GAS PHASE SYNTHESIS OF FINE SILICA PARTICLES IN A TUBE REACTOR

JIŘÍ SMOLÍK, PAVEL MORAVEC

Institute of Chemical Process Fundamentals of the Czech Academy of Sciences,
Rozvojová 135, 165 02 Prague

Received June 18, 1996.

Silica particles were synthesised by oxidation of tetraethylorthosilicate (TEOS) vapour in tube furnace reactors of 27 and 37 mm inner diameter. Particles production was studied as a function of reactor diameter, residence time of the reaction mixture in the reactor, TEOS concentration, geometric mean diameter and geometric standard deviation of generated particles. Smaller and more monodisperse particles were prepared in the larger reactor. Particle size and dispersity increases with temperature and TEOS concentration whereas number concentration is quite insensitive to the experimental conditions investigated.

INTRODUCTION

Silica particles are currently produced by flame-hydrolysis of silicon tetrachloride vapour [1]. This process has been used for preparation of preforms for optical wave guides [2] and on an industrial scale for the production of fused silica [1, 3]. An alternate route for the synthesis of fine silica particles uses tetraethylorthosilicate (TEOS) as a precursor. The previous investigations include high temperature decomposition of TEOS [4], silica particle generation during SiO_2 film formation by TEOS plasma-enhanced Chemical Vapour Deposition (CVD) [5], and atmospheric-pressure CVD using ozone [6].

At our laboratory the study of the production of silica particles by thermal decomposition of TEOS vapour in the presence of oxygen was performed [7]. The study showed that particle generation is greatly influenced among other factors by the reactor geometry. In this work further study of this problem is performed using tube reactors of various diameters. The influences of temperature, TEOS vapour concentration and residence time were also investigated.

EXPERIMENTAL PART

The experiments were carried out using the apparatus shown schematically in figure 1. The air, supplied from a compressor, passed through a coalescing filter for removal of the rest of the oil aerosol, a pressure regulator, a molecular sieve packed dryer and a highly efficient filter that removed any fine particles. After that it was divided into three streams. The flow rates were controlled by electronic mass flowmeters. The first stream was saturated by TEOS vapours in a saturator at a temperature of 20 °C controlled by a thermostat. Then it was diluted by a supplementary stream of air to ensure the required TEOS concentration and flow rate at the reactor inlet. The reactors used were glass tubes 55 cm long with 27 and 37 mm inner diameter (i.d.), situated inside an electrically heated furnace. Reaction products were mixed with additional stream of air in the diluter closely connected to the reactor outlet to decrease their temperature and also particle number concentration to the level appropriate for particle size distribution measurement. The sample of diluted aerosol was monitored by TSI model 3932 Differential Mobility Particle Sizing (DMPS) system, consisting of TSI model 3071 Electrostatic Classifier (EC), and TSI model 3022 Condensation Particle Counter (CPC). Samples of particles were also

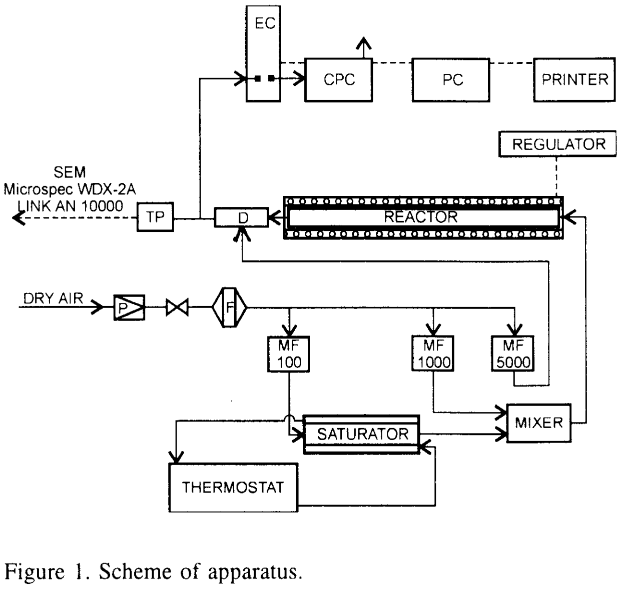

Figure 1. Scheme of apparatus.
D - diluter; F - filter; MF - mass flowmeter; TP - thermoprecipitator.

collected for SEM (Scanning Electron Microscopy - CamScan 4DV) and chemical analysis using hot wire plate thermoprecipitator. Chemical analysis was performed by Energy Dispersive X-Ray Detector (LINK AN 10000) and Wavelength Dispersive Spectrometer (Microspec WDX-2A).

In presence of oxygen the thermal decomposition of TEOS takes place in the reactor according to the reaction [8]:

$$Si(OC_2H_5)_4 + 12O_2 \rightarrow SiO_2 + 8CO_2 + 10H_2O \quad . \qquad (1)$$

Table 1. Range of experimental conditions.

	reactor 27 mm	reactor 37 mm
residence time (s)	7.7 - 42.2	8.9 - 31.4
temperature (°C)	500	450 - 520
c_{TEOS} (mol l^{-1})	2.3×10^{-6}	2.3×10^{-6} - 9.3×10^{-6}

Particles generation was studied as a function of temperature, TEOS concentration, residence time of the reaction mixture in the reactor, and reactor geometry. The range of experimental conditions is shown in table 1.

RESULTS

The synthesised particles were white and spherical in shape. An analysis on Energy Dispersive X-Ray Detector and Wavelength Dispersive Spectrometer showed that it is SiO_2. A SEM photo of the sample of particles is shown in figure 2.

The influence of reactor geometry and residence time

In the first run of experiments we investigated the effect of reactor geometry. The experiments were carried out using two reactors with 27 and 37 mm i.d. (6.75 and 9.25 mm volume to surface ratio) for temperature 500 °C and TEOS concentration 2.3×10^{-6} mol l^{-1}.

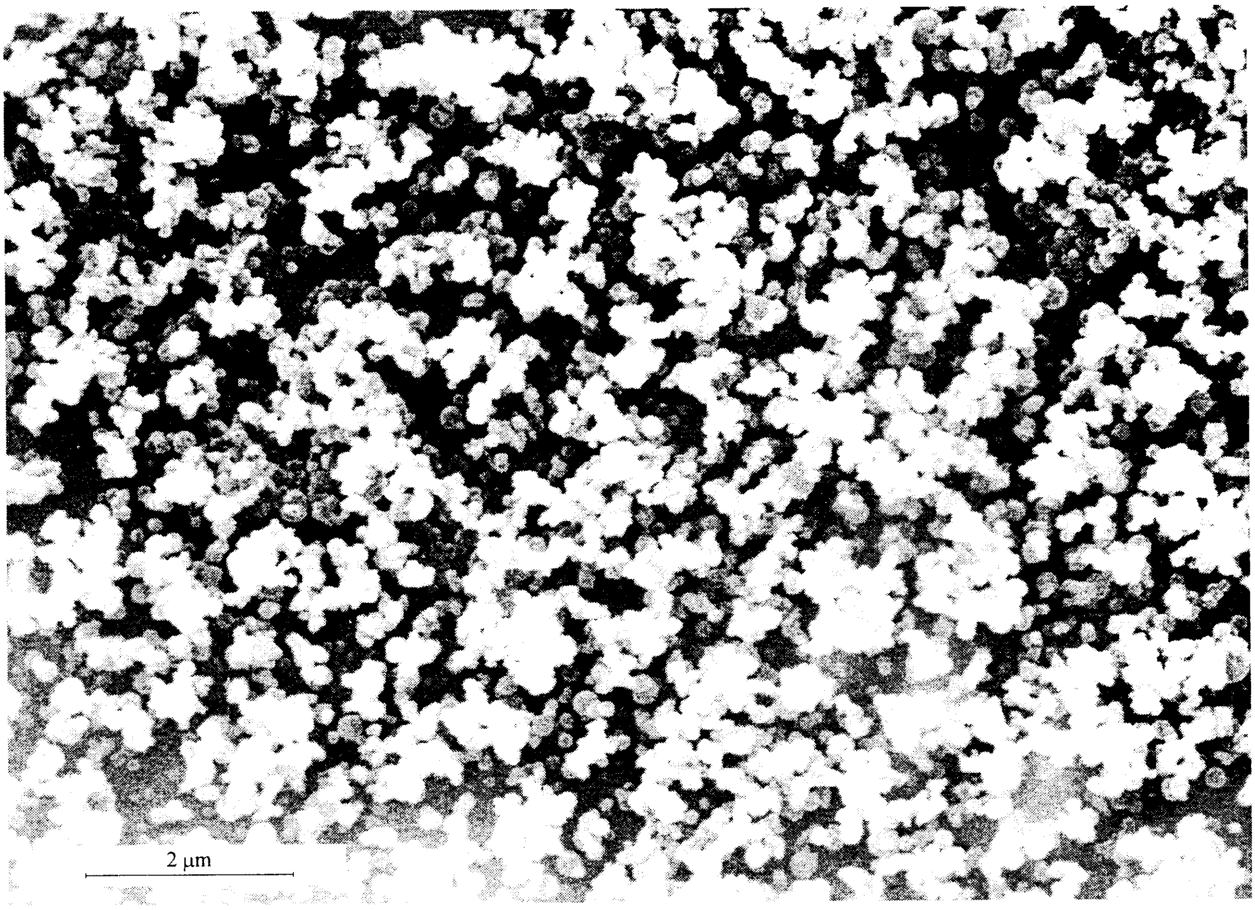

Figure 2. SEM photo of particles generated at reactor 27 mm i.d. T = 500 °C, TEOS concentration 3.9×10^{-6} mol l^{-1} and residence time 10.3 seconds.

Number concentrations (N_t), geometric mean diameters (GMD) and geometric standard deviations (GSD) of the particles generated in these experiments as a function of residence time, are shown in figures 3 - 5. Particles generated in both reactors at higher flow rates of reaction mixture (residence time less then 11 seconds for reactor 27 mm i.d. and less then 15 seconds for reactor 37 mm i.d.) were monodisperse (GSD less than 1.4). At lower flow rates (residence time longer than 15 seconds for reactor 27 mm i.d. and longer than 16 seconds for reactor 37 mm i.d.) size distributions of generated particles were bimodal. If we compare results from both reactors smaller and more uniform particles were produced in the larger reactor. This effect can be caused by competitive CVD process on the wall of the reactor that decreases the TEOS concentration in the bulk flow. It would cause higher nonuniformities in TEOS concentration in the smaller reactor that can results in more polydispersed product. Dispersity can be also influenced by diffusive deposition of the aerosol particles on the reactor surface and reentrainment of bigger particles in the form of dendrites from the reactor wall. These effects would be again more important, especially for residence times shorter than 15 seconds, in the smaller reactor [6].

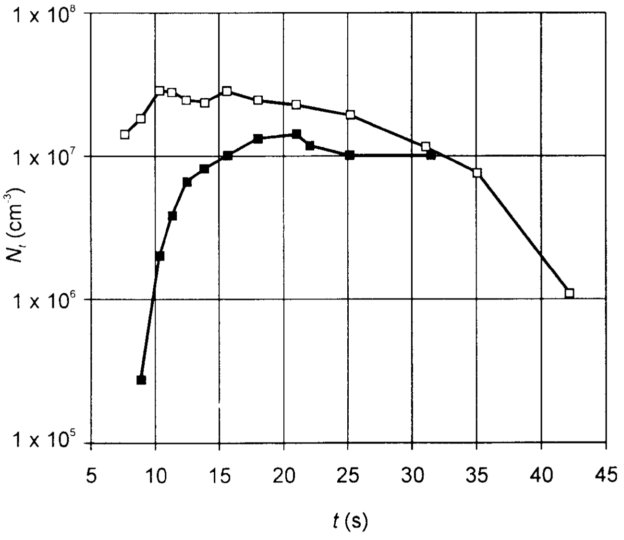

Figure 3. Number concentration vs. residence time. T = 500°C, TEOS concentration 2.3×10^{-6} mol l^{-1}.
☐ – r = 27 mm, ■ – r = 37 mm

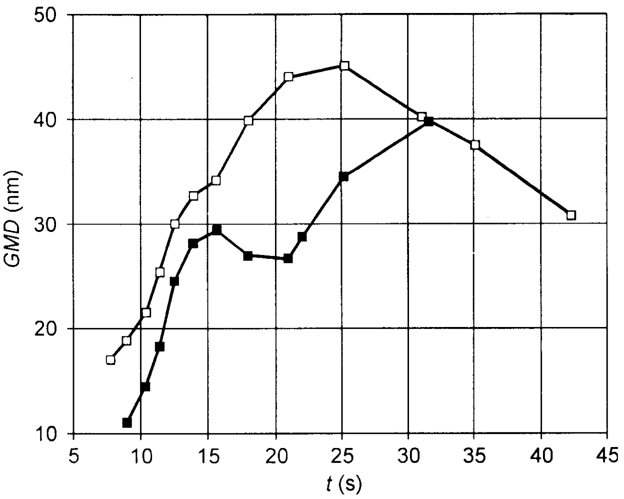

Figure 4. Geometric mean diameter vs. residence time. T = 500°C, TEOS concentration 2.3×10^{-6} mol l^{-1}.
☐ – r = 27 mm, ■ – r = 37 mm

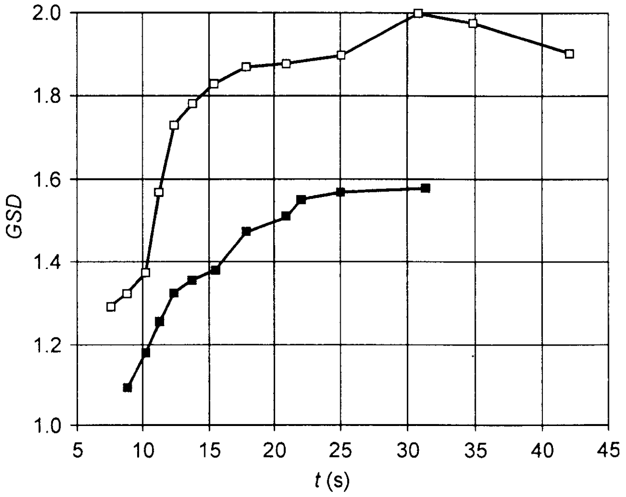

Figure 5. Geometric standard deviation vs. residence time. T = 500°C, TEOS concentration 2.3×10^{-6} mol l^{-1}.
☐ – r = 27 mm, ■ – r = 37 mm

The lower particle number concentrations observed in the larger reactor were probably caused by insufficient cooling of reaction mixture at the outlet of the reactor that resulted in thermophoretic deposition of particles on the wall of the diluter. This effect was more profound at higher flow rates (shorter residence times) at which some white deposit on diluter wall was found.

The influence of temperature and TEOS concentration

The effect of temperature and TEOS concentration on particle production was investigated in the reactor 37 mm i.d. The experiments were carried out at residence time 21 s for temperature range 450-520 °C and TEOS concentrations ranging from 2.3×10^{-6} to $9.3 \times$ $\times 10^{-6}$ mol l^{-1}. Before the experiments we measured by thermocouple axial profiles of temperature in the reactor for different flow rates. Typical profiles of temperature are shown in figure 6. In our experiments the temperature was measured in the middle of axial coordinate of the reactor. The results of experiments are shown in figure 7 - 9. The number concentrations of generated particles were quite insensitive to the reaction conditions used (figure 7) but the size of particles increased both with temperature and TEOS concentration (figure 8). With increasing temperature and TEOS concentration more polydispersed product was obtained, as can be seen in figure 9.

Fitting the experimental data the following relationship that describes the variation of GMD with temperature and TEOS concentration was found

$$\mathrm{GMD} = -229.9 + 0.490T + 0.589.10^{7}c_{\mathrm{TEOS}} \ , \qquad (2)$$

where units in nm, °C and mol l^{-1} are used. The validity of the equation (2) is limited only to investigated experimental conditions, see table 1. As can be seen in figure 10, 84 % of correlated values differ from experimental data less than 10 %.

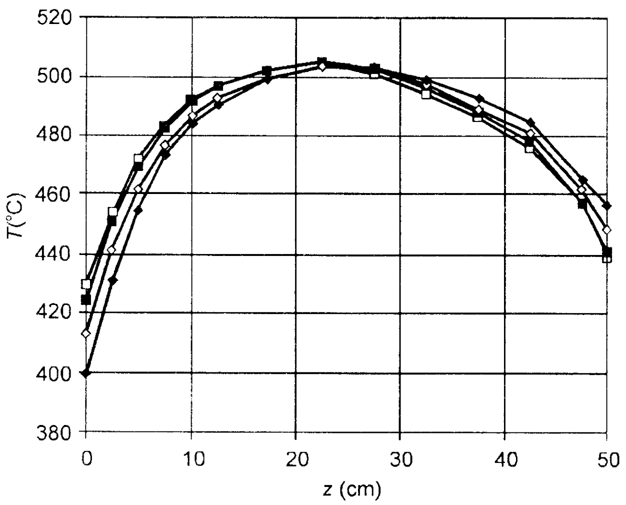

Figure 6. Axial temperature profiles in tube reactor for various flow rates of reaction mixture.
□ – Q = 0 ml min^{-1}, ■ – Q = 100 ml min^{-1},
◊ – Q = 400 ml min^{-1}, ♦ – Q = 700 ml min^{-1}

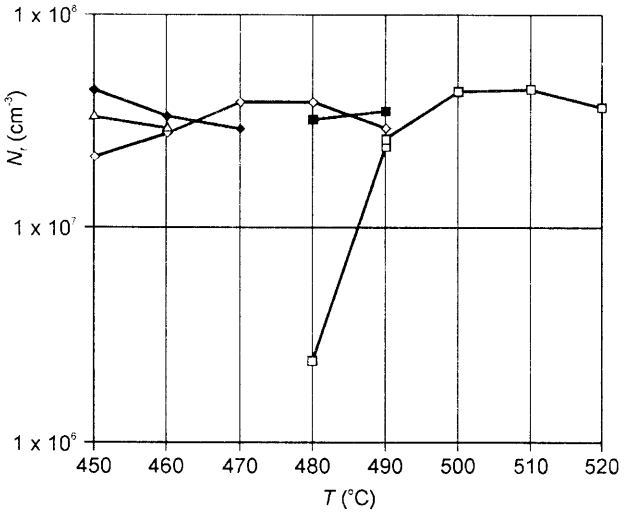

Figure 7. Number concentration vs. temperature for various TEOS concentrations (mol l^{-1}).
reactor 37 mm, □ – $c = 2.3 \times 10^{-6}$, ■ – $c = 3.5 \times 10^{-6}$,
◊ – $c = 4.7 \times 10^{-6}$, ♦ – $c = 7.0 \times 10^{-6}$, Δ – $c = 9.3 \times 10^{-6}$

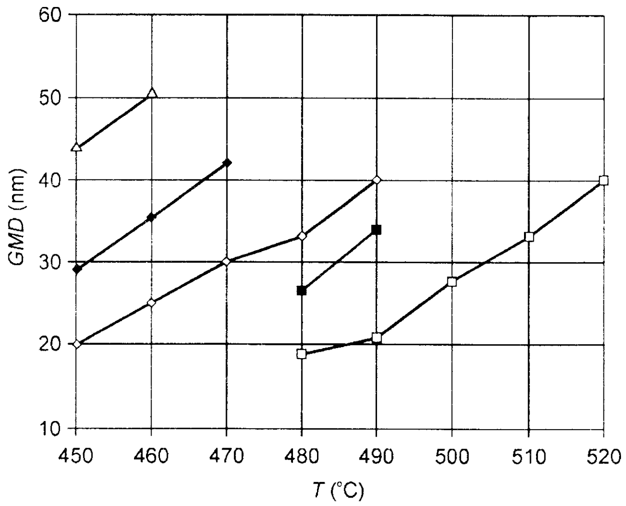

Figure 8. Geometric mean diameter vs. temperature for various TEOS concentrations (mol l^{-1}).
reactor 37 mm, □ – $c = 2.3 \times 10^{-6}$, ■ – $c = 3.5 \times 10^{-6}$,
◊ – $c = 4.7 \times 10^{-6}$, ♦ – $c = 7.0 \times 10^{-6}$, Δ – $c = 9.3 \times 10^{-6}$

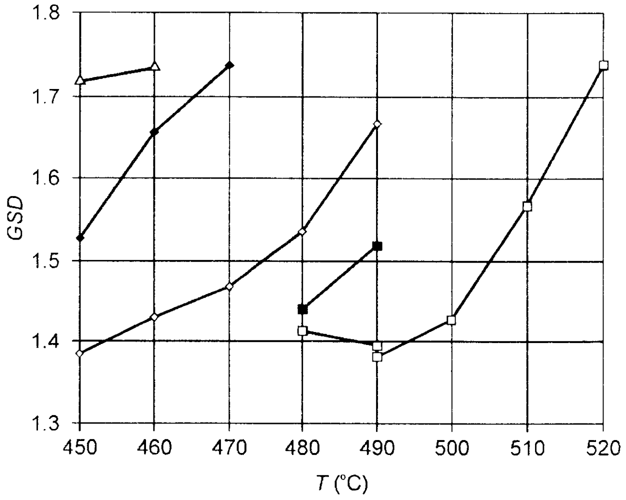

Figure 9. Geometric standard deviation vs. temperature for various TEOS concentrations (mol l^{-1}).
reactor 37 mm, □ – $c = 2.3 \times 10^{-6}$, ■ – $c = 3.5 \times 10^{-6}$,
◊ – $c = 4.7 \times 10^{-6}$, ♦ – $c = 7.0 \times 10^{-6}$, Δ – $c = 9.3 \times 10^{-6}$

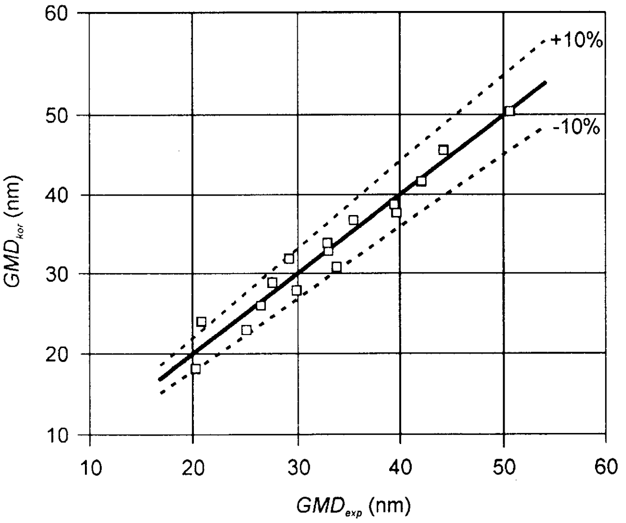

Figure 10. Correlated vs. experimental values of geometric mean diameter in dependence on temperature and TEOS concentration.

CONCLUSION

Ultrafine silica particle production by oxidation of TEOS vapour in tube flow reactor was investigated as a function of reactor geometry, residence time of reaction mixture, temperature and TEOS concentration. The experimental conditions for monodisperse particle synthesis were found. The size of the particles can be controlled by residence time in the reactor, temperature and concentration of TEOS vapour. It is also influenced by the reactor diameter.

Acknowledgement

This work was supported by Academy of Sciencies of the Czech Rrepublic, Project no. 472 105. SEM and X-Ray analyses were performed by Dr. Blahoslav Kolman from the Institute of Plasma Physics.

References

1. Kirk-Othmer: *Encyclopedia of Chemical Technology*, 2nd ed., Vol. 18, p. 64, John Wiley & Sons, Inc., New York, London, Sydney and Toronto 1969.
2. Kašík I., Matějec V.: J. Aerosol Sci. *26*, 399 (1995).
3. Gurav A., Kodas T., Pluym T., Xiong Y.: Aerosol Sci. Technol. *19*, 411 (1993).
4. Okuyama K., Kousaka Y., Tohge N., Yamamoto S., Wu J. J., Flagan R. C., Seinfeld J. H.: AIChE J. *32*, 2010 (1986).
5. Wu J. J., Tinker M. T., Miller R. J.: Proc. Electrochem. Soc. *91*, 347 (1991).
6. Okuyama K.: Proc. Trends in Aerosol Research III (Edited by A. Schmidt-Ott), p. 34, Sonderforschungbereich 209, Universität Duisburg 1993.
7. Smolík J., Moravec P.: J. Mater. Sci. Lett. *14*, 387 (1995).
8. Boyd I. W.: Proc. Thin Films and Microstr., p. 212-213, Springer Verlag, Berlin 1987.

Submitted in English by the authors.

PŘÍPRAVA NANOČÁSTIC SiO_2 V TRUBKOVÉM REAKTORU CVD PROCESEM

JIŘÍ SMOLÍK, PAVEL MORAVEC

Ústav chemických procesů AV ČR,
Rozvojová 135, 165 02 Praha 6-Suchdol

Zabývali jsme se přípravou ultrajemných částic SiO_2 tepelným rozkladem par tetraethylorthosilikátu (TEOS) za přítomnosti kyslíku v reakční směsi. Produkce částic byla studována v trubkovém reaktoru v závislosti na průměru reaktoru, zdržné době reakční směsi, koncentraci TEOS a na teplotě. Proces byl charakterizován koncentrací generovaných částic a distribucí jejich velikostí, t.j. středním geometrickým průměrem (SGP) a střední geometrickou odchylkou (SGO). Byly nalezeny experimentální podmínky vhodné pro přípravu monodisperzních částic (SGO < 1.4, SGP < 30 nm). Menší a monodisperznější částice byly připraveny v reaktoru o průměru 37 mm. Se zvyšující se teplotou a koncentrací TEOS roste velikost a disperzita částic, zatímco koncentrace generovaných částic se ve zkoumaném rozmezí experimentálních podmínek výrazně nemění.