Journal of Ceramic Processing Research. Vol. 10, No. 4, pp. 553~558 (2009)

J O U R N A L O F
Ceramic Processing Research

Control of the size and morphology of nano-size silica particles using a sodium silicate solution

Sang-Wook Ui[a], Seung-Jae Lim[a], Sang-Hoon Lee[b] and Sung-Churl Choi[a,*]

[a]*Divison of Materials Science and Engineering, Hanyang University,Seoul 133-791, Republic of Korea*

[b]*Deparment of Environmental Engineering, Graduate School of Engineering, Hanyang University, Seoul 133-791, Republic of Korea*

In general nano-sized silica powders are synthesized using the Stber method. A system of chemical reactions has been developed which permits the controlled growth of spherical silica particles of a uniform size by the hydrolysis of alkyl silicates and subsequent condensation of silicic acid in alcoholic solutions. In this study nano silica powders were synthesized using a low cost sodium silicate instead of high cost alkoxide or organo-metallic compound. Cetyltrimethylammonium bromide (CTABr) was used as an additive to control the particle shape and produce a large surface area. The particle shape and specific surface area were controlled with various molar ratios of CTABr, ethyl acetate, DI water and water glass. The nano silica powders were characterized using BET(Brunauer, Emmett & Teller, specific surface area, powder pore size and distribution), and a scanning electron microscope.

Key words: Silica, powder, synthesis, sol-gel, surfactant, SiO_2, Sodium silicate solution.

Introduction

Silica, commonly named silicon oxide, is configured with four to six oxygen atoms and also comes in other forms. Recently the metal and oxide powder of the precursors have become useful materials in various fields because they have new physicochemical properties which do not appear in the corresponding bulk materials [1].

Propertis of the silica corpuscular powder is widely applied in the mechanical industry and as precise systems for chemical catalysts, ceramics, restriction, chromatography, pigments, electronic components, mechanical materials, photoelectricity elements and colloids. Applied fields for the silica corpuscular powder are expanding gradually because of the physicochemical merits of it.

Silica powder has demonstrated various properties according to its purity, shape, size and distribution and these have been investiqated.

Particle shape, size, and monodispersity were analyzed with an SEM, and the specific surface area, pore diameter and pore distribution were calculated from N_2 adsorption using the BET method.

Currently there are various methods to manufacture silica such as the gas-reaction method, precipitation, solvent elimination and a sol-gel method. Silica can be synthesized in a similar was to ceramic particles. The Sol-gel method has the merit of producing silica, by controlling the size and distribution at low temperatures. In this study water-glass was used as a precursor instead of expansive materials such as alkoxide or organometallic compounds. The effect of surfactant CTABr's density, reaction velocity and water-glass density were investiqated.

*Corresponding author:
Tel : +82-2-2220-0505
Fax: +82-2-2291-6767
E-mail: choi0505@hanyang.ac.kr

Experiments

Materials. Sodium silicate solution (SIGMA-ALDRICH contains ~14%NaOH ~27% SiO2), 1N-hydrocholric acid solution (DAEJUNG), hexadecyltrimethylammonium bromide (CTAB) 99%+, and Ethy acetate 99.5% (SAMCHUN) were purchased.

Synthesis procedures were divided into three different groups on the basis of the water glass.

Procedure 1 : Fig. 1 shows the general method to make porous silica using CTABr. A Sol-gel was used to synthesize silica powder and control the particle size with shape control. Fig. 2 shows the standard experimental process. In the first step, the synthesized precursors were a sodium silicate solution and HCl. The reaction mixture was prepared by pipetting water-glass at 0.05 ml/s into a glass beaker containing the water and HCl solution.

The solution was stirred for 20 hours and a gel formed. The gel was washed in a filter paper with distilled water or centrifuged to remove NaCl and other impurities. The gel was dried in a drying oven at 90 °C for 22 hours, microwaved for 30 minutes, and sieved to 20 μm.

Table 1 shows reaction condition.

Procedure 2 : Fig. 3 shows the second method of the spherical particle synthesis.

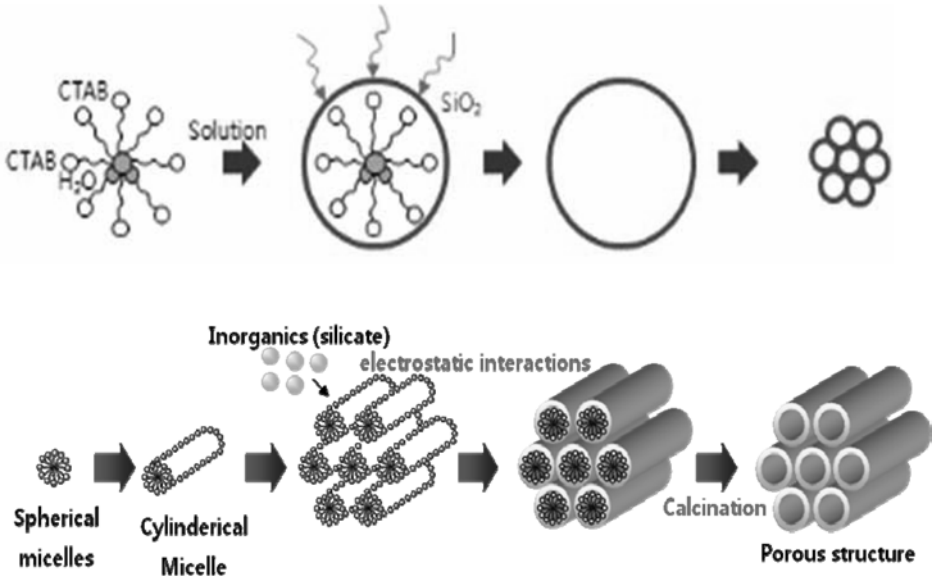

Fig. 1. The micelle formation mechanism.

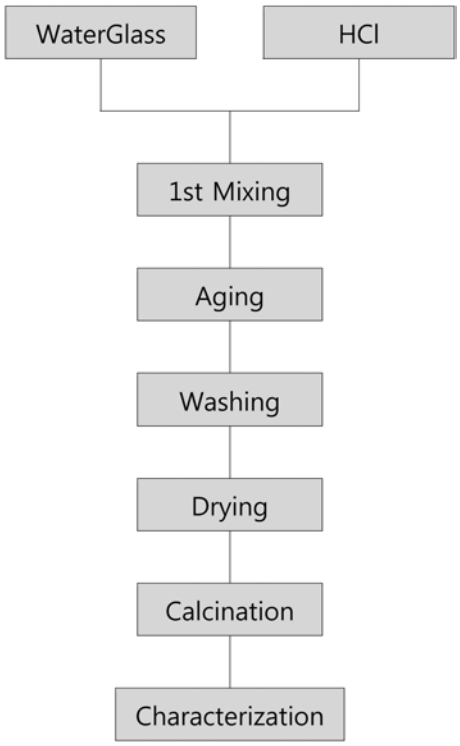

Fig. 2. Schematic diagram of synthesis (1).

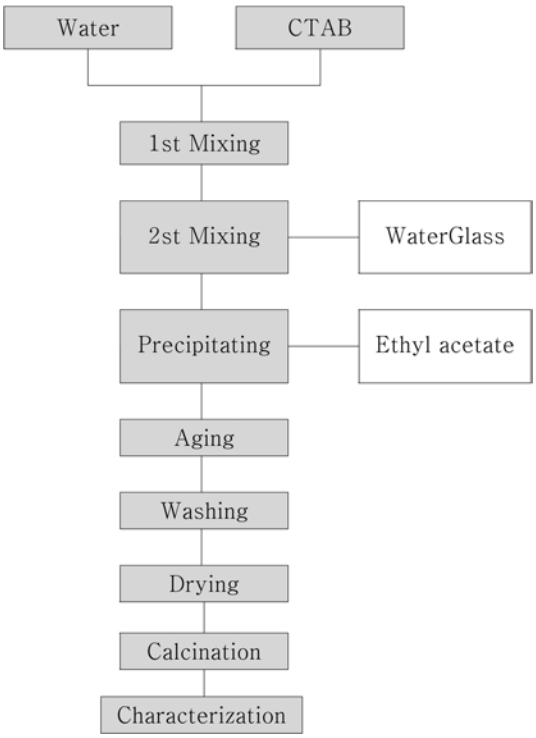

Fig. 3. Schematic diagram of synthesis (2).

Table 1 Reaction condition (1)

Sample	Water	WaterGlass	HCl
A	20	2.1	5

In a typical synthesis, the reaction mixture for the synthesis of water glass was prepared in a glass vessel. CTABr and sodium silicate solution were dissolved in distilled water. Ethyl acetate (99.5% Samchun) was added and, the mixture was stirred with a magnetic bar at 400 rpm. After 30 minutes, a precipitate began to form and the mixture was incubated at ambient temperature for 24 hours. In this process, the separation of solid particles from the solution occurred by sedimentation, which enabled removal of the supernatant. The suspension of the solid product was transferred into a polypropylene bottle and aged at 90 °C for 50 h. The shortening of this step led to a slight deterioration of the structural parameters.

The aged solids were recovered by filtration of the warm reaction mixture, and they were washed extensively with distilled water and ethanol, and dried at ambient

temperature. The CTABr was removed by calcination at 600 °C for 20 h in flowing air.

Table 2 shows reaction condition.

Procedure 3 : Fig. 4 shows the second method of the spherical particle synthesis. Silica particles were synthesized by the sol-gel method under the conditions specified in Table. 3.

Specifically, 1N HCl and CTAB were placed into 20 mol water and stirred at 400 rpm with a magnetic bar. When the pH was less than one, 1 M sodium silicate solution was added slowly to the solution and stirred for 2-3 minutes with a pipet. At this step, the pH increased rapidly as indicated in Fig 5.

The solution was aged for 90 minutes after stirring and the precipitated reactant was washed by filtering with DI-water to remove NaCl The precipitate was dried at 50 °C, which is very important for the sol-gel process because silica particles may aggregate if not dried slowly enough. submicrometer pores in silica particles in the solution generated capillary-force by drying solution. Therefore slow drying was performed in this study. Calcination was performed at 600 °C for 10 hours and sampled.

Table 2 Reaction condition (2)

Sample	Water	CTABr	Ethyl acetate	WaterGlass	HCl
B	20	0.025	1.33	2.1	5

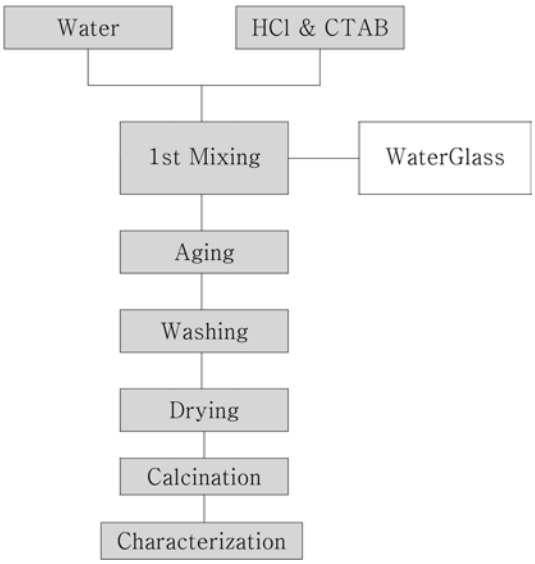

Fig. 4. Schematic diagram of synthesis (3).

Table 3 Reaction conditions (3)

Sample	Water	CTABr	WaterGlass	HCl
C	20	0.025	1	1.5
D	20	-	1	2.7
E	20	0.028	1	1.5
F	20	0.014	1	2.7

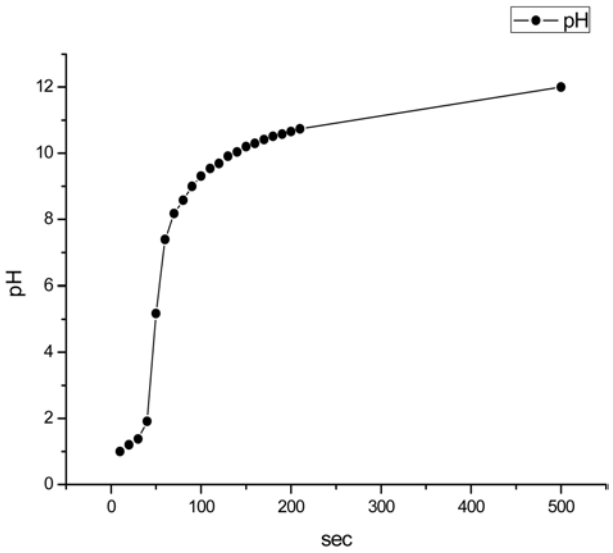

Fig. 5. Transformation of the reaction velocity.

Results and Discussion

According to the scheme of this study, cubic and spherical silica particles were manufactured using water glass with the hydrolysis of silicon alkoxide. The mechanisms of the condensation reactions are the following [2-4].

Hydrolysis reaction : $\equiv Si\text{-}OC_2H_5 + H_2O \leftrightarrow \equiv Si\text{-}OH + C_2H_5OH$ (1)

Alcohol polymerization : $\equiv Si\text{-}OC_2H_5 + \equiv Si\text{-}OH \leftrightarrow \equiv Si\text{-}O\text{-}Si\equiv + C_2H_5OH$ (2)

Water polymerization : $\equiv Si\text{-}OH + Si\text{-}OH \leftrightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O$ (3)

Total reaction : $Si(OC_2H_5) + 2H_2O \leftrightarrow SiO_2\downarrow + 4C_2H_5OH$ (4)

The synthesis of metallic salts with water-glass and HCl resulted in particles with NaCl. The NaCl can be removed by centrifugation or filtering and drying in a drying oven or microwave [5].

Reaction velocity

Fig. 5 show the transformation of the reaction velocity. We can know that almost reaction already made it before 100 seconds.

Mophology

Fig. 6 illustrates the scanning electron microscope_ (SEM) images of silica particles from different manufacturing methods after washing and drying.

The synthesized silica was manufactured in 20 to 100 nm cube(Fig. 6A)[6-8].

We were able to identify relative uniformity of particles with 20-30 nm diameters(Fig. 6C). Theoretically, a micelle forms with a cylinderical shape using CTABr, however this is difficult. As demonstrated by SEM, we were able to produce rod-like silica with 20 nm width and 70 nm length(Fig. 6B) [9]. A silica monolayer was observed with an approximate thickness of 20 nm(E-1,E-2). Larger particles were observed

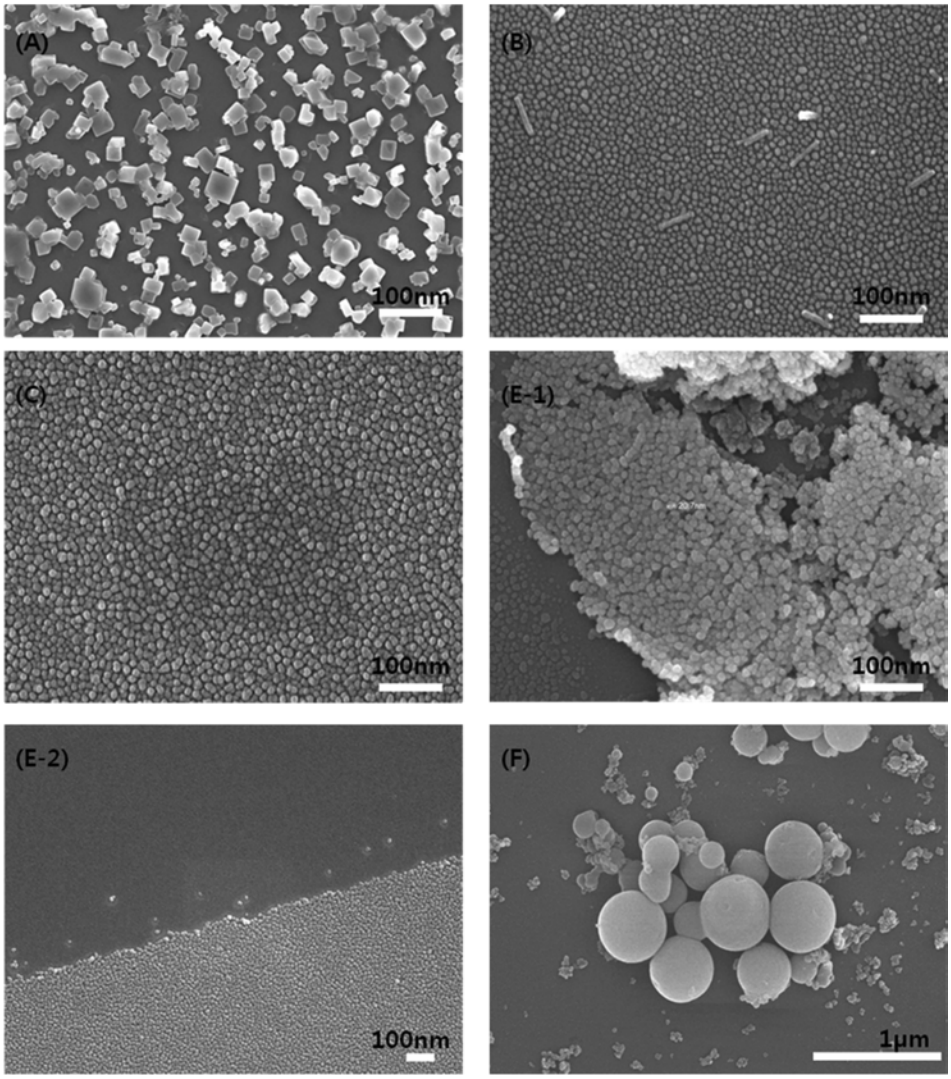

Fig. 6. SEM images of (A) cubic,- (B) spherical and rod-like, (C, E-1, E-2) spherical and (F) irregular spherical SiO_2 shapes.

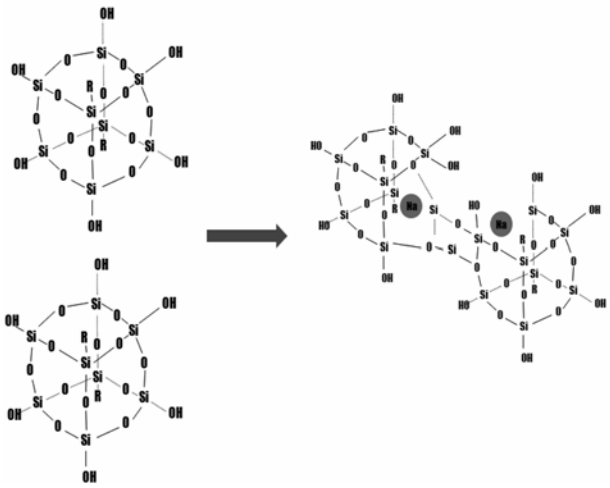

Fig. 7 Necking phenomenon mechanism of silica by Na+

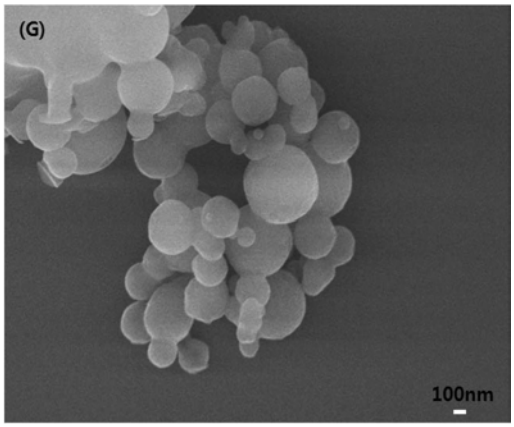

Fig. 8. SEM image of necking silica particles.

at a controlled concentration and necked particles were generated more with TEOS because the NaOH in the water glass obstructed the production of homogeneous particles.

Morphological control was achieved through deposition of self-assembled spherical and rodlike silicate micelles. The formation of the mesoporous silica particle began with the nucleation of the silica surfactant interactions [4].

Fig. 7, 8 show necking phenomenon mechanism of silica.

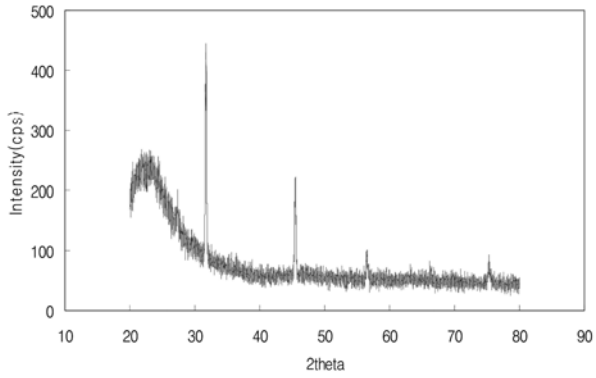

Fig. 9. XRD data of NaCl confirmed before washing.

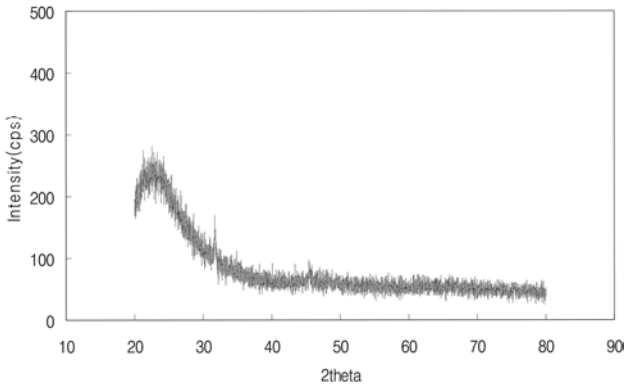

Fig. 10. XRD data of NaCl removed after washing.

XRD

Filtering to remove NaCl was more effective than using a centrifugal separator or filtration, as shown in the XRD spectra of Figs. 9 and 10 with different molarities.

With a lower density of water-glass, the amount of HCl acid decreased, the surface area was wider and the homogeneity of the particles increased.

Surface Area

A linear increase of the absorbed volume at low pressures was followed by a steep increase in nitrogen uptake at a relative pressure of $0.6 < p/p_0 < 0.8$ for (Fig. 11A) which was due to capillary condensation inside the mesopores [10-12].

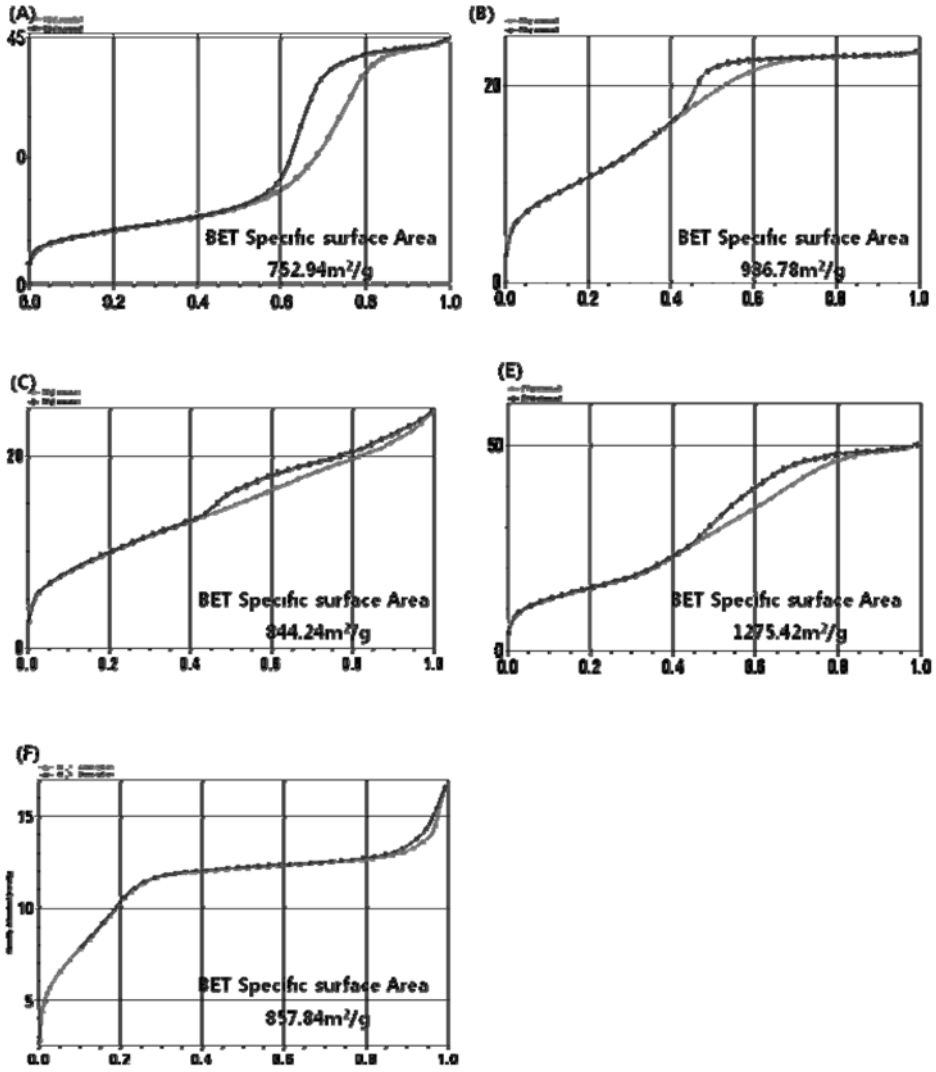

Fig. 11. Specific surface area of silica by BET.

Table 4 Reaction conditions (1,2,3)

Sample	Water	Waterglass	CTABr	HCl	Ethyl acetate	Gelation	Morphology	Surface area (m^2/g)	Particle size (nm)
A	-	2.1	-	5	-	O	cubic	752.94	20~100
B	20	2.1	0.025	5	1.33	O	rod circle	936.78	Width 20 Length 70
C	20	1	0.025	1.5	-	O	circle	844.24	20~30
D	20	1	-	2.7	-	X	-	-	-
E	20	1	0.028	1.5	-	O	circle	1275.42	20~30
F	20	1	0.014	2.7	-	O	circle	857.84	100~600

Conclusions

Silica particles were synthesized by a sol-gel method and the effective density, reaction time and R(H_2O/surfactant) control were obtained for the synthesis. The following items were observed. Table. 4 shows condensational total reaction conditions.

1. In the event that the molar ratio of HCl and H_2O increased the particle size decreased.
2. Nano silica powder with a high surface area was produced using a cationic surfactant CTABr.
3. The nano-sized silica powders with very high specific surface area and low density were obtained using a low price water glass solution as a silica source.
4. This study investigated the silica particle size by SEM and the specific surface area and pore size distribution were tested using BET.

Acknowledgements

This research was supported by the Hanyang Fusion Materials Program funded by the Ministry of Education, Science and Technology, Korea. This study was also supported by the Korea Science and Engineering Foundation under grant No. R01-2008-000-12298-0.

References

1. T. Jesionowski, *Synthesis and characterization of spherical silica precipitated via emulsion route.* Journal of Materials Processing Technology, 203[1-3] (2008): p. 121-128.
2. A. Arkhireeva and J.N. Hay, *Synthesis of sub-200 nm silsesquioxane particles using a modified Stöber sol-gel route.* Journal of Materials Chemistry,. 13[12] (2003): p. 3122-3127.
3. A. Berggren and A.E.C. Palmqvist, *Particle size control of colloidal suspensions of mesostructured silica.* Journal of Physical Chemistry C,. 112[3] (2008): p. 732-737.
4. Q. Cai *et al.*, *Dilute solution routes to various controllable morphologies of MCM-41 silica with a basic medium.* Chemistry of Materials,. 13[2] (2001): p. 258-263.
5. S.H. Kim, B.Y.H. Liu and M.R. Zachariah, *Ultrahigh surface area nanoporous silica particles via an aero-sol-gel process.* Langmuir,. 20[7] (2004): p. 2523-2526.
6. Y.S. Han *et al.*, *Synthesis of cubic type hollow silica particles.* Materials Letters.
7. Y.K. Hwang *et al.*, *Microwave synthesis of cubic mesoporous silica SBA-16.* Microporous and Mesoporous Materials,. 68[1-3] (2004): p. 21-27.
8. W. Tanglumlert *et al.*, *Structural aspects of SBA-1 cubic mesoporous silica synthesized via a sol-gel process using a silatrane precursor.* Journal of the American Ceramic Society,. 90[12] (2007): p. 3992-3997.
9. S. Han *et al.*, *Synthesis of rod-like mesoporous silica with hexagonal appearance using sodium silicate as precursor.* Colloid and Polymer Science,. 282[7] (2004): p. 761-765.
10. K. Kosuge *et al.*, *Morphological Control of Rod- and Fiberlike SBA-15 Type Mesoporous Silica Using Water-Soluble Sodium Silicate.* Chemistry of Materials,. 16[5] (2004) p. 899-905.
11. X. Pang and F. Tang, *Morphological control of mesoporous materials using inexpensive silica sources.* Microporous and Mesoporous Materials,. 85[1-2] (2005): p. 1-6.
12. J.X. Wang *et al.*, *Study on a novel template synthesis method for hollow silica nanospheres.* Acta Chimica Sinica,. 63[14] (2005): p. 1298-1302.