PREPARATION OF MONODISPERSE SILICA PARTICLES: CONTROL OF SIZE AND MASS FRACTION

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We extend the work of Stober, Fink and Bohn (J. Colloid Interfac Sci. 26 (1968) 62) to establish the ranges of reagent concentrations which result in the precipitation of monodisperse silica particles from ethanol solutions containing ammonia, water, and tetraethyl orthosilica. A correlation is presented which can be used to predict final particle sizes over concentrations of 0.1–0.5 M TEOS, 0.5–17.0 M H_2O and 0.5–3 M NH_3. The maximum particle size achievable for these conditions at $25°C$ is ≈ 800 nm and near the maximum, monodispersity is difficult to maintain. The effects of reaction temperature are studied and particle size distributions are analyzed. A seeded growth technique for preparing larger particles and/or increasing solids mass fraction up to a theoretical limit of ≈ 24 wt% of silica is described.

1. Introduction

The work of Stober et al. [1] showing that the hydrolysis of silicon alkoxides leads to the precipitation of essentially monodisperse SiO_2 particles has led to use the alkoxides of many metals in the preparation of a variety of ceramic precursor powders [2,3,7]. These studies have shown that while solids are easily precipitated from a wide range of starting alkoxides, the narrow size distributions achieved with silica are difficult to reproduce. Often when conditions are found which result in mondispersity the suspension mass fractions are so low as to preclude their use in the fabrication of ceramic bodies large enough for even model studies. As part of an effort to overcome these difficulties, we present here an extensive study on the preparation of powders by the hydrolyses of tetraethyl orthosilicate (TEOS) in aqueous ethanol solutions containing ammonia.

In previous work on this system by Stober et al. [1] and Van Helden et al. [4], final particle sizes are presented in a graphical form which are difficult to read and cover limited concentration ranges. We have expanded on these studies to

detail the set of reagent concentrations and reaction temperatures which result in the precipitation of particles with narrow size distributions. Our results are presented as a correlation to aid others wishing to tailor particle size for particular needs. In addition, we describe a seeded growth technique which can be used to prepare suspensions of particles with narrow size distributions at mass fractions of 17%.

2. Experimental

TEOS (Fisher Scientific Co., Reagent Grade) was vacuum distilled before use for particle synthesis. Dehydrated ethyl alcohol (US Industrial Chemicals Co.) and ammonium hydroxide (J.T. Baker Chemical Co., Reagent Grade) were used as received. Titrations indicated an ammonia concentration of 14 M. Ammonia saturated ethanol solutions were prepared by passing the ammonia through a drying column and then bubbling it through ethanol. The resulting ammonia concentration, determined just prior to use, was about 3 M at room temperature.

For each experiment the necessary amounts of ethanol, ammonium hydroxide, ethanol saturated with ammonia and deionized water (18 MΩ cm prepared with a Barnstead Nanopure Deionization Apparatus) were mixed in the reaction vessel and placed in a constant temperture bath. After the solution had come to temperature, the TEOS was added quickly. However, extremely rapid additions, as required, for example, when using titanium alkoxides as a starting material [5], were not needed.

A series of experiments demonstrated that the final particle size and size distribution were not functions of the degree of agitation during the reaction. In all subsequent experiments low to moderate mixing speeds were used.

Both round bottom flasks equipped with paddle stirrers and polyethylene bottles mixed with magnetic stirbars were used as reactors with no alteration in final product. The majority of the results reported here were carried out with reactor volumes of 100–150 ml. However, vessels with volumes up to 4 l have been used with no observable effects on final particle size or size distribution. All vessels were washed with a 2% HF solution then rinsed with deioized water before use.

For the growth experiments, seed suspensions were prepared as described above. After the reaction had come to completion (3–8 h after the first addition of TEOS), TEOS and water were added to the suspension in a 1:2 mole ratio. This mole ratio is required as the production of one mole of SiO_2 from one mole of TEOS consumes two moles of water and produces four moles of ethanol. Additions of up to twice the number of moles of TEOS in the original solution were repeated at 8 h intervals for up to 10 additions.

Particle sizes were determined from electron micrographs taken on a Phillips 400 transmission electron microscope. The diameters of over a hundred particles were used in calculations of the average size and standard deviation of each sample. A carbon replica of a diffraction grating (SPI Supplies) was used as a magnification standard.

The solids density was detrmined on samples dried at 100°C for 24 h with a Quantachrome Micropycnometer, in which helium was used to measure the volume displaced by the particles.

3. Results and discussion

In their early work Stober et al. [1] and later Van Helden et al. [4] and Bridger et al. [6] presented results which established that the hydrolysis of TEOS in ethanol solutions containing water and ammonia can result in particles with narrow size distributions. This has stimulated a great deal of work in using the resulting amorphous SiO_2 particles as model colloids and in studies of ceramic fabrication processes. In addition, titanium, zinc, aluminium, and zirconium alkoxides, to name a few, have been used in attempts to prepare cermaic precursor powders of similar morphologies [2,7]. However, it is commonly reported that narrow size distributions are difficult to achieve. Indeed, even in the silica system, which is by far the most extensively studied, when attempting to prepare larger particles or suspensions with high mass fractions, extrapolations of the results of Stober et al. and Van Helden et al. can lead to heterodisperse suspensions.

In this paper we wish to establish in a more quantitative fashion the concentration ranges over which monodispersity is achieved and develop a correlation which can be used to predict final particle sizes for a given set of ammonia, water and TEOS concentrations. To achieve this, a wide range of initial reaction conditions were studied.

Primarily, the effects of initial concentrations on final particle size were investigated at a reaction temperature of 25°C. Our approach was to hold the TEOS concentration fixed and then vary ammonia and water concentrations in a systematic manner. Typical results of particle morphology are shown in fig. 1. The dependence of final particle size on ammonia and water concentrations are displayed in figs. 2 and 3, for fixed TEOS concentrations of 0.17 M and 0.3 M, respectively. It will be noted that the size goes through a maximum as both ammonia and water concentrations are raised. Similar behavior was observed for all TEOS concentrations studied (0.1–0.5 M) where a maximum particle size was achieved at approximately 7 M water and 2 M ammonia. This maximum moves to higher ammonia and water concentrations as TEOS con-
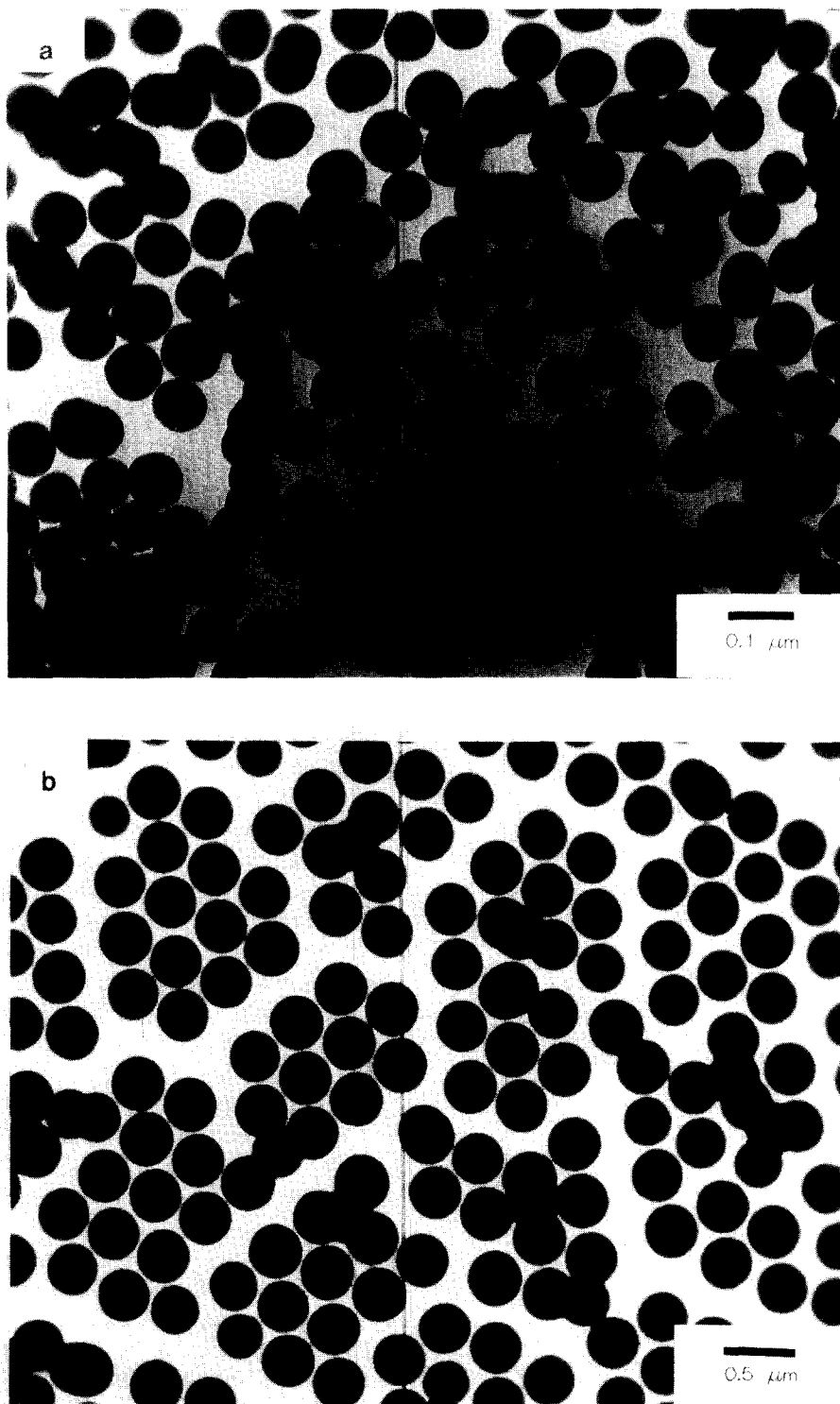
Fig. 1. (a) SiO_2 particles of average size 79.9 nm $\pm$ 7.3% from a solution containing 0.2 M TEOS, 1.0 M NH_3 and 2.0 M H_2O in ethanol and (b) SiO_2 particles of average size 392 nm $\pm$ 2.6% synthesized at 25°C from a solution containing 0.25 M TEOS, 0.5 M NH_3, and 7.5 M H_2O in ethanol.
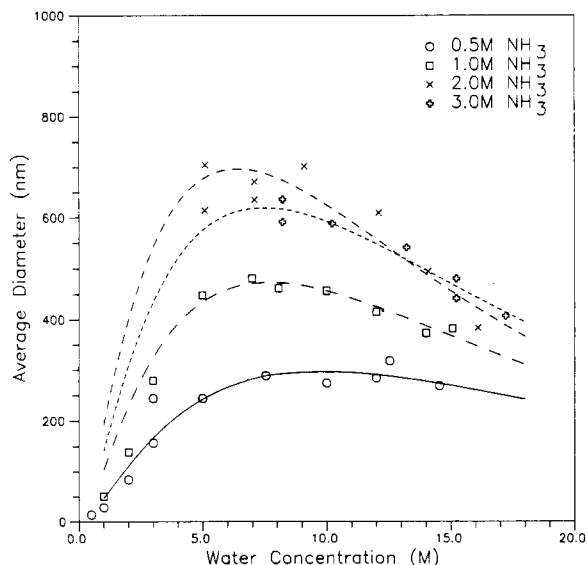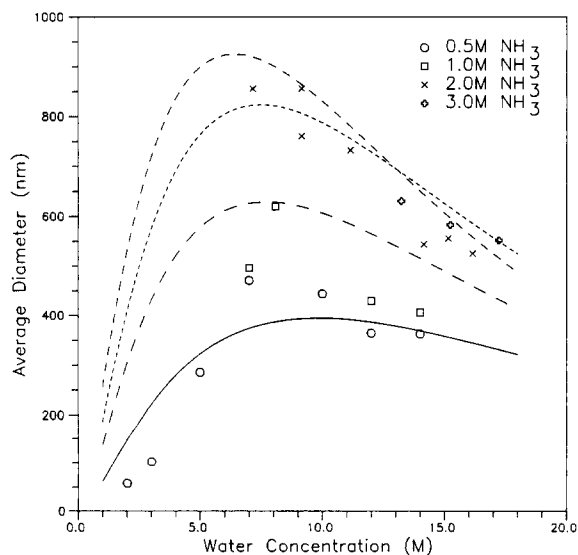
Fig. 2. Average particle size as function of ammonia and water concentrations at a constant TEOS concentration of 0.17 M at 25 °C. See text for synthetic details. Curves calculated from eq. (1) for constant TEOS and NH_3 concentrations as indicated.

Fig. 4. Average size of particles precipitated at 25°C from solutions containing 0.17 M TEOS, 1.0 M NH_3 over an extended range of H_2O concentration. Curve is calculated from eq. (1).

centration is increased. However, the maximum achievable size remained at approximately 800 nm for all TEOS concentrations studied.

Fig. 3. Average particle size as functions of ammonia and water concentrations at a constant TEOS concentration of 0.3 M at 25°C. See text for synthetic details. Curves calculated from eq. (1) for constant TEOS and NH_3 concentrations in indicated.
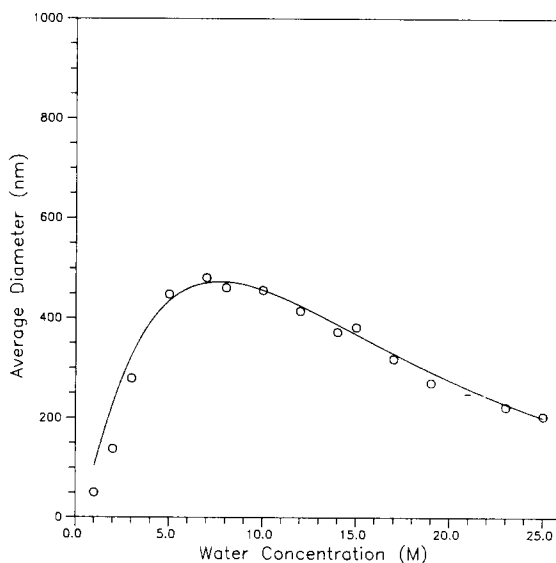
Limited data was obtained for water concentrations above 17 M. In fig. 4, final particle sizes are presented for 0.17 M TEOS and 1 M ammonia and H_2O concentrations up to 25 M. No phase separation was observed at these water concentrations and the particle size appears to approach a plateau size at high water concentration.

This result is in contrast to the work of Bridger et al. [6] who observed a phase separation at water concentrations greater than 15 M at a TEOS concentration of 0.28 M. Phase separation is expected to be a complex function of TEOS, NH_3 and H_2O concentration as well as temperature. Consequently, as Bridger et al. carried out their reaction at water concentrations well above those typically studied in our work and at 30°C, this result is not surprising. However, in agreement with the trends reported in fig. 4, they report that at a NH_3 concentration near 1.7 M, the final particle diameter decreased from 290 to 67 nm as water concentration increased from 15 to 26 M.

Within minutes of the time the reaction had been initiated, we observed that the reacting solution became a turbid white for water concentrations greater than approximately 2 M. At very low

water concentrations, a few hours were required to observe opacity in the reaction mixture. This increased apparent induction time can be accounted for by the small final particle size where it was not until late in the reaction that the particles achieved a size capable of scattering visible light. The overall reaction time determined by electron micrographs of growing particles was on the order of 3 h for intermediate reagent concentrations (0.17 M TEOS, 1.3 M NH_3, 3.3 M H_2O) and decreased as the water concentration was raised reaching a reaction time of approximately 40 min at 24 M H_2O [8].

Results gathered on over 100 sample preparations synthesized at 25°C and concentration ranges of 0.1–0.5 M TEOS, 0.5–17.0 M H_2O and 0.5–3.0 M NH_3 were used in the development of a correlation relating final particle size to intial reagent concentrations. The resulting expression, which has been developed to fit the experimental observations and thus contains no mechanistic information, is written,

$$d = A[H_2O]^2 \exp\left(-B[H_2O]^{1/2}\right), \qquad (1)$$

with

$$A = [TEOS]^{1/2}\big(82 - 151[NH_3]$$
$$+ 1200[NH_3]^2 - 366[NH_3]^3\big),$$

and

$$B = 1.05 + 0.523[NH_3] - 0.128[NH_3]^2,$$

where d is the average diameter in nanometers and the reagent concentrations are given in mol/l. Fig. 5 shows the predicted diameter from the correlation plotted versus the experimentally observed diameters. The majority of the data falls within the lines representing a deviation of 20%.

Due to the complexity of the functional dependence of particle size on reagent concentrations, a better correlation would be difficult to achieve without using an even less straightforward fitting function. The curves drawn in figs. 2–4 are calculated using eq. (1). It should be noted that the data used in developing the correlation did not include results for water concentrations greater than 17 M. Thus the predictions up to 25 M water as shown in fig. 4 suggest that eq. (1) can be used
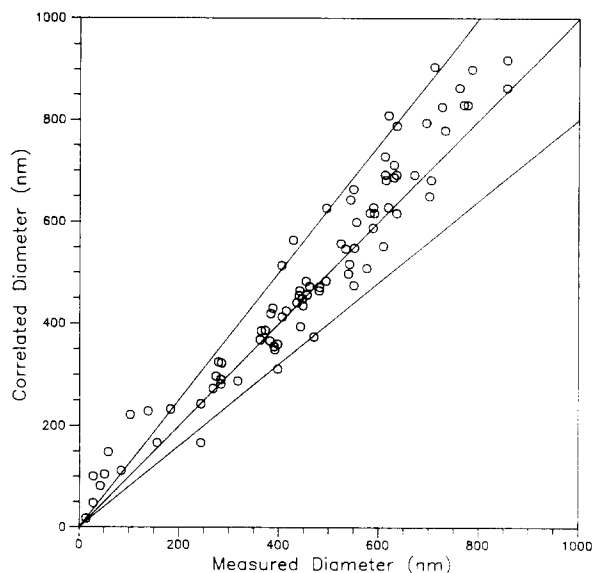

Fig. 5. Diameters calculated from eq. (1) as a function of experimentally determined diameters. A perfect correlation would correspond to the center line. The two outer lines represent a ±20% error in the correlation.

in limited extrapolations outside the range of values for which it was designed. It can be seen that the correlation deviates most strongly at small particle sizes and at higher TEOS concentrations. Fitting the data at the low water concentrations where small particles are generated is difficult without the introduction of a more complex fitting function. At elevated TEOS concentrations, the particle sizes were less reproducible and broader size distributions were observed. The correlation as presented in eq. (1) has been chosen to act as a practical guide and thus will be useful when designing reaction conditions required to achieve a desired size.

As a general rule, spherical particles with a narrow size distribution as shown in fig. 1 were obtained over the range of concentrations used in the development of eq. (1). The use of distilled TEOS was found to produce a more uniform particle morphology than using the TEOS as supplied by the vendor. Near the maximum achievable size for any given TEOS concentration, monodispersity was often not achieved and bimodal final particle size distributions were common (fig. 6). Stober et al. [1] reported a similar type of behavior for the larger particle sizes which they
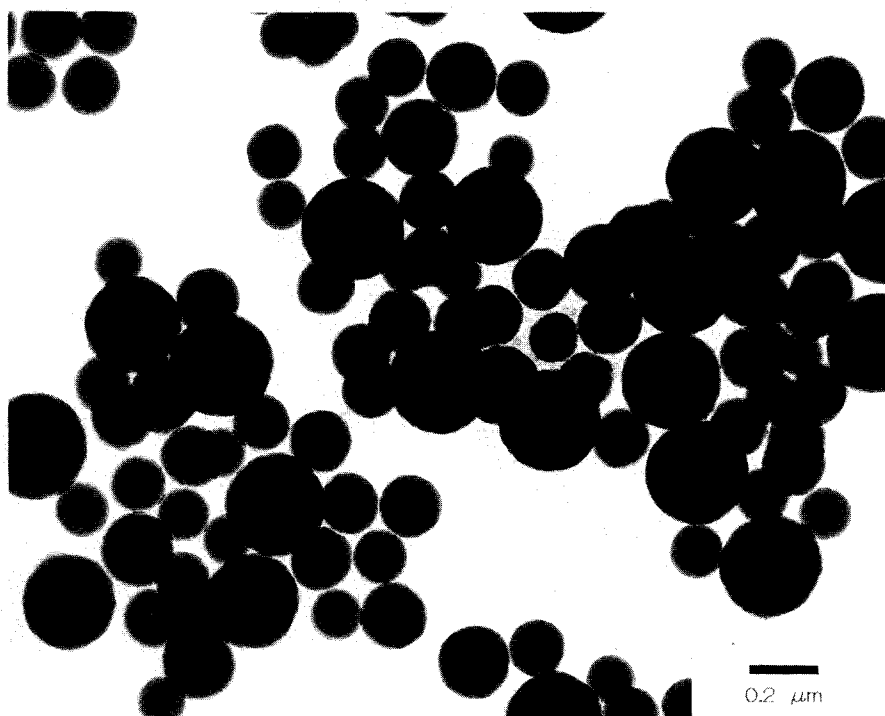
Fig. 6. Bimodal particle size distribution precipitated at 25 °C from a solution containing 0.4 M TEOS, 0.5 M NH_3, and 5.5 M H_2O.

prepared. We also observed heterodisperse particle size distributions at high TEOS and ammonia concentrations, mostly at 0.5 M TEOS and 2.0–3.0 M ammonia. These samples showed signs of being flocculated.

In the range where monodispersity was achieved, we found, in agreement with Van Helden et al. [4], that the standard deviation expressed as a percentage of average size decreased with increasing particle size (fig. 7). Surprisingly, these results appear to follow a function which is independent of initial reagent concentrations. For example, particles synthesized with 0.17 M TEOS and 1 M NH_3 and with 3.0 and 19.0 M H_2O had final particle diameters of 279 and 270 nm respectively. The standard deviations in therespective particle size distributions were 5 and 8%. This similarity in the breadth of final particle sizes occurred even though the water concentrations were substantially different and the total reaction times were 180 min for 3.0 M H_2O but only 45 min for reaction containing 19.0 M H_2O.
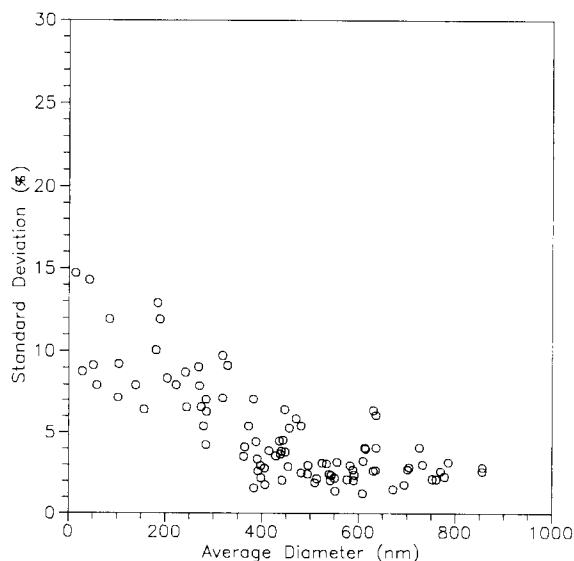

Fig. 7. Standard deviation in particle size distribution expressed as a percentage of average size as a function of average size.
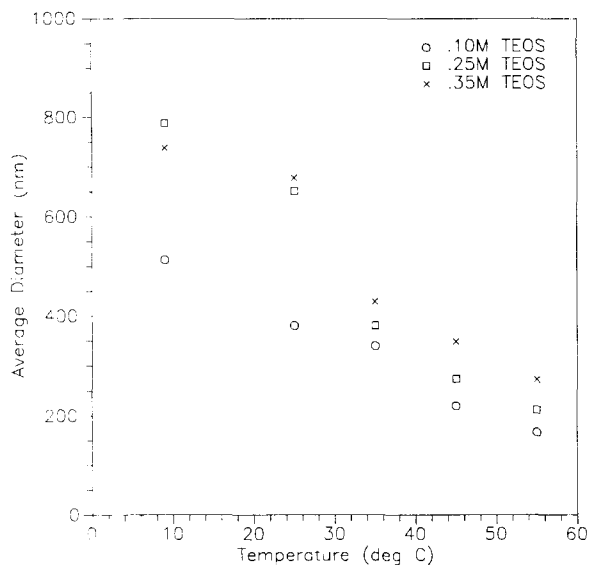
Fig. 8. Particle size as a function of reaction temperature for solutions containing 1.0 M NH_3, 7.0 M H_2O and TEOS concentrations of 0.10, 0.25 and 0.35 M.

The effect of reaction temperature in final particle properties was explored over a temperature range from 9 to 55°C. The reactions were carried out in 1.0 M ammonia, 7.0 M water and TEOS concentrations ranging from 0.1 to 0.35 M. The results (fig. 8) indicate that final particle size decreases monotonically as temperature increases. At the lowest temperature studied monodispersity was not always maintained, where as at elevated temperatures narrow size distributions were found for all TEOS concentrations.

Elemental analysis carried out on the particles washed in deionized water and dried at 90°C for 48 h yielded 0.15 wt% carbon, 0.67 wt% hydrogen and 43.32% silicon. These results compare favorably with those of Van Helden et al. [4]. Assuming all of the carbon originates from unhydrolyzed ethoxy groups which remain after the reaction has come to completion, we calculate that the final particles contain 92.7% SiO_2, 0.25% OC_2H_5 groups and 5.75% H_2O.

Density determinations made using a helium pycnometer yielded a solids density of 2.04–2.10

g/cm^3 for particles in the 80–900 nm diameter range. It is felt that the helium samples micropores inside the particles. Consequently, the measured density does not represent the particle's bulk density (as defined by the mass of a single particle divided by its volume which has been calculated on the basis of the electron microscope diameter). The density determined by pycnometry does, however, fall in the range of densities reported by Van Helden et al. [4] and Vrij et al. [9] as determined by measuring suspension densities as a function of solids mass fraction, a method expected to give densities very similar to those determined via pyconometry. Particle bulk densities were estimated by following the esterification procedure of Van Helden et al. [4] which replaces all silanol groups on the internal and external surfaces with steryl alcohol groups. After rigorously washing the resulting hydrophobic particles free of steryl alcohol and drying them at 90°C for 48 h, the particle densities were again determined by helium pycnometry. These paticles had a density of 1.9–1.95 g/cm^3. Based on this density and the assumption that the C_{18} chains from the steryl alcohol ($\rho \approx 0.77$ g/cm^3) plug all pores effectively excluding helium, we calculate a bulk unesterified particle density of 1.78–1.86 g/cm^3. These values are in line with the calculations of previous investigators [4,6,9] and indicate a particle porosity of 11–15%.

From these results we conclude that SiO_2 particles of narrow size distribution can be reproducibly synthesized over a size range of 20–800 nm diameter. While the "best" conditions will depend on what size particles are desired, the particles with the smallest percentage standard deviation are achieved for average sizes greater than about 300 nm. Near the maximum achievable size for any TEOS concentration, broad or multimodal particle size distributions are often obtained. For the TEOS system, particles of size greater than approximately 800 nm are difficult to synthesize without resorting to the seeded growth technique described below, and we recommend that a set of experiments be carried out in the region of the maximum to determine the exact conditions which produce large monodisperse particles if this growth technique cannot be followed.
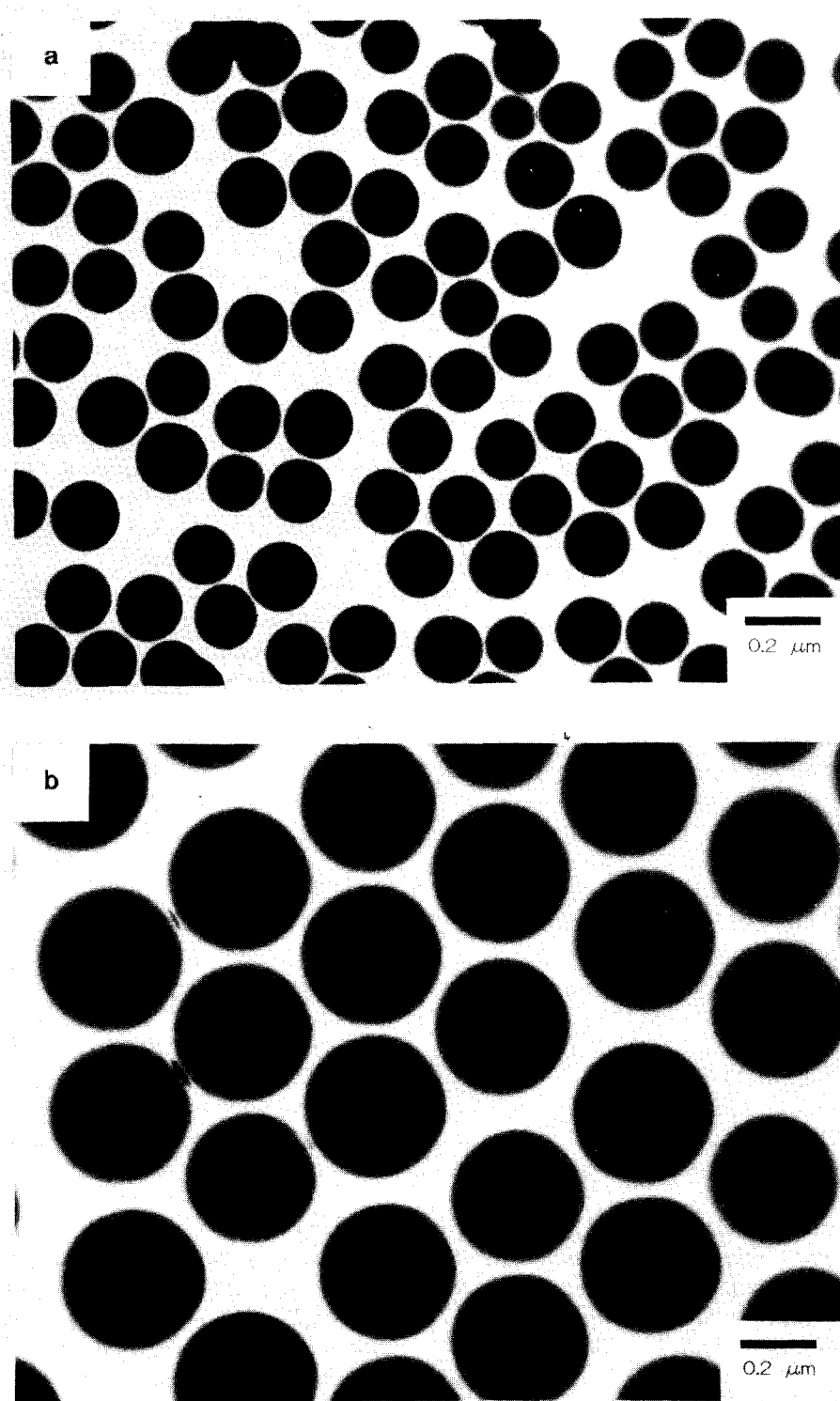
Fig. 9. (a) Seed particle synthesized at 55°C from a solution containing 0.2 M TEOS, 1.0 M NH$_3$, and 6.0 M H$_2$O. (b) Particles growtn from seed particles shown in (a) by 10 single additions of TEOS and corresponding water. See text for explanation of single addition nomenclature.

4. Seeded growth

While very narrow particle size distributions can be obtained with a one step growth process, the solids content in the resulting suspension achieves a maximum values of 3% at a TEOS concentration of 0.5 M. We have found that attempts to increase the solids weight fraction above this value by simply increasing the initial TEOS concentration results in heterodisperse particle size distributions. In order to achieve both larger particles and/or larger final mass fractions, we have developed a seeded growth technique which results in monodisperse particles at solids contents with a theoretical limit of 24%.

In this technique, a seed suspension is prepared using the techniques described above. The size of the seed does not influence the mondispersity of the final product and thus should be selected on the basis of the desired final size and mass fraction. TEOS and H_2O are added to the seed suspension in a 1 : 2 mole ratio after the seed suspension has stopped reacting. During ensuing hydrolysis and condensation, the number of colloidally stable particles remains constant but their size increases. While the use of distilled TEOS is necessary to achieve uniform seed particles, we found

Fig. 10. Standard deviation after each growth step of particles, shown in fig. 11 ○, single additions, × double additions.

that the use of as supplied TEOS in subsequent growth steps was not detrimental to the size distribution or morphology of the final product.

In a typical experiment, two suspensions with average diameter of 170 nm and mass fractions of 1.5% were prepared. To the first sample, an amount of TEOS equal to that originally present in the solution (4.0 ml in a total reaction volume of 90.0 ml) and the corresponding volume of water (referred to below as a single addition) were added at 8 h intervals. To the second sample, twice the original volume of TEOS and the corresponding volume of water were added at each interval (referred to below as a double addition). After 10 additions each, the first sample reached a mass fraction of 10.6%, and the second a mass fraction of 14.3%. The particles in each case remained spherical and increased in size (fig. 9). In line with the results presented for conventionally grown particles, it was found that the percentage standard deviation of the seeded growth particles decreases as their size increases (fig. 10).

It was found that during seeded growth the size of the particles can be related to the total volume of TEOS added to the solution by a simple equation.

$$d = d_0 (V/V_0)^{1/3}, \tag{2}$$

where d is the average diameter, d_0 is the average diameter of the seed particles, V_0 is the moles (or equivalently, volume) of TEOS used to produce the seed particles and V is the total moles of TEOS added to the solution (including V_0). This equation fits the results of the two experiments very well (fig. 11).

The form of eq. (2) suggests that the volume of the growing particles increases in proportion to the number of moles of TEOS added to the solution. As a result, the number and the density of the particles must remain constant while they are growing. As would be expected, however, for a seeded growth process, if the added amount of TEOS exceeds a critical value, nucleation will result in the growth of a second population of colloidally stable particles. The critical TEOS value depends on initial particle size and number density, and reaction temperture. For example, at 55°C seed particles (prepared with 1 M NH_3, 5
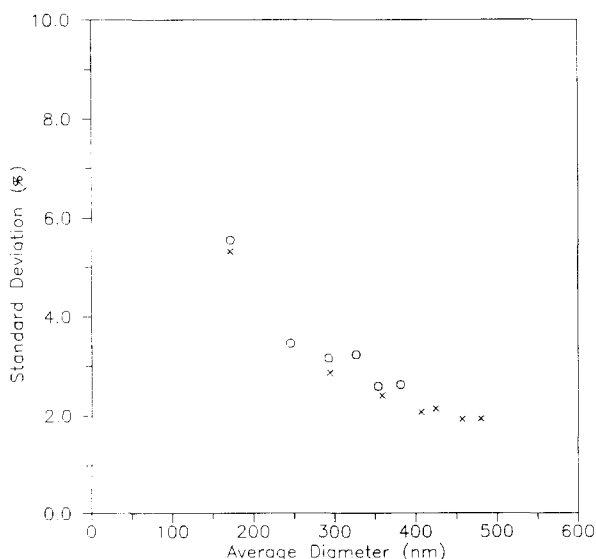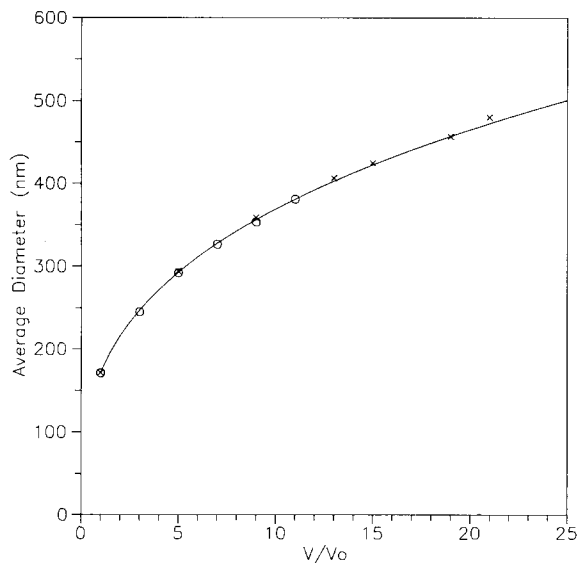
M H_2O and 0.2 M TEOS) were grown successfully into stable particles in suspensions having volume fractions of greater than 10% by using both single and double additions of TEOS for 10 growth steps. However, at 25°C, double additions to seed particles prepared under the same conditions resulted in a heterodisperse particle size distribution (fig. 12).

We routinely use this seeded growth technique to prepare 4 l of suspensions with mass fractions in the 11–15% (w/w) range. The technique works well for particles with final diameters of 50–900 nm. When small final particles are desired, even smaller seed particles must synthesized. For example, to prepare 50 nm particles at a final mass fraction of 11%, seeds with a diameter of approximately 18.5 nm must be synthesized. Conditions resulting in particles in particles in this size range can be easily determined for eq. (1) or by looking at the data presented in figs. 2–4. Growth of particles of any size appears to present no

Fig. 12. Heterodisperse particle size distribution produced at 25°C with 10 double additions of TEOS to a seed suspension prepared from 0.2 M TEOS, 1.0 M NH_3 and 5.0 M H_2O in ethanol.

particular difficulties as long as the critical TEOS concentration described above is not exceeded.

5. Mechanism of formation

While the primary purpose of this paper is to establish experimental conditions which result in silica particle with narrow size distributions, these results also begin to lay a solid foundation on which to develop mechanistic models of particle growth. Relevant observations drawn from our studies include the data presented in figs. 7 and 10 which indicate that as the particles grow their size distribution becomes narrower. This suggests the growth mechanism is self sharpening (i.e., small particles grow faster than large particles). Secondly, because the density (porosity) of the final particles and their external granular morphology are independent of particle size or whether prepared in a single or multistep process, it can be concluded that the growth mechanism does not alter dramatically during the course of the reaction. Finally, if precipitation is to result in monodisperse particles, the growing particles must, at some point, achieve colloidal stability. That is, as van der Waals attractive forces are ever present, a substantial repulsive pair interaction potential must develop to forestall flocculation and the resulting heterodispersity in size distribution.

These observations and kinetic studies reported elsewhere [8,10,11] have led us to postulate that particle growth occurs primarily through an aggregation mechanism. Monodispersity is achieved through size dependent aggregation rates where the probability of aggregation between two particles of the same size decreases as the particles grow. Such aggregation laws are predicted by the DLVO theory of colloidal stability [12] where the repulsive interparticle potential is due to charges bound to particle surfaces. This model suggests that silica nuclei formed in a supersaturated solution are colloidally unstable and aggregate. As the particle size distribution moves to larger average sizes, the bigger particles stop interacting and grow primarily through aggregation with smaller particles and freshly formed nuclei. While this model fits the qualitative observations drawn from

the data presented in this paper and predicts the correct kinetic trends, further work is required to unravel the dependence of the rates of hydrolysis, condensation, nucleation, and aggregation on reagent concentrations and reaction temperature. Work along these lines suggests that the nucleation and aggregation mechanism can be developed into a quantitatively predictive model [8].

6. Conclusions

In this paper we present conditions which result in the precipitation of SiO_2 particles from aqueous ethanol solutions containing ammonia and TEOS. This work extends earlier studies to broader reagent concentration ranges and summarizes the data in a more quantitative fashion than has been available previously in the literature. While the resulting correlation contains no mechanistic information, it can be used as an engineering tool in the preparation of single sized SiO_2 powders. Surprisingly, we find that the percentage standard deviation of the resulting particles is independent of initial reagent concentrations and is solely a function of final particle size. The seeded growth technique described here has been used to prepare large quantities of SiO_2 particles at mass fractions up to 17 wt%. It is found that the number and density of the particles in the suspension remains constant during the growth steps thus allowing for accurate prediction of increases in particle size and mass fraction for each addition of TEOS.

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