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A small angle X-ray scattering study on high pH silica precipitations

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Abstract

Silica precipitations were carried out at high pH (7–10) and elevated temperatures (60–90°C) by means of simultaneous dosing of diluted water glass and sulphuric acid into a stirred thermostatted reaction vessel. In order to investigate the development of the vulnerable silica structures during the processes, every 5–10 min small samples were taken from the reaction mixture and analysed using small angle X-ray scattering. It was found that a narrow particle size distribution was maintained throughout the entire preparation procedure (or at least from about 1 h until the end of the process), despite the fact that the primary silica particles were growing continuously. In addition, a continuous decrease in the total number of primary particles was observed, indicating that the primary particles were involved in clustering and aging processes, and that (except for the initial reaction stages) newly dosed silica does not form new particles but is deposited onto the already existing particles. Ostwald ripening, which is regarded as the most important aging mechanism, probably proceeds relatively rapidly under the applied process conditions, leading to a persistent high degree of monodispersity.

Keywords: Precipitation; Silica; Small-angle X-ray scattering

1. Introduction

Silicas are used in a very wide range of applications. For example, silicas serve as “fillers” in rubber materials, such as tyres, and they are applied as a catalyst support and as a drying agent. Silicas are also used as abrasives and in separation technology (membranes, chromatography, filtration). Each of these applications requires a type of silica with specific properties. Important parameters are the mechanical strength, specific surface area, pore volume, and pore size distribution. To develop a tailor-made silica for a specific application, it is important to be able to control these properties. Therefore it is important to understand the chemical processes that occur during the preparation of silicas.

Silicas are prepared from either silicon alkoxides or water glass. Since water glass, a solution of SiO_2 and NaOH in water, is a considerably cheaper silicon source than silicon alkoxides, the vast majority of industrially produced silicas are prepared from water glass. Only in special cases, when high purity silicas are required, are alkoxides used as starting material.

In both cases, silica preparation is based on a condensation reaction between $\text{Si}(\text{OH})_{4-x}\text{O}_x^{x-}$ species, which results in the formation of an Si–O–Si bridge [1,2]. (With silicon alkoxides, this reaction is preceded by hydrolysis of the alkoxides.) From the literature it is known [1,2] that further condensation reactions lead to the formation of cyclic oligomers, followed by growth of primary particles. The size of these particles varies

between less than 1 nm to more than 100 nm, depending on the reaction conditions. Subsequently, these particles may aggregate into clusters, and eventually a percolating network may be formed (gelation), provided that the concentration of primary particles is sufficiently high. Finally, redistribution of silica may occur as a result of aging processes. As all these processes, and thus the primary particle size and the structural properties of the aggregates and the gel, are strongly influenced by the reaction conditions, an enormous variety of silicas with very different properties can be prepared just by variation of the temperature, pH value, concentrations, or by the addition of other species to the reaction mixture. Therefore it is not surprising that our knowledge of the growth, aggregation and aging of silicas and the influence of the reaction conditions thereon is still far from complete.

The investigation of the vulnerable silica structures during the preparation of silicas demands the use of non-invasive analysis techniques which do not require sample drying prior to analysis. Small angle X-ray scattering (SAXS) is one of the very few techniques that meet these requirements. Moreover, rapid data collection is possible by the use of high brilliance synchrotron radiation, which enables “real-time” analysis of the dynamic chemical processes.

In previous studies carried out by our group [3–5] the formation of silicas from water glass solutions was investigated at pH 4. Water glass was mixed into the acidic solution, and subsequently the reaction vessel was left unstirred. This pH value was chosen since particle growth and aging can be examined conveniently and independently under these conditions, because of the relatively low reaction rates, and because the time scale for aging processes is orders of magnitude larger than for particle growth.

However, precipitated silicas are industrially prepared at very different conditions [6]. Water glass and diluted sulphuric acid are added continuously into the reaction vessel at rather high pH values (7–10). Consequently, the amount of silicon atoms in the reaction vessel is not constant but increases with time. The amount of electrolyte (sodium sulphate) increases as well. Furthermore,

the reaction mixture is stirred vigorously. The aim of this study was to investigate the chemical processes occurring during preparation of silicas under these industrial conditions.

2. Experimental details

2.1. Preparation of silicas

Synthesis of precipitated silicas was carried out following procedures described in the patent literature [6]. Diluted solutions of water glass and sulphuric acid were added simultaneously into the thermostatted and vigorously stirred reaction vessel, which had been filled with an initial amount of water, the so-called “heel” (Fig. 1). The pH was tuned at a constant value between 7 and 10 by matching the acid and water glass flows, and a constant temperature was maintained, typically in the range 60–90°C. After approximately 1 h gelation occurred; the viscosity rose sharply and a percolating gel would have been formed if the stirrer had been stopped. Later on, the viscosity

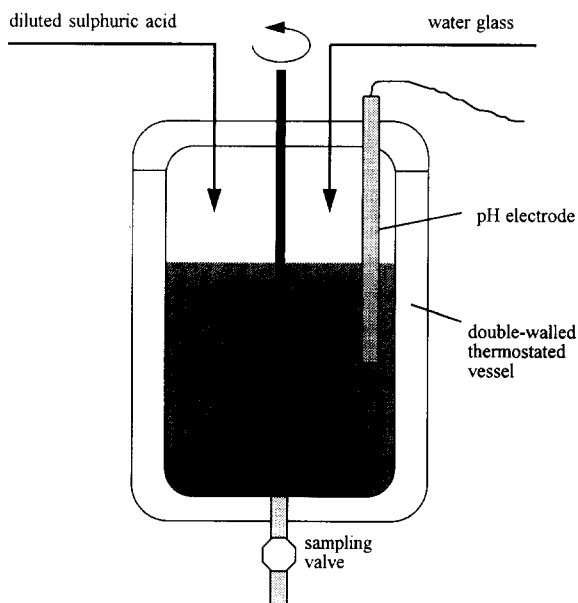


Fig. 1. Schematic overview of the experimental set-up of a silica precipitation.

dropped again. After 165 min the simultaneous dosing of water glass and acid was stopped.

2.2. Small angle X-ray scattering

SAXS experiments were carried out at station 2.1 of the Synchrotron Radiation Source of Daresbury Laboratories (UK), using a collimated X-ray beam with a wavelength of 0.154 nm. The scattered intensity was measured as a function of the scattering angle by means of a position-sensitive quadrant detector. The camera length was 8.0 m, resulting in a Q window of 0.074–0.80 nm^{-1} (long).

During the synthesis described above every 5–10 min a small sample was taken from the reaction mixture through a sampling valve at the bottom of the vessel. A droplet of the sample was quickly transferred into the SAXS cell between two thin (about 10 μm) Mylar windows, and subsequently placed in the X-ray beam. SAXS spectra were collected in 5 min.

3. Results and discussion

Fig. 2 shows a $\log(I)$ – $\log(Q)$ plot of a series of SAXS spectra collected during a typical high pH (7–10) and high temperature (60–90°C) silica precipitation. After some dosing time a spectrum has developed exhibiting at the high Q side a pattern of maxima and minima superimposed on a straight line with slope -4 . This side maxima pattern is characteristic of spherical monodisperse particles [7–9]. As can be observed in Fig. 3, the position of the maxima and minima is rather sensitive to the size of the particles. Since the minima and maxima are smoothed as a result of the non-zero silica concentration and, moreover, would readily be averaged out by appreciable deviations from monodispersity, the observation of side maxima is quite remarkable. It indicates that the primary particle size distribution is rather narrow ($\Delta R/R$ is estimated at 15%) at any moment between dosing times of about 50 and 165 min, and also during acidification to pH 4. It also implies that the spheres are smooth, which is also supported by the slope of -4 . In theory [7], other regular

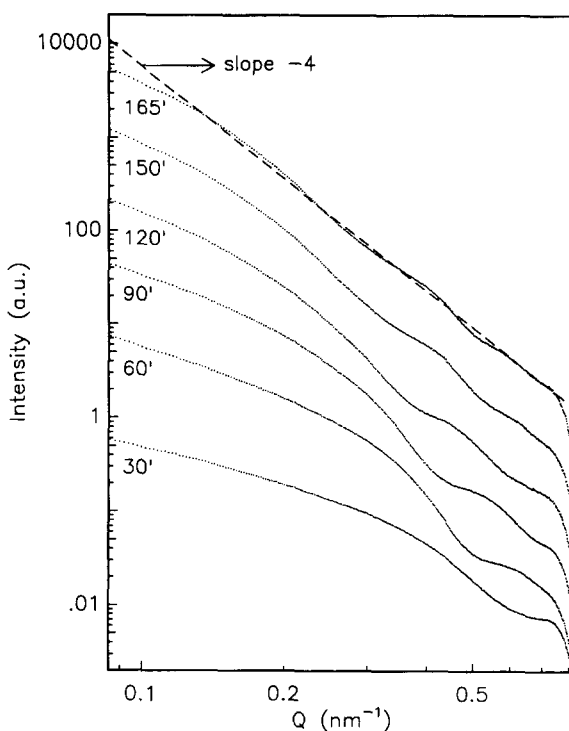


Fig. 2. SAXS profiles of samples taken at various dosing times during a typical silica precipitation at high temperature (60–90°C) and pH (7–10).

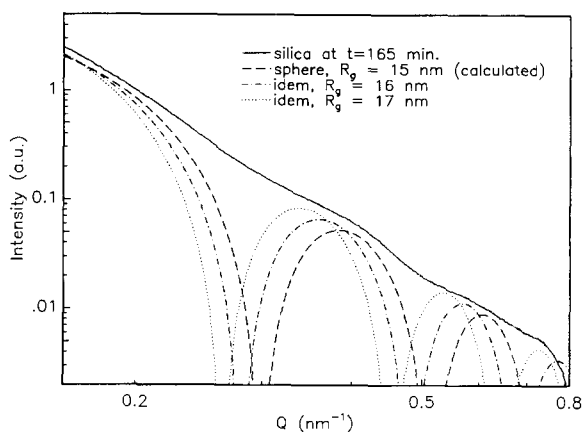


Fig. 3. Part of the final SAXS spectrum (taken after 165 min of simultaneous addition of water glass and sulphuric acid), and calculated SAXS patterns for very diluted monodisperse spheres with radii of gyration of 15, 16 and 17 nm.

particle shapes would be possible as well, such as ovals or cubes, but there is no reason why amorphous silica would assume such shapes [1].

From the present data no conclusions can be drawn yet about the first hour of the synthesis; SAXS experiments with a shorter camera, covering larger Q values, will shed more light on the silica particles during this period.

Fig. 2 also shows clearly that the side maxima pattern gradually shifts to lower Q values with increasing dosing time, which indicates that the primary particles are continuously growing. For each SAXS spectrum the radius of gyration of the primary particles was determined from the position of the minima and maxima. This can be done most conveniently and rather accurately (experimental error about 0.2 nm) from a $\log(IQ^4) - \log(Q)$ plot. The results derived from the SAXS spectra in Fig. 2 (and from some additional spectra) are shown in Fig. 4. Clearly, the primary particle size increases virtually linearly with dosing time.

From experimental observations such as the sharp increase in viscosity it is known that aggregation of the primary particles occurs around and after the “gelation point”, leading to the formation of relatively large clusters (the formation of a percolating system is prevented by vigorous stirring). In principle the radius of gyration of the largest clusters can be determined from the position in an (ultra) small angle scattering spectrum where, at the low Q side, the curve levels off and a constant scattered intensity is reached. However, this point does not fall within the Q range of Fig. 1. It can only be concluded that the largest clusters are larger than 40 nm.

Because the primary particles are not fractal, their mass increases with $\frac{4}{3}\pi R_g^3$. Consequently the number of primary silica particles in the reaction vessel is proportional to the amount of water glass added divided by R_g^3 . The latter quantity is also displayed as a function of time in Fig. 4. Obviously, the number of primary particles decreases with dosing time, at least after 1 h. This means that new nuclei are only formed in the initial stages of the reaction, before the gel point. In later stages all additionally dosed silica is deposited onto the already existing particles. Moreover, the number of these particles is slowly being reduced. This can

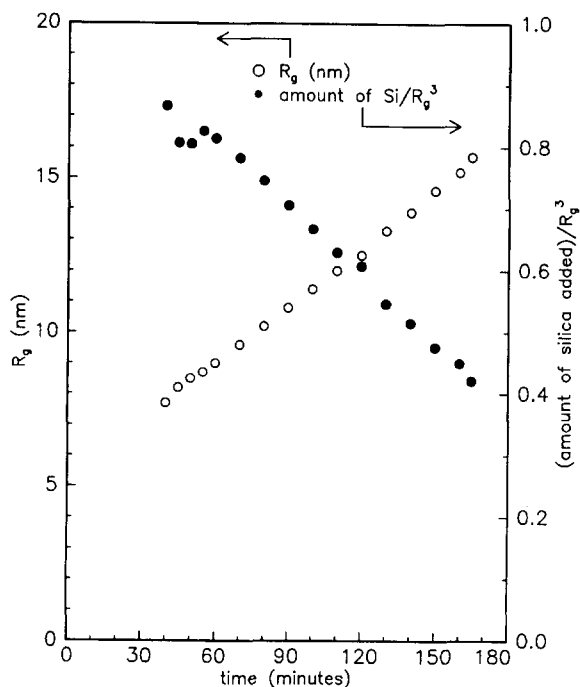


Fig. 4. The average radius R_g of gyration and the amount of water glass added divided by R_g^3 (which is proportional to the number of silica particles in the reaction vessel) as a function of dosing time, calculated from the SAXS spectra recorded during the precipitation presented in Fig. 2.

be caused by two processes. Firstly, the number of particles will decrease if two particles form an interparticle bond. However, they will still be “seen” by SAXS as separate particles unless the “necks” between the particles are filled up. If diffusion limitations do not play a role, it is expected that these “necks” will be filled rapidly owing to preferential condensation on these concave surfaces. Secondly, Ostwald ripening [1], which is regarded as the main contribution to the aging process, will diminish the number of primary particles. Because of the difference in surface energy, silica at the highly curved convex surfaces of the smaller particles redissolves relatively easy and recondenses preferentially at the more slightly curved surfaces of the larger particles, or in the “necks” between interconnected particles, together with the newly added silica in the continuously dosed water glass solution.

However, it must be stressed once again how

surprising it is that the side maxima pattern is visible, and therefore that the rather high degree of monodispersity is maintained throughout the whole period from the gelation point to the end of the precipitation, although the primary particles not only are growing continuously, but also form clusters. In the first instance, both coalescence followed by preferential silica deposition in the necks between the particles and Ostwald ripening are expected to give rise to loss of monodispersity. In the former case this could occur as a result of the formation of irregularly shaped intermediate silica structures with partially filled necks. Apparently, relatively few such structures are present, either because the necks are filled rapidly, or because the interparticle connections remain rather weak so that the individual particles remain clearly discernible. The latter situation may occur if there are virtually no condensation reaction limitations and, hence, the process is diffusion limited.

The SAXS results suggest that Ostwald ripening is a fairly rapid process under the applied reaction conditions, for, if redissolution of the smaller silica particles had been proceeding slowly, a broad range of particle sizes would have been present in the reaction vessel, and thus the side maxima pattern would not have been found in the SAXS profiles.

4. Conclusions

SAXS experiments recorded during silica precipitations performed at high pH (7–10) and high temperatures (60–90°C) by means of simultaneous dosing of water glass and sulphuric acid have shown clearly that the primary SiO₂ particles grow continuously during the precipitation. In addition, it appeared that at any moment between about 1 h dosing time and the end of the precipitation (after 165 min) the primary particles have a rather

narrow size distribution. This is a surprising result, since the particles are continuously involved in a number of processes: growing, forming interparticle bonds, and aging. It is also shown that the total number of particles in the reaction vessel decreases gradually. This implies that, at least after about 1 h dosing time, no new particles are formed, but all silica in the newly dosed water glass is deposited on the already existing particles. Moreover, the decrease in the number of primary particles, in combination with the persistence of the narrow particle size distribution, probably indicates that Ostwald ripening is a relatively rapid process.

Acknowledgment

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