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Synthesis of Monodispersed Silica Powders II. Controlled Growth Reaction and Continuous Production Process

Herbert Giesche

New York State College of Ceramics at Alfred University, School of Ceramic Engineering and Science,
2 Pine Street, Alfred, New York 14802–1296, USA

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Abstract

The present paper will describe the preparation of monodispersed silica particles by a controlled growth process. This procedure has several advantages compared with the original Stöber (batch) process. A simple calculation allows seeds of a given size to be grown exactly to a pre-set final particle size. Spherical and exceptional monodispersed particles of up to 3·6 μm in diameter and a very high (particle) mass fraction of up to 10 vol.% silica could be prepared by this process. Moreover, a simple tube reactor is shown, which allows those particles to be produced on a continuous basis.

Im Folgenden wird ein kontrollierter Wachstumsprozeß beschrieben, der verschiedene Vorzüge gegenüber dem ursprünglichen Batch-Prozeß von Stöber besitzt. Eine einfache Berechnung erlaubt es, eine vorgegebene Partikelgröße exakt herzustellen. Kugelförmige und außerordentlich einheitliche Partikel von bis zu 3·6 μm Durchmesser und sehr hohen Feststoffkonzentrationen von bis zu 10 vol.% SiO$_2$ konnten hergestellt werden. Ferner wird ein einfacher Rohrreaktor vorgestellt, der die kontinuierliche Synthese solcher Pulver erlaubt.

Le présent article décrit la préparation de particules de silice monodispersées par un procédé de croissance contrôlée. Cette dernière méthode présente plusieurs avantages en comparaison avec le procédé original en batch de Stöber. Un simple calcul permet de faire croître avec exactitude des grains d'ensemencement d'une taille donnée jusqu'à une taille finale de particules pré-déterminée. Des particules monodispersées sphériques jusqu'à 3·6 μm de diamètre et une fraction massique (en particules) très élevée jusqu'à 10 vol.% en silice pourraient être préparées par ce procédé. De plus, un simple réacteur tubulaire est décrit, lequel permet de produire ces particules de façon continue.

1 Introduction

In the last decades several techniques have been developed to synthesize powders exceedingly uniform in size, shape and composition.[1–6] Organic as well as inorganic particles have been prepared. The importance and advantages of monodispersed submicron powders were shown not only in the scientific field of physical chemistry dealing with the dynamic behaviour and stability of dispersions, but also in various industrial applications, e.g. catalysts, ceramics, pigments, pharmacy, photographic emulsions, etc. However, when it comes to industrial applications, several problems arise. The reproducible production of larger quantities of such colloids at reasonable cost remains the greatest difficulty. This has many reasons, for example the reproducibility depends very much on a precise control of the nucleation step in the precipitation reaction. The costs are high because of the expensive chemicals and the highly diluted mixtures in most of the systems. The only exception refers to latex colloids, which are being produced on industrial scales by established processes.

The present study will demonstrate a controlled growth procedure and a continuous production process of monodispersed silica powders, a solution to some of the above-mentioned difficulties. Recently a few papers have been published,[7–10] demonstrating the general possibility of a seeded

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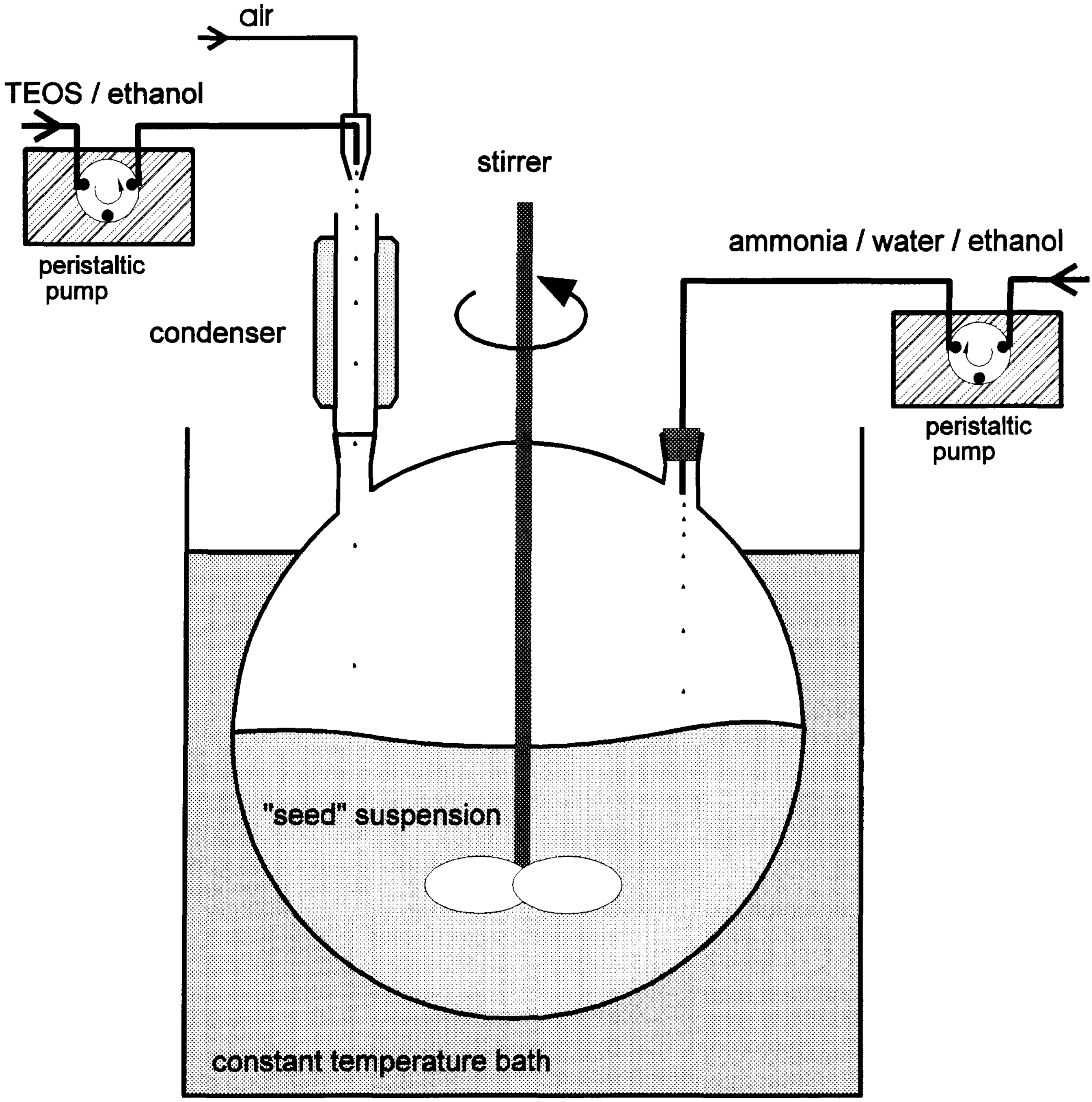


Fig. 1. Schematic drawing of the experimental set-up for the controlled growth procedure.

growth in the Stöber silica process.[11] The particle size described in those publications was always below 0·5 μm ∅ (diameter), well within the range of the original Stöber process. The process presented here, however, controls the growth much more precisely and as a result particle sizes of several microns in diameter could be prepared, a range not obtained by the original process. Moreover, the cost efficiency could be increased by raising the silica concentration to about 10 vol.% and by the possibility of a continuous production process, a very important aspect for any industrial scale-up. In general, continuous powder preparation has received more and more attention during the last years and various submicron ceramic materials have been prepared by continuous processes, e.g. $Y(OH)CO_3$,[12] $AlOOH$,[13] $SrTiO_3$,[14] or TiO_2, SiO_2, ZrO_2, Ta_2O_5 and Y_2O_3–ZrO_2.[15,16]

2 Experimental

2.1 Materials

Tetraethylorthosilicate (TEOS) (Wacker, Burghausen, Germany) was distilled immediately before use. Prior to the distillation, CaO was added in order to capture HCl impurities, which often remained from the synthesis of TEOS ($SiCl_4$ + C_2H_5OH). Ethanol (E. Merck, Darmstadt, Germany) was denatured with methyl ethyl ketone. Ammonia

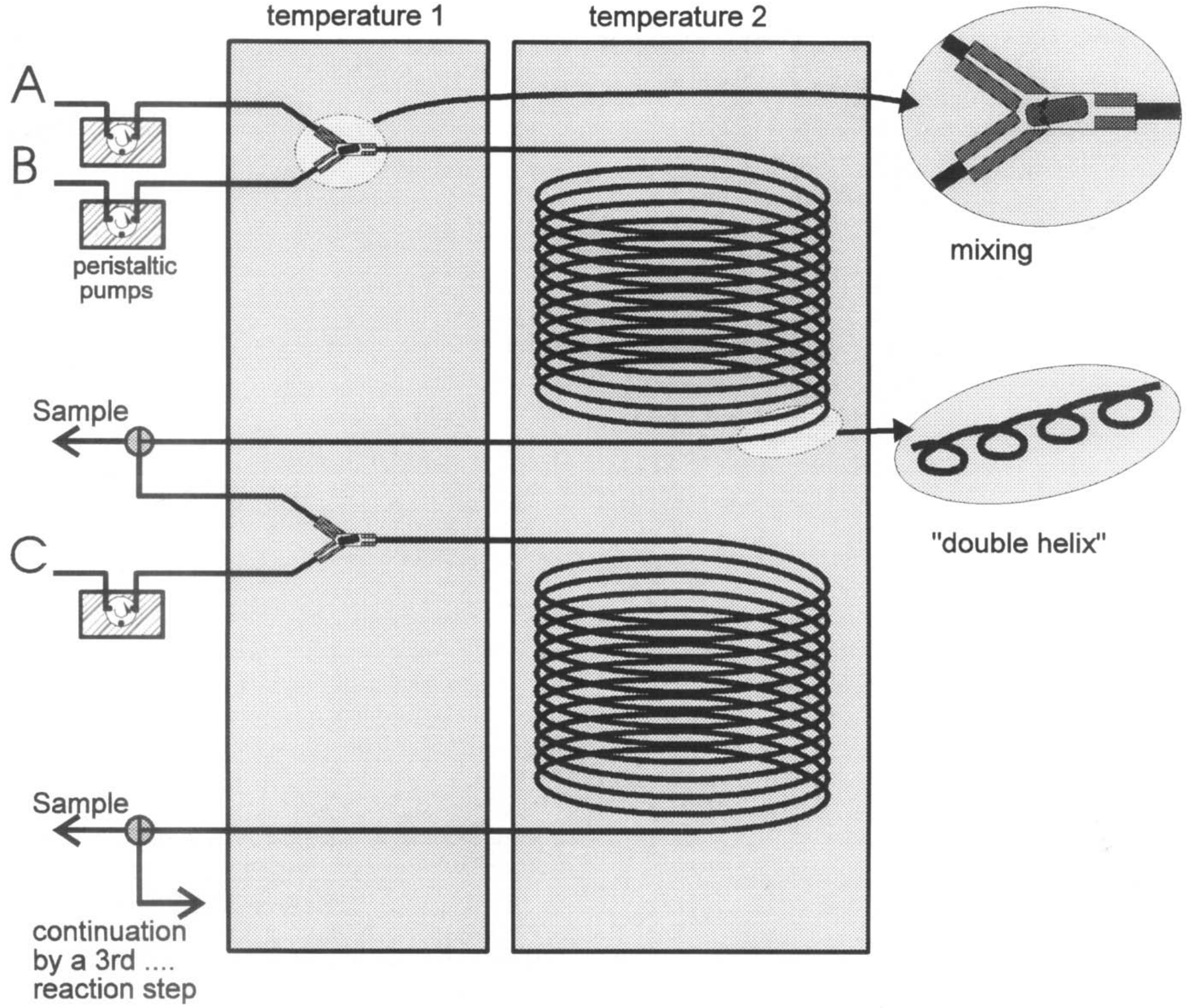


Fig. 2. Schematic drawing of the continuous reactor system.

solution (25%; E. Merck, Darmstadt, Germany) was analytical grade. All other chemicals (organotrialkoxysilanes), supplied by E. Merck or Wacker, were of reagent grade and were used without further purification.

2.2 Growth process

For the growth experiments, seed suspensions were prepared as described in Part I.[17] After the reaction was completed, further TEOS, H_2O and NH_3 was added to the suspension. This can be done stepwise, as described by Bogush *et al.*[8] or by the nearly continuous process described in Section 2.3. Figure 1 shows a schematic drawing of the set-up. The previously prepared seed suspension was gently stirred in the flask (100–200 rpm), while TEOS premixed with ethanol on the one side and $H_2O/NH_3/EtOH$ on the other side was added dropwise. The rate of addition could be adjusted by two peristaltic pumps. It was important to avoid any hydrolysis and condensation reaction in the TEOS/ethanol drops before they reached the seed suspension. Any pre-hydrolysis can cause a secondary nucleation. In order to avoid this effect the TEOS outlet and the condenser were adjusted carefully to obtain free falling droplets. In addition, the ammonia present in the gas phase was kept away from the TEOS orifice by rinsing the TEOS outlet with dry air.

2.3 Continuous process

Figure 2 shows a schematic drawing of the continuous production. The set-up primarily consisted of three sections: a pumping, a mixing and a reaction zone. The flow of the two components, A, ammonia/water/ethanol, and B, TEOS/ethanol, were adjusted by two peristaltic pumps. After thoroughly mixing the two liquids at room temperature or at 273 K (0°C) the reaction further proceeded at 313 K (40°C), set by a second temperature bath. The length of time at which the reaction proceeded at T_1 and T_2 could be adjusted by the length and size of the tubing as well as by the pumping speed.

In some cases a second (or further) reaction step(s) was (were) added in order to adjust the particle size, to increase the mass fraction, or to modify the surface of the silica particles prepared in the first step. The process proceeded in a similar way as already described for the first continuous preparation step; however, mixture A was substituted by the previously prepared silica dispersion and mixture B was replaced either by a further amount of TEOS or various organotrialkoxysilanes (mixture C).

2.4 Electron microscopy (TEM and SEM)

TEM micrographs were obtained at a JEOL TEM 1200 EX electron microscope (JEOL, Japan). The acceleration voltage of the electron beam was 100 kV. TEM was employed to determine the particle size and structure of the silica beads. Copper carrier grids were covered with a formvar film. One drop of the properly diluted particle dispersion was put onto these grids and dried.

SEM micrographs were obtained at a PSEM 500 (Philips, Kassel). In a similar way one drop of the particle dispersion was dried on an aluminium sample block and finally coated with a thin gold film in order to avoid charging effects.

Particle size distribution histograms were determined from the micrographs with the help of a Zeiss TGZ3 analyser.

3 Results and Discussion

3.1 Controlled particle growth

In a series of experiments the influences of several experimental parameters on the growth reaction were studied. The ammonia, water and TEOS concentrations, and the reaction temperature directly affected the reaction kinetics, whereas other parameters like the seed size and concentration, the addition rate of TEOS or the mixing conditions, had an indirect influence on the outcome.

The growth sequence of one example is shown in the TEM and SEM micrographs in Fig. 3. Silica seed particles of 17·5 nm ∅ were synthesized according to the original Stöber process[11,17,18] at 333 K (60°C) and water, ammonia, and TEOS concentrations of 10 mol dm^{-3}, 0·2 mol dm^{-3}, and 0·1 mol dm^{-3}, respectively. Thereafter (next day) the reaction temperature was lowered to 313 K (40°C) and the ammonia content adjusted to $\approx$ 0·5 mol dm^{-3}. TEOS diluted with ethanol (1 : 2 volume ratio) was added as described in the experimental part. The addition rate was controlled to approximately double the starting Si content within 5 h. The resulting particle size could easily be calculated from the known seed size, seed concentration and the added amount of TEOS.

Taking a variable density into account (e.g. in the case of different seed materials) the following formula described the interrelationship:

$$\frac{M_{\text{seed}}}{\varnothing^3_{\text{seed}}\rho_{\text{seed}}} = \left(\frac{M_{\text{seed}}}{\rho_{\text{seed}}} + \frac{M_{\text{TEOS}}}{\rho_{\text{SiO}_2}}\frac{FW_{\text{SiO}_2}}{FW_{\text{TEOS}}}\right)\frac{1}{\varnothing^3_{\text{new}}}$$

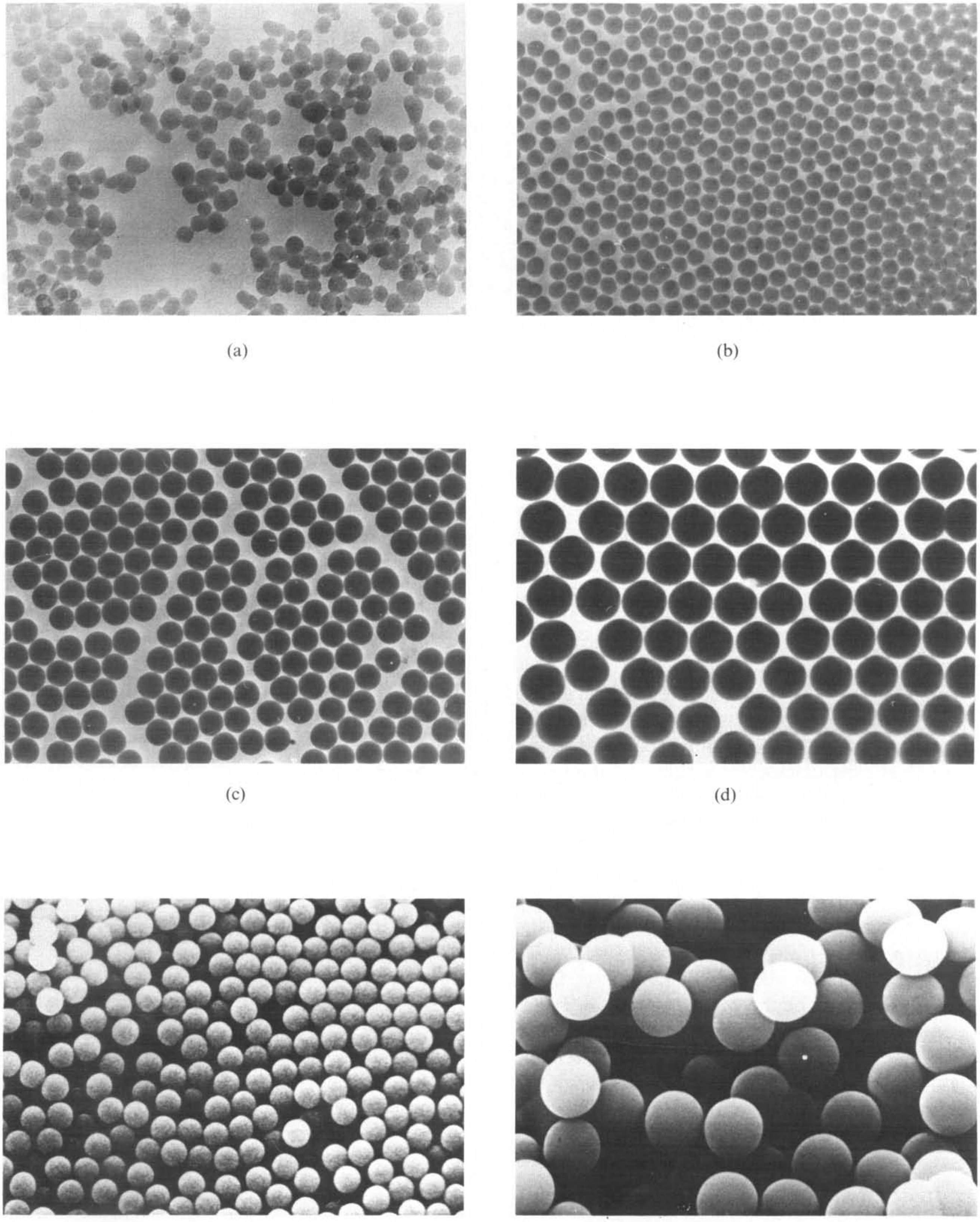
where M = mass; ∅ = diameter; ρ = density; FW = formula weight.

The equation simplified for seeds of the same density as the grown shell to:

$$\left(\frac{\varnothing_{\text{seed}}}{\varnothing_{\text{new}}}\right)^3 = \frac{M_{\text{TEOS, seed}}}{M_{\text{TEOS, total}}} = \frac{\text{starting content Si}}{\text{final content Si}}$$

In accordance with this formula, a particle size of 55 nm ∅, (see Fig. 3(b)) was reached after the Si content was increased by a factor of 30. In analogy, particle sizes of 160, 510, 1660 or 3620 nm ∅ were prepared by the continued growth of the above sample (see Fig. 3(c)–(f)). Throughout the process the ammonia content was checked by titration with HCl and adjusted to a value of $\leq$0·7 mol dm^{-3}. The water content was kept at about 8 mol dm^{-3}. The total Si concentration, SiO_2 seeds + added TEOS, was slightly increased throughout the growth process and a maximum value of Si $\approx$ 1 mol dm^{-3} was set for particle sizes above 1 μm ∅.

The TEM and SEM micrographs shown in Fig. 3 demonstrated the exceptional degree of monodispersity of these samples. The absolute values of standard deviations of the particle size increased only slightly during the particle growth. However, the relative standard deviation thus steadily decreased, falling below 2% relative for particle sizes >300 nm ∅. A certain increase of the absolute value has to be attributed to a 'systematic' error in the determination method of particle sizes, as shown elsewhere.[17,18] Another broadening effect of the size distribution can be attributed to an incomplete or inhomogeneous mixing during the addition of the TEOS. Thus microfluctuations in the TEOS concentration lead to different growth rates for each particle. In principle however, and demonstrated with only minor restrictions in the experiments, the absolute value of the size distribution will stay nearly constant during the growth process. Van Blaaderen *et al.*[7] demonstrated the same result by studying the growth of a bimodal seed population. They found that the absolute difference between the two seed size distributions remained constant throughout the growth and they concluded that the particle growth proceeded through a reaction-limited con-



(a) (b) (c) (d) (e) (f)

Fig. 3. TEM micrographs of silica particles grown from (a) 17·5 ± 2·9 nm ∅ seeds to various final particle sizes; (b) 55 ± 3·5 nm, (c) 160 ± 4·0 nm, (d) 510 ± 8·7 nm, (e) 1·66 ± 0·02 μm, and (f) 3·62 ± 0·04 μm ∅. Some doublet particles were observed in (f), thus the growth was stopped at this size. Original magnifications: (a) × 367 000; (b) × 114 000; (c) × 57 000; (d) × 28 500; (e) × 6 000; (f) × 6 000.

densation process of hydrolysed monomers or small oligomers.

In general, further growth of the silica particles could be accomplished under all reaction conditions, which yielded monodispersed particles in the original one-step Stöber process (see Part I). However, not all conditions gave acceptable results for all seed (particle) sizes and/or concentrations. The addition rate of TEOS was the most critical point under different reaction conditions. As shown in Part I, eqn (1), the particle growth rate was slow at low ammonia, or water concentrations or at low temperatures. Therefore, the addition of further TEOS had to be very slow in those experiments. When the TEOS was added 'too' fast, the concentration of the hydrolysed silicic acid units increased constantly until the critical self-nucleation concentration was reached and a new particle (seed) generation would appear, thus 'destroying' the monodispersity of the first seed population.

On the other hand, experiments at high ammonia and water concentrations or high temperatures did not solve all problems. Due to the very fast reaction in those cases, it was difficult to homogeneously disperse the freshly added TEOS before the latter was hydrolysed to a large extent and the resulting high local concentrations of silicic acid caused secondary nucleation too.

The stability of the dispersion towards agglomeration was another point which had to be carefully controlled. At low ammonia concentrations (low pH) the particle surface potential might be too low to sufficiently stabilize the particles. In addition the overall reaction proceeded much slower under these conditions and thus the time for any agglomeration to take place was much longer. In contrast, when the ionic strength of the solution was increased at high ammonia concentrations and consequently the double layer thickness decreased, the electrostatic repulsion barrier, or finally the stability of the dispersion was reduced too. In conclusion, intermediate ammonia concentrations were advantageous and NH_3 concentrations between 0·1 and 1 mol dm^{-3} were chosen for all further growth experiments.

In a similar way it was obvious that the diffusion distance of the hydrolysed TEOS to the seed particle surface might be too large for highly diluted seed dispersions or large seed sizes. At a constant SiO_2 concentration of seeds the available particle surface area decreased ($\propto \varnothing^{-1}$) and the diffusion distance towards this surface increased ($\propto \varnothing$) with seed size. Thus the seed concentration had to be increased at larger particle sizes in order to compensate for these effects. However, the seed concentration could not be set too high, since this would increase the probability of agglomeration and thus the formation of doublet particles. A practical limit of $[SiO_2]_{max}$ = 1 mol dm^{-3} seemed to be adequate for most of the experiments in order to keep the degree of agglomeration sufficiently low. However, this limit is somewhat arbitrary. As shown later, the concentration could be increased to more than 3 mol dm^{-3}, if the dispersion stability was assured.

Table 1. Maximum addition rate of TEOS for different silica seed sizes

Seed size (μm)	*Maximum addition of TEOS h^{-1}*
0·5	1/4 of silica seeds already present[a]
0·75	1/6
1·0	1/8
1·25	1/10
1·5	1/12

[a] For example, 6 g silica seed ≅ 0·1 mol Si ⇒ maximum addition rate of TEOS is 0·025 mol h^{-1} for a seed size of 0·5 μm or 0·01 mol h^{-1} for a seed size of 1·25 μm.

Despite all these factors, the most critical and most important factor of a perfect growth process remained the addition rate and procedure of TEOS. As shown before, intermediate reaction rates (conditions) were preferred in order to avoid mixing problems or an undesirable slow growth rate. Table 1 summarizes the maximum TEOS addition rates for an ammonia concentration of 0·5 to 0·7 mol dm^{-3}, a water concentration of about 8 mol dm^{-3}, and a reaction temperature of 313 K (40°C). The seed concentration for those experiments was below 1 mol dm^{-3} SiO_2, preferably at 0·5 to 0·8 mol dm^{-3}. Again, these values should be seen more as a practical guide and not as a strict limit. They very much depend on the kind of mixing and even exceeding the values for a short time does not instantly cause a secondary nucleation. Interestingly, calculation of the maximum particle growth rate from the values given in Table 1 resulted in a constant value of 40 nm h^{-1}. The latter corresponded to the particle growth rate after a reaction time of about 1 h or ≈80% reaction turnover in the comparable batch experiment (see Part I). However, the number of experimental data was not sufficient and too inaccurate to prove any correlation in this question.

3.1.1 High particle concentration

Nowadays various materials can be synthesized as monodispersed submicron powders. However, the preparation of larger quantities at reasonable cost is still a major difficulty. The high costs for the chemical is one aspect in certain cases, but the very low mass fraction in nearly all precipitation systems is the other important factor. The silica preparation according to the original Stöber process is already higher in its mass fraction by a factor of 10 or more than most other systems for the production of monodispersed particles. Nevertheless the mass fraction can be further improved during the controlled growth process.

The TEOS or Si concentration is limited in the original Stöber process to about 0·5 mol dm^{-3}. Above this value particles become more and more irregularly shaped or agglomerated. The latter effect is probably due to a disturbed nucleation and growth reaction at higher TEOS concentrations. In contrast, in the controlled growth process described here the well-adjusted balance between reaction rate (conditions) and the rate of TEOS addition kept the concentration of free silicic acid low enough to avoid any further nucleation. As a result, the reaction proceeded homogeneously on the present seed surfaces. Finally, the total Si concentration, SiO_2 seeds, TEOS, and free silicic acid, could be increased well above 0·5 mol dm^{-3}. Rather a value of $[Si] \approx 1$ mol dm^{-3} was advantageous for a perfect growth of particles larger than 1 μm in diameter and from the industrial point of view, even higher values would be desirable. A theoretical limit is given by the kind of alkoxide used in the reaction and the necessary H_2O for the reaction. For example, 208 g TEOS and 36 g water will yield 60 g silica and 184 g ethanol. Taking the densities of silica (2·0 g cm^{-3}) and ethanol (0·79 g cm^{-3}) into account, a maximum volume fraction of 11·4% ($\approx$3·8 mol dm^{-3}) results. The corresponding value when tetramethoxysilane is used instead of TEOS reaches about 15 vol.%.

Experiments showed that volume fractions of up to 10% SiO_2 could be prepared when pure TEOS instead of the prediluted mixtures (TEOS/ethanol) were added during the growth procedure already described. However, the process can not be controlled as perfectly as before and especially the fast and homogeneous distribution of the added TEOS can cause problems. Only minor difficulties arose at particle sizes of about 0·3 to 0·5 μm ∅ and ammonia concentrations <0·6 mol dm^{-3}, whereas at larger sizes an increased particle agglomeration was observed and at higher ammonia concentrations the reaction rate became too fast, causing a second nucleation and/or flocculation.

3.1.2 Particle surface modification

Last but not least, the silica particles could likewise be surface modified in a final reaction step. Instead of the further growth by addition of TEOS, different organotrialkoxysilanes were added to the particle dispersion. The silanes having various functional groups, e.g. octyl, phenyl, glycidoxypropyl, aminopropyl, or mercaptopropyl groups changed the surface properties of the silica particles. The different surface characteristics were confirmed, e.g. by electrophoretic mobility measurements, or the alkyl- or phenyl-modified samples were highly hydrophobic and resulted in a flocculated suspension.

In a similar way different organic dyes could be incorporated in a shell around the silica particles. Thus pigment particles of controlled colour, size (submicron) and surface properties were prepared.[19]

3.2 Continuous synthesis

Large-scale production of monodispersed silica particles can be accomplished in two ways; firstly a scale-up of the batch process, or secondly, a continuous preparation process. Already batches of several hundred litres have been prepared (Kinkel, J. N., pers. comm.) and the controlled growth already described allows variations between different batches to be perfectly adjusted and equalised. However, it still remains a batch process and a continuous process would have several advantages for an industrial production. Ferguson & Ring[20] studied a modified form of the Stöber process, a continuously stirred tank reactor. However, their particle size distribution was very broad (0·4–2 μm ∅) and samples could no longer be called monodispersed. In contrast, the tube reactor presented here yielded samples nearly as monodisperse as prepared by the batch process.

The principal set-up of the tube reactor consisted of mixing, reaction and collection sections. In order to adjust or modify certain particle properties, several of these set-ups can be combined to a 'reaction cascade'. For example, the particle size could be adjusted, an additional coating layer precipitated as a shell around the first particle, or the particle surface could be modified with various organofunctional silanes (e.g. alkyl, aromatic, mercapto, amino, hydroxy, acid groups, etc.).

Since the hydrolysis, condensation and particle growth reaction were studied in great detail in Part I, the two remaining experimental questions were the initial mixing of the two reaction components and the flow in the reaction tubing. A schematic drawing of the mixing cell is shown as an insert in Fig. 2. The total cell volume of the Y-tube device was less than 0·6 cm^3 and a vibrating magnetic stirring bar assisted the mixing. The inner diameters of the incoming and outgoing tubings were 1 mm and 0·3 mm for the silane (TEOS) source. These diameters together with the flow rates were very important. For example, at low flow rates or at larger tubing diameters a clogging

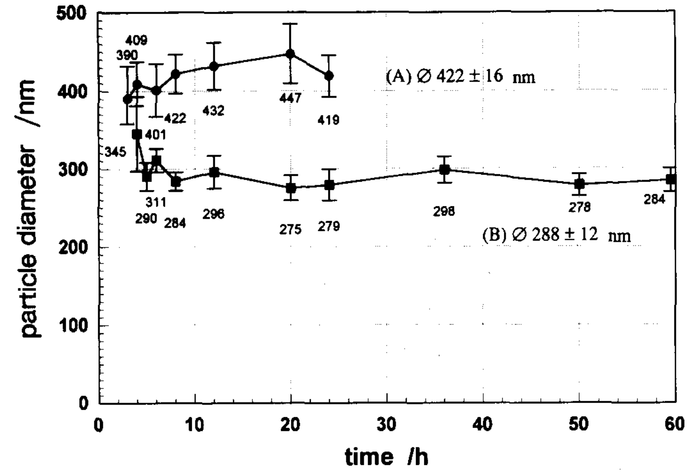


Fig. 4. Variation of the mean particle size during the continuous production process. Error bars show standard deviations (width) of the particle size distributions of each sample, based on a number average. Corresponding experimental data are connected by a line to indicate the variation of the mean particle size with time. The average ± standard deviation of the latter values is shown at the end of each line. The following reaction conditions were studied: (A) NH_3, H_2O and TEOS concentrations 0·8, 8·0 and 0·2 mol/dm^{-3}, respectively, T_1 = 273 K (0°C), T_2 = 313 K (40°C), total flow rate 2·8 cm^3 min^{-1}, 100 m reaction tube of 3 mm Ø, residence time ≈4 h; and (B) NH_3, H_2O and TEOS concentrations 1·5, 8·0 and 0·2 mol/dm^{-3} respectively, T_1 = 273 K (0°C), T_2 = 313 K (40°C), total flow rate 8 cm^3 min^{-1}, 50 m reaction tube of 6 mm Ø, residence time ≈3 h. Numerical values of the experiments are given in Table 2.

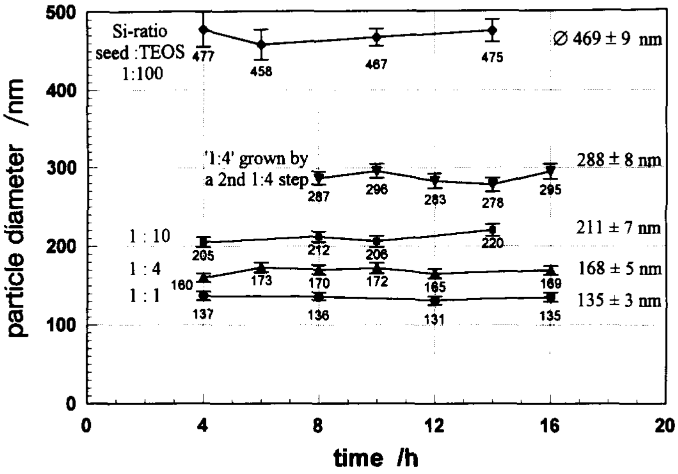


Fig. 5. Variation of the mean particle size during the continuous production process, when different seed/TEOS rations were chosen or when a second growth step was added. Error bars show standard deviations (width) of the particle size distributions of each sample, based on a number average. Corresponding experimental data are connected by a line to indicate the variation of the mean particle size with time. The average ± standard deviation of the latter values is shown at the end of each line. Silica seeds of 100 ± 4·1 nm were employed and the same reaction conditions chosen as in Fig. 4 (A). Numerical values of the experiments are given in Table 3.

of the silane tubing was noticed, whereas at higher flow rates a back-run reaction to the silane reservoir and/or a start of the precipitation already in the mixing cell could be avoided. The reaction velocity was another important factor, controlled by the chosen reactant concentrations. In addition, the velocity could also be influenced by the temperature. The temperature in the mixing section was set at 273 K (0°C), in order to slow down the reaction, whereas the reaction zone was kept at 313 K (40°C), thus accelerating the reaction by a factor of ≈5. The reaction rates could be calculated according to the results presented in Part I of this study and together with the flow rate and tubing size the necessary length of the reaction zone tubing could be calculated to assure a final silica conversion of >99%.

In addition to the previously described effects, the arrangement of the reaction tubing had a major influence on the outcome. To begin with the tubing was wound up in a parallel arrangement around a cylinder of ≈20 cm Ø (see Fig. 2). The evolution of the reaction could be watched using a transparent polypropylene tubing. During the experiment the colour of the clear solution to start with became bluish and then milky white after a certain reaction time or tubing length, respectively. At still later reaction times a phase separation was noticed within the tubing after some time. The white particle dispersion accumulated at the bottom of the tubing, leaving a clear supernatant in the upper part and the resulting particle size distribution became very broad at this point. Even reducing the tubing diameter from 6 to 3 mm did not resolve this problem completely. Therefore a different arrangement was tested. Two tubes were twisted around each other as in a double helix. The latter was then rolled up onto the cylinder. With the new arrangement no separation was observed for 6 as well as 3 mm Ø tubing's. TEM micrographs of the resulting samples indicated a reasonable monodispersity as well as a constant mean particle size during the experimental run (see Fig. 4 and Table 2).

Several possibilities existed to control the final particle size. Firstly, in the same way as presented

Table 2. Variation of the mean particle size during the continuous production process (see Fig. 4)

Reaction time (h)	*(A) particle diameter ± standard deviation (nm)* ■	*(B) particle diameter ± standard deviation (nm)* ●
3		390 ± 42
4	345 ± 48	409 ± 28
5	290 ± 18	
6	311 ± 15	401 ± 34
8	284 ± 12	422 ± 25
12	296 ± 21	432 ± 30
20	275 ± 16	447 ± 38
24	279 ± 20	419 ± 27
36	298 ± 17	
50	278 ± 14	
60	284 ± 15	

Table 3. Mean particle size during the seeded continuous production process (see Fig. 5)

Reaction time (h)	*Particle diameter ± standard deviation (nm)* *Si molar ratio of seed: TEOS*				
	1 : 1 ●	*1 : 4* ▲	*(1 : 4) + 1 : 4*[a] ▼	*1 : 10* ■	*1 : 100* ◆
4	137 ± 5·6	160 ± 5·5		205 ± 6·4	477 ± 22
6		173 ± 6·2			458 ± 19
8	136 ± 5·0	170 ± 6·0	287 ± 8·5	212 ± 6·8	
10		172 ± 6·5	296 ± 9·1	206 ± 7·4	467 ± 11
12	131 ± 5·4	165 ± 6·0	283 ± 9·3		
14			278 ± 8·8	220 ± 7·5	475 ± 14
16	135 ± 5·7	169 ± 5·6	295 ± 9·7		

[a] Second growth step (1 : 4) ~4 h after the first 1 : 4 growth.

for the batch process (Part I), the ammonia and water concentrations influenced the particle size. Also a controlled number and size of seed particles could be employed. A previously prepared silica dispersion replaced mixture A in the experiment. Thus the final particle size could be predicted very well from the seed size and the ratio of silica seed concentration to the added amount of TEOS, according to the formula given for the controlled growth experiments. Figure 5 presents several runs with various seed to TEOS ratios. As a third method, the particle size after the first precipitation step could be adjusted by a second growth step (see Fig. 5 (▼) and Table 3). In industrial production the size after the first step can be analysed online, and appropriate adjustment of the TEOS addition rate in the second step will produce final powders of a constant and pre-set size.

Not only the size but also the mass fraction could be increased in the second growth step. For example, the two-step seed experiment shown in Fig. 5 (▼) resulted in a final silica content of about 1 mol dm^{-3} (3 vol.%). Correspondingly, the particle surface could be modified in a final reaction step with various organofunctional silanes in just the same way as described in the controlled growth process.

4 Conclusions

A controlled growth process for the preparation of monodispersed silica particles was demonstrated, covering a wide range of particle and dispersion properties, which can not be obtained by the original Stöber process. The procedure allowed the partical size to be adjusted and exactly controlled. An exceedingly high degree of monodispersity could be achieved, since the absolute width of the size distribution did not (or only slightly) broaden during the growth process. Larger silica particles of up to 3·6 μm ∅ and high mass fractions of up to 10 vol.% SiO_2 were prepared.

Results of the previous paper (Part I) and the growth process were transferred to a continuous production set-up, a simple tube reactor. The reactor was run for 60 h, yielding monodisperse silica samples of a constant mean particle size. Properties of the final product could be influenced and adjusted by using several tube reactors in a reaction cascade. Thus the particle size and the mass fraction of the dispersion could be increased or adjusted to a pre-set value, or in a final step the particle surface could be modified with organofunctional groups

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