, even if the stoichiometric molar ratio of TEOS to water in the hydrolysis reaction was 4, it was observed in our experiment that the actual molar ratio of TEOS to water should be greater than 10. In addition, the spherical particles of the silicon oxide could be obtained with the solvents of methanol, ethanol and n-propanol, but not with n-butanol solvent. However, it was interesting that the particle morphology of silicon oxide was independent of the feeding time and power input.

ACKNOWLEDGEMENT

This research was supported in part by Korea Institute of Science Technology.

NOMENCLATURE

A_c	: surface area of single particle
C	: silicon oxide concentration at bulk
C_s	: solubility of silicon oxide
D_a	: impeller diameter
G	: linear growth rate ($=dR/dt$)
k_m	: mass transfer coefficient
k_r	: surface reaction constant
n	: impeller speed [rps]
N_p	: power number
N_{Re}	: Reynolds number
P	: power dissipation [$\text{Kg m}^2/\text{s}^3$]

Greek Letters

ρ	: particle density
ρ_s	: solution density
μ	: viscosity of solution

REFERENCES

- Barringer, E. A. and Bowen, H. K., "Formation, Packing and Sintering of Monodisperse TiO_2 Powders", *J. Am. Ceram. Soc.*, **65**, C-199 (1982).
- Bell, A. and Matijevic, E., "Growth Mechanism of Hydrated Chromium(III) Oxide Spherical Particle of Narrow Size Distribution", *J. of Phys. Chem.*, **78**, 2621 (1974).
- Brinker, C. J. and Scherer, G. W., "Sol-Gel Science", Wiley Pub. Co., Inc., NY (1990).
- Dutta, A. and Tarbell, J. M., "Closure Models for Turbulent Reaction Flows", *AIChE J.*, **35**(12), 2013 (1989).
- Fitchett, D. E. and Tarbell, J. M., "Effect of Mixing on the Precipitation of Barium Sulfate in an MSMR Reactor", *AIChE J.*, **36**(4), 511 (1990).
- Jean, J. H. and Ring, T. A., "Processing Monosized TiO_2 Powders Generated with HPC Dispersant", *Am. Ceram. Soc. Bull.*, **65**, 1574 (1986).
- Karpinski, P. H., "Importance of the Two-Step Crystal Growth Model", *Chem. Eng. Sci.*, **40**, 641 (1985).
- Kim, W. S. and Tarbell, J. M., "Effect of PVA and Gelatin Additives on Barium Sulfate Precipitation in an MSMR Reactor", *Chem. Eng. Comm.*, **101**, 115 (1993).
- Kim, W. S. and Tarbell, J. M., "Micromixing Effects on Barium Sulfate Precipitation in an MSMR Reactor", *Chem. Eng. Comm.*, in print (1996).
- Lee, S. K., Ikeda, M. and Muzutani, N., "Influence of Alcohol Solvent in the Formation of Monodispersed Particles by Hydrolysis of Zirconium Tetra n-Butoxide", *J. of Ceram. Soc. Japan*, **99**(4), 300 (1991).
- Lee, S. K., Shinozaki, K. and Muzutani, N., "Effects of Stabilizing Agents on Synthesis of Monodispersed Al_2O_3 Powder by Hydrolysis of Aluminium Sec-Butoxide", *J. of Ceram. Soc. Japan*, **100**(9), 1140 (1992).
- Leung, W. H. and Nancollas, G. H., "A Kinetic Study of the Seeded Growth of Barium Sulfate in Presence of Additives", *J. of Inorg. Nucl. Chem.*, **40**, 1871 (1978a).
- Leung, W. H. and Nancollas, G. H., "Nitrotri(methylenephosphonic Acid) Adsorption on Barium Sulfate Crystals and Its Influence on Crystal Growth", *J. of Crystal Growth*, **44**, 1631 (1978b).
- Liu, S. T. and Nancollas, G. H., "The Crystal Growth of Calcium Sulfate Dihydrate in the Presence of Additives", *J. of Colloid and Interface Sci.*, **44**(3), 442 (1973).
- Liu, S. T. and Nancollas, G. H., "The Crystal Growth and Dissolution of Barium Sulfate in the Presence of Additives", *J. of Colloid and Interface Sci.*, **52**(3), 582 (1975).
- McCabe, W. L. and Smith, J. C., "Unit Operations for Chemical Engineering", McGraw-Hill, London (1976).
- McCartney, E. R. and Alexander, A. E., "The Effect of Additives upon the Process of Crystallization. I. Crystallization of Calcium Sulfate", *J. of Coll. Sci.*, **13**, 383 (1958).
- Mehta, R. V. and Tarbell, J. M., "Four Environment Model of Mixing and Chemical Reaction: Part II, Comparison with Experiments", *AIChE J.*, **33**(7), 1089 (1987).
- Nakanishi, K. and Takamiya, Y., "Growth of Seeded Silica from TEOS in Ethanol", *J. of Ceram. Soc.*, **72**, 421 (1988).
- Nielsen, A. E., "Kinetics of Precipitation", Pergamon Press, Oxford, UK (1964).
- Ogihara, T., Mizutani, N. and Kato, M., "Growth Mechanism of Monodispersed ZrO_2 Particles", *J. Am. Ceram. Soc.*, **86**, 476 (1988).
- Ohara, M. and Reid, R. C., "Modeling Crystal Growth Rate from Solutions", Prentice-Hall, Inc., Englewood, NJ (1973).
- Okamura, H., Barringer, E. A. and Bowen, H. K., "Preparation and Sintering of Monosized Al_2O_3 - TiO_2 Composite Powder", *J. Am. Ceram. Soc.*, **69**, C-22 (1986).
- Stober, W., Fink, A. and Bohn, E., "Controlled Growth of Monodispersed Silica Spheres in the Micron Size Range", *J. of Coll. & Interface Sci.*, **26**, 62 (1968).