



Formation of Silica Nanoparticles by Hydrolysis of TEOS Using a Mixed Semi-Batch/Batch Method

KI DO KIM AND HEE TAIK KIM

*Department of Chemical Engineering, Hanyang University, 1271 Sa 1-Dong,
Ansan Kyunggi-do 425-791, South Korea*

khtaik@hanyang.ac.kr

Received January 24, 2002; Accepted May 20, 2002

Abstract. A new method for preparing silica nanoparticles, which consists of a two-stage semi-batch/batch hydrolysis reaction of tetraethylorthosilicate (TEOS), is presented. A relatively slow rate of hydrolysis of the TEOS occurred during the semi-batch process, which resulted in larger silica particles with a narrower size distribution. This was in direct contrast to the batch process. An example of reduction in particle size for an initial semi-batch and subsequent batch reaction is shown. On completion of the initial semi-batch step, the silica particles had a diameter of 106 nm. As the subsequent batch reaction proceeded, the mean size of the particles decreased to 23 nm. In this work, it was found that the optimal conditions for the silica nanoparticles using this mixed method were as follows; (TEOS: 0.5 M, H₂O: 6.0 M, NH₄OH: 0.2 M, feed rate: 5.0 ml/min, temperature: 42.5°C). In conclusion, a mixed semi-batch/batch system suggested a new probability for the synthesis of nanoparticles.

Keywords: silica, TEOS, semi-batch/batch, hydrolysis, optimal condition

1. Introduction

Monodisperse silica colloidal particles that are uniform in size, shape and composition have wide application not only in the field of physical chemistry dealing with dynamic behavior and stability of particle systems, but also in industries involving catalysts, chromatography, ceramics, pigments, photographic emulsion, etc. [1–4]. Monodisperse silica particles can be prepared by hydrolysis and condensation of alkoxysilanes in a mixture of alcohol, water, and ammonia. Since Kolbe [5] discovered the formation of monodisperse silica particles through the hydrolysis and condensation of tetraethylorthosilicate (TEOS) in ethanol with ammonia as catalyst, many studies have been made on this reaction system [6, 7]. Some mechanisms were put forward. Bogush and co-workers [8] regarded the nucleation and growth of silica particles as an aggregation process of small sub-particles several nanometers in size. Matsoukas and Gulari [9] proposed that particle

nucleation was the result of the reaction between two hydrolyzed monomers, such that the particles grew only by monomer addition.

The controlled hydrolysis and condensation of TEOS in dilute alcohol solution using a batch precipitation technique gives fine particles of SiO₂. Typically, small-scale batch hydrolysis is done under a nitrogen atmosphere in a vessel fitted with a magnetic stirrer. Precipitation parameters, such as reactant concentration, the concentration ratio (*R*) of water and TEOS, reaction temperature, and ageing conditions, affect the resulting particle size, size distribution, morphology, and state of particle agglomeration. In general, a batch process [10] in which system the reactants (TEOS/H₂O/NH₄OH/Et(OH)) are initially charged into a reactor, are well mixed, and are left to react for a certain period is used for small-scale operation, for testing new processes that have not been fully developed, for the manufacture of expensive products, and for processes that are difficult to convert to continuous operations.

The batch process has the advantage of high conversions that can be obtained by leaving the reactant in the reactor for long periods of time. In addition, it is simple and needs little supporting equipment. But it also has the disadvantages of high labor costs per unit production, and it is not efficient to obtain nanophase particles with a narrow size distribution. These nanophase materials have several technical applications like catalysis, lowering the sintering temperature, increasing the sintering rate, controlling the microstructure in high performance ceramic materials and magnetic applications.

On the contrary, a semi-batch process [10, 11] in which system one reactant (TEOS/Et(OH)) are fed into a reactor containing the other reactant ($\text{H}_2\text{O}/\text{NH}_4\text{OH}/\text{Et(OH)}$) at a constant feed rate gives greater control over the resulting particle size, shape, and size distribution than batch process, because of the system's short nucleation time and the slow hydrolysis rate of the reaction. In addition, it has the advantages of good temperature control and good control of reaction speed because the reaction proceeds as reactants are added. It is a flexible system but is more difficult to analyze than the other reactor types. In this study, therefore, a mixed semi-batch/batch system combining the merits of the semi-batch and batch methods were used to obtain silica nanoparticles with a narrower size distribution than in either the batch or semi-batch system. Above all, the advantage of this mixed method is that the particle size can be reduced by controlling the reaction conditions of second batch reaction, although the size of particles prepared by first semi-batch reaction is not desirable or large. In addition, it also has the merit that is possible to make a mass production.

The objectives of this work were: (1) to suggest a new method for synthesizing silica nanoparticles from the hydrolysis of alkoxide, (2) to establish the optimal conditions for preparing nanoparticles, and (3) to find the main parameters affecting the properties of silica nanoparticles.

2. Experimental

2.1. Starting Solutions

In this work, TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$, 99.99%, Aldrich Chemical Co.), ethanol (99.9%, Sigma Chemical Co.), and ammonia water (NH_4OH , 28%, Yakuri Pure Chemicals Co. Ltd.) were used as starting materials without any purification. The solutions were prepared in a glove box at room temperature under inert atmosphere.

The relative humidity in the glove box was kept below about 3.0%.

2.2. Preparation and Analysis of SiO_2 Particles

Monodispersed spherical SiO_2 nanoparticles were prepared by the hydrolysis of TEOS using a two-stage mixed semi-batch/batch method. The overall experimental procedure and the schematic diagram of a semi-batch and batch reactor are shown in Fig. 1, respectively. A micro feed pump (EYELA, MP-3) with a constant flow rate (0.3–5.0 ml/min) fed the starting solution A (TEOS and ethanol) into the reactor with another solution B (water, ammonia, and ethanol), thereafter, the mixture prepared by a semi-batch reaction as the first stage was agitated for 60 min under an N_2 atmosphere.

After the first stage reaction (semi-batch) was finished, the batch reaction as the second stage was started. Solutions A and B were again added into the reactor containing the solution and the particles prepared by the first stage reaction. The reaction mixture was vigorously stirred for 60 min. The SiO_2 dispersion were transferred out of the reactor and the powders were washed with ethanol by repeated centrifugation (at 3,000 rpm for 5 min) and dried at 70°C for 12 hours. A laser particle size analyzer (Otsuka electronics, LPA-3000, 3100) was used to determine the mean particle size and size distribution presented in figure of this paper. To confirm the results, scanning electron microscopy (SEM, JEOL JSM-T330, Japan) was also used.

3. Results and Discussion

3.1. Effect of the Concentration of Water and Ammonia

Figures 2 and 3 show the effect of the amount of water and ammonia on the particle size and standard deviation. The solid symbols are the experimental data measured from the first stage (semi-batch) and the open symbols are those obtained from the second stage (batch). The particle size and standard deviation at the second stage were smaller than those at the first stage. As the concentration of water and ammonia at the first stage increased, the decrement of particle size from the first stage to the second stage increased. (see Figs. 2(a) and 3(a)) However, the excess concentration of water

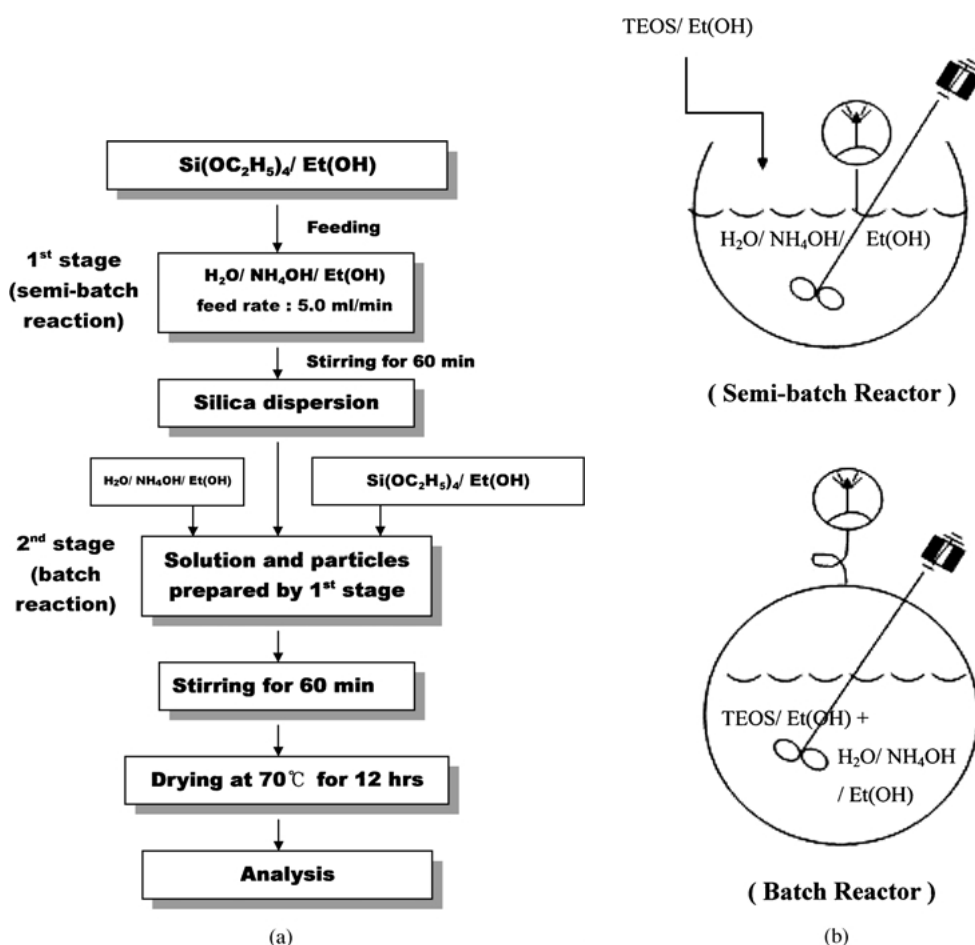


Figure 1. Experimental procedure of silica nanoparticle preparation by two-stage mixed method (a) and the schematic diagram of semi-batch and batch system (b).

and ammonia caused to increase the standard deviation of particle size as shown in Figs. 2(b) and 3(b). In addition, there was an increase in particle size with increasing water concentration ($\text{H}_2\text{O}/\text{TEOS}$) and ammonia concentration. To minimize the particle size, the value of mole ratio ($=[\text{H}_2\text{O}]/[\text{TEOS}]$) and ammonia concentration must be decreased. Thus, the optimal conditions of mole ratio and NH_4OH concentration for obtaining the smallest mean particle size and the narrowest size distribution were 12 and 0.2 M, respectively.

Matsoukas and Gulari [12] reported that the effect of ammonia concentration is not only to promote hydrolysis, but also to promote the polymerization (condensation) rate, resulting in faster kinetics, and larger particle sizes. In many other studies, the same result was observed. However, they reported that the increase in water concentration leads to smaller particles. On the

contrary, large particle size was obtained in the higher water concentration regime in this work. We can explain this as follows. If a high water concentration is used, the nucleation rate is high, so a lot of small sub-particles are prepared within a short period. However, the hydrogen bond of silica sub-particles under the condition of a higher water concentration is stronger than that of a lower water concentration because of excess water in the former case. Therefore, sub-particles in the higher water concentration agglomerate with each other and grow into large particles.

3.2. Effect of Feed Rate and Reaction Temperature

Figure 4 shows the effect of feed rate (0.3–5.0 ml/min) on particle size and standard deviation at concentration of 0.5 M TEOS, 6.0 M H_2O , and 0.2 M NH_4OH .

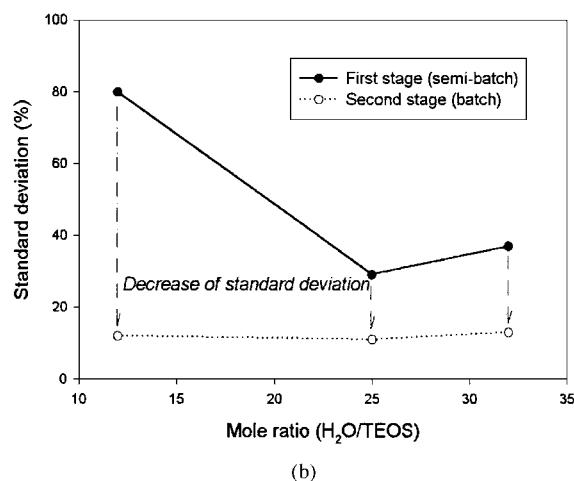
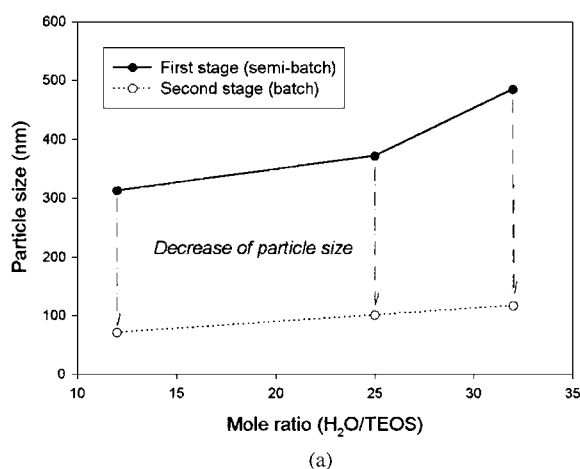


Figure 2. The effect of mole ratio ($H_2O/TEOS$) on particle size (a) and standard deviation (b).

After the second batch reaction was complete, all the particle sizes and standard deviations at the first stage decreased. In addition, as the feed rate increased, the particle size decreased (see Fig. 4(a)). However, the standard deviation at second stage (open symbols) did not vary with the feed rate of reactant as shown in Fig. 4(b). Thus, it was found that the feed rate for obtaining the smallest particle size was 5.0 ml/min.

Figure 5 shows the effect of reaction temperature on particle size and standard deviation. As shown in Fig. 5, all the particle sizes and standard deviations at the first stage (solid symbols) decreased after the second stage (open symbols) was complete, and the decrement of particle size and standard deviation increased at room temperature. In addition, as the reaction temperature

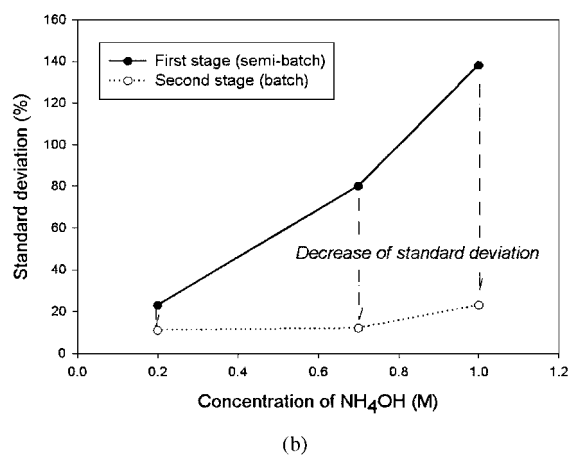
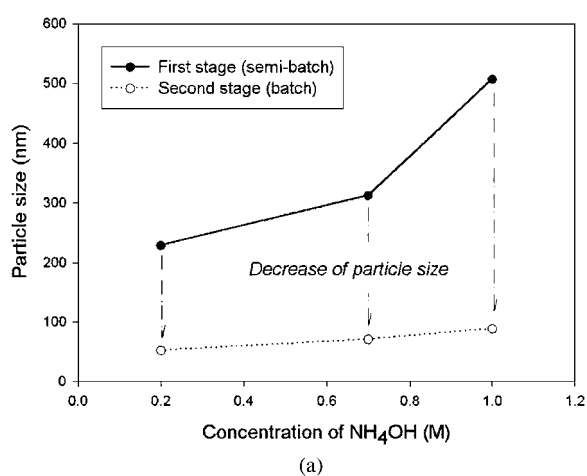
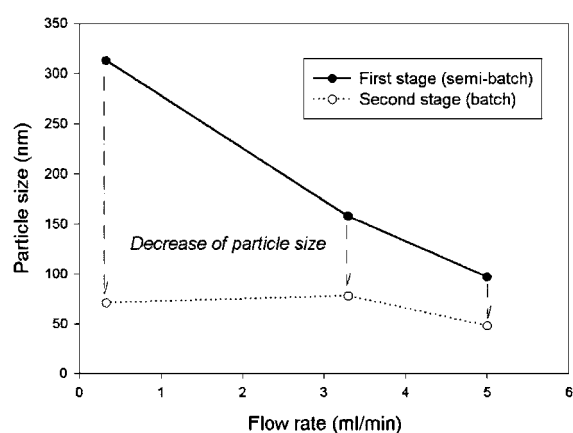
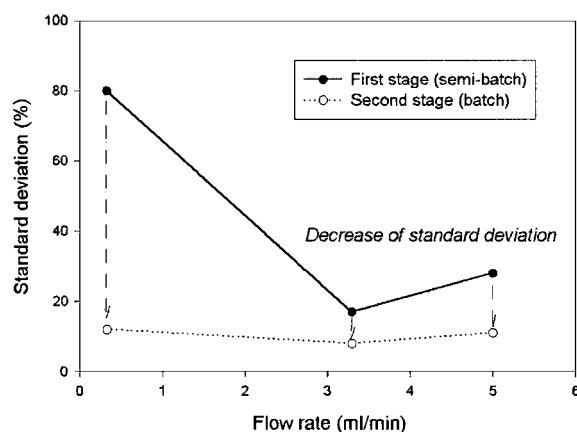


Figure 3. The effect of concentration of NH_4OH on particle size (a) and standard deviation (b).

increased, the particle size decreased. This tendency for size reduction with temperature can be explained by two ways [13]. Firstly, the equilibrium solubility (C_s) of $Si(OH)_4$ as an intermediate product obtained by the hydrolysis of TEOS increases due to the high reaction temperature. As a result, the particle size decreases because the growth of particles proceeds until the reaction stops due to equilibrium solubility (C_s) and the time for growing the particles is shortened by the increase of equilibrium solubility (C_s). Consequently, the growth period at a high reaction temperature is shorter than that at low temperature. Secondly, if reaction temperature goes up, the value of nucleation rate increases. Therefore, the high nucleation rate at elevated reaction temperature prohibits nuclei from growing into a large particle. And small particles are obtained at high reaction temperature.



(a)

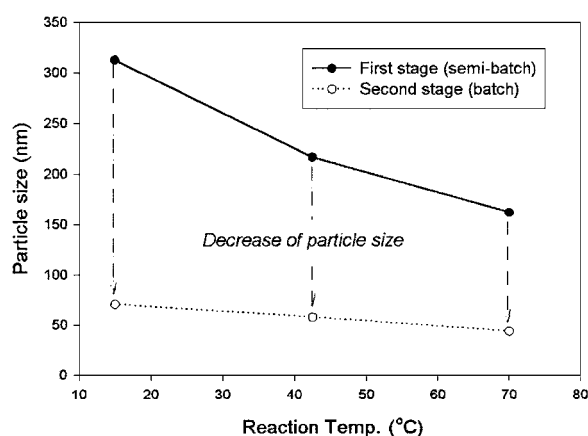


(b)

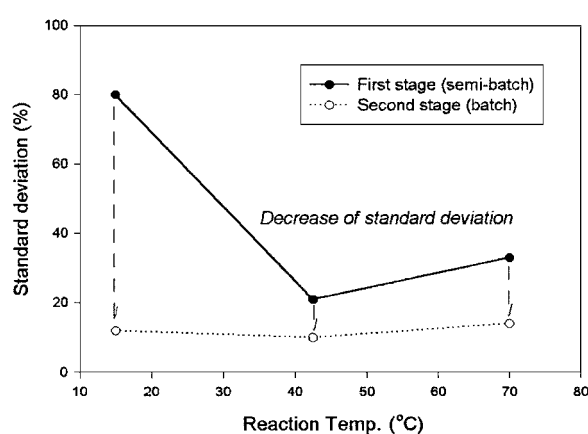
Figure 4. The effect of feed rate on particle size (a) and standard deviation (b).

3.3. Effectiveness of Two-Stage Mixed Method for Reducing the Particle Size

The effect of the mole ratio ($\text{H}_2\text{O}/\text{TEOS}$), ammonia concentration, feed rate, and reaction temperature on the particle size and standard deviation was shown in the above section. The operational parameters and optimal conditions for the synthesis of nanoparticles are summarized in Table 1. The change of the silica particle size prepared by the above optimal conditions (Table 1) with reaction time is presented in Fig. 6. At the completion stage of the initial semi-batch reaction, the particles had a mean diameter of 108 nm. When a batch reaction was continued to 120 min as a second step, the size of the silica particles decreased to 23 nm. Figures 7 and 8 show the SEM photos obtained from the each stage and final particle size distribution, respectively.



(a)



(b)

Figure 5. The effect of reaction temperature on particle size (a) and standard deviation (b).

This reduction of particle size by mixed method can be explained in LaMer and Dinegar's model [14]. They proposed the self-nucleation model of monodispersed particle production. There are three regimes in the generation of monodispersed particles for use as ceramic powders. The first period is induction time, during which the reaction slowly generates growth units of the solid. The concentration in solution builds up until

Table 1. Optimal experimental conditions for each parameter.

Parameters	Optimum
Mole ratio ($\text{H}_2\text{O}/\text{TEOS}$)	12
NH_4OH (M)	0.2
Feed rate (ml/min)	5.0
Reaction Temp. (°C)	42.5

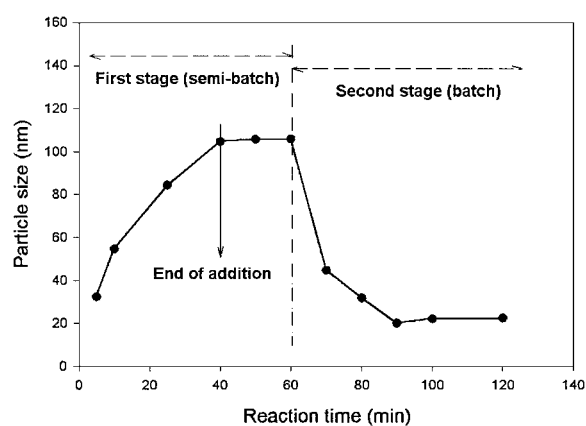


Figure 6. Change of the particle size with reaction time during 1st and 2nd stages (preparation conditions; TEOS: 0.5 M, H₂O: 6.0 M, NH₄OH: 0.2 M, feed rate: 5.0 ml/min, temperature: 42.5°C).

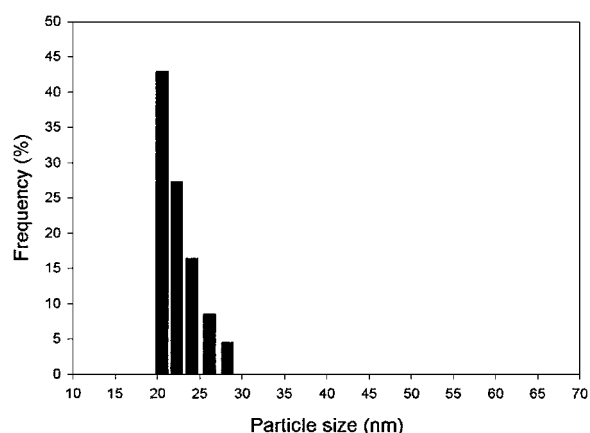
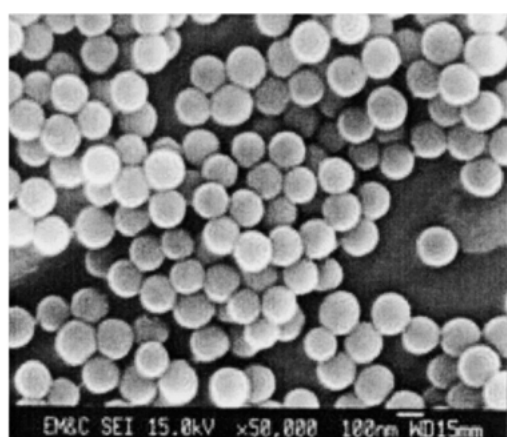
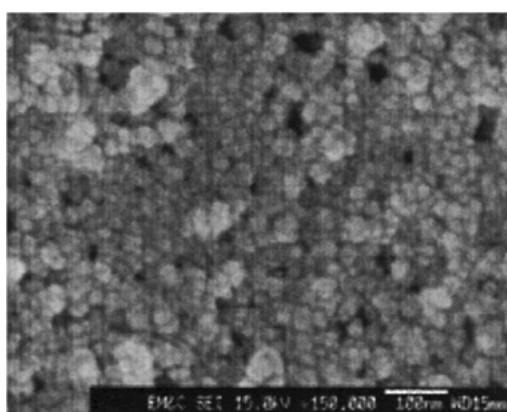


Figure 8. Final particle size distribution of SiO₂ particles prepared by optimum conditions.



(a)



(b)

Figure 7. SEM micrographs of SiO₂ particles prepared by optimum conditions. (a) After the first stage (semi-batch) reaction and (b) after the second stage (batch) reaction.

a minimum critical supersaturation (C_{\min}^*) is reached, when nucleation occurs. A relatively short nucleation period produces a narrow size distribution of nuclei and relieves the supersaturation to below the critical values, preventing further nucleation. After nucleation, growth proceeds until the reaction stops due to equilibrium solubility (C_s).

Figure 9 depicts the change of the solute concentration (Si(OH)₄) and particle morphology during the mixed semi-batch/batch system. There is a difference between a semi-batch system and a batch system, considering a LaMer and Dinegar's model. Using a semi-batch system, reactant solution A (TEOS and ethanol) is fed into the reactor containing reactant solution B (water, ethanol and ammonia) by a micro feed pump. Therefore, accumulation rate of growth units to a minimum critical supersaturation concentration (C_{\min}^*) is slower than that of a batch process. And the short

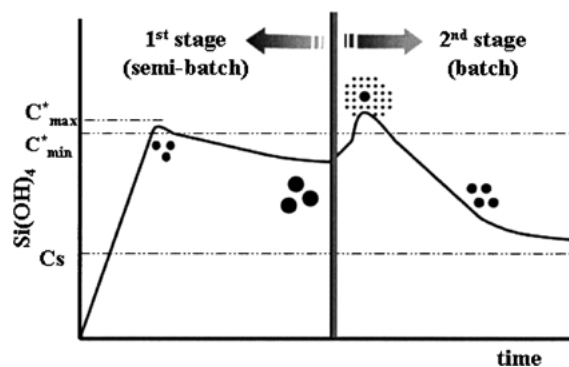


Figure 9. Change of the Si(OH)₄ concentration and particle morphology with reaction time during two-stage mixed method.

nucleation occurs because reactant A is not sufficiently supplied to keep the solute concentration above the minimum critical supersaturation (C_{\min}^*). Finally, the growth of particles takes place in semi-batch system for a long time. On the contrary, using a batch system, accumulation rate of growth units to a minimum critical supersaturation concentration (C_{\min}^*) is faster than that of a semi-batch system because reactant A (TEOS and ethanol) and B (water, ethanol and ammonia) is fed into the reactor instantaneously. Consequently, the reason for size reduction by mixed method is that the silica particles prepared by batch process are smaller than the particles obtained by the semi-batch process because the growth time of silica particles in the batch system is shorter than that of the semi-batch system. In addition, very small particles are generated by second batch reaction at a one time, resulting in the reduction of mean particle size.

4. Conclusions

1. Silica nanoparticles were prepared by the hydrolysis of TEOS using a mixed semi-batch/batch method. The particle size and standard deviation of silica nanoparticles were controlled by changing four parameters. Of all the parameters, the main parameters affecting the decrease of particle size were mole ratio ($\text{H}_2\text{O}/\text{TEOS}$) and ammonia concentration.
2. The particles prepared by using the two-stage (semi-batch/batch) method had a smaller mean particle size and narrower size distribution than those obtained from the single stage.
3. The optimum conditions obtained by the experimental results were as follows; (Mole ratio ($\text{H}_2\text{O}/\text{TEOS}$): 12, Concentration of NH_4OH (M): 0.2, Feed rate (ml/min): 5.0, Reaction temperature

($^{\circ}\text{C}$): 42.5). In conclusion, the smallest particle size (23 nm in diameter) of SiO_2 was obtained and the above two-stage method suggested a new way of probability for the synthesis of silica nanoparticles.

Nomenclature

C_{\min}^*	Concentration of minimum critical supersaturation for nucleation (mol/l)
C_{\max}^*	Concentration of maximum critical supersaturation for nucleation (mol/l)
C_s	Equilibrium solubility (mol/l)

References

1. J.G. Overbeek, *Adv. Colloid Interface Sci.* **15**, 251 (1982).
2. G.R. Wiese and T.W. Healy, *Trans. Faraday Soc.* **66**, 490 (1970).
3. K. Unger, *J. Chromatogr.* **61**, 359 (1986).
4. M.D. Sacks and T.Y. Tseng, *J. Am. Ceram. Soc.* **67**, 526 (1984).
5. G. Kolbe, *Das Komplexchemische Verhalten der Kieselsäure* (Dissertation, Jena, 1956).
6. W. Stober, A. Fink, and E. Bohn, *J. Colloid Interface Sci.* **26**, 62 (1968).
7. V.A. Blaaderen, V.J. Geest, and A.J. Vrij, *J. Colloid Interface Sci.* **154**, 481 (1992).
8. G.H. Bogush and C.F. Zukoski, *J. Colloid Interface Sci.* **142**, 1 (1991).
9. T. Matsoukas and E. Gulari, *J. Colloid Interface Sci.* **132**, 13 (1989).
10. H.S. Fogler, *Elements of Chemical Reaction Engineering: Rate Laws and Stoichiometry* (Prentice-Hall, Englewood Cliffs, NJ 1986), p. 59.
11. S.K. Park, K.D. Kim, and H.T. Kim, *J. Ind. Eng. Chem.* **6**, 365 (2000).
12. T. Matsoukas and E. Gulari, *J. Colloid Interface Sci.* **124**, 252 (1988).
13. K.D. Kim and H.T. Kim, *J. Ind. Eng. Chem.* **6**, 281 (2000).
14. V.K. Lamer and R.H. Dinegar, *J. Am. Chem. Soc.* **72**, 4847 (1950).