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Silica Gel from Water Glass: a SAXS Study of the Formation and Ageing of Fractal Aggregates

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Abstract

The influence of pH, cations, F^- and temperature on the aggregation, gelation and ageing of aqueous silica gels has been investigated using small-angle X-ray scattering (SAXS). At both low and intermediate pH (pH = 4 and 6–8, respectively), fractal aggregates are formed during gelation from silicic monomers or small oligomers. The fractal dimensionality is 2.20 (5), to be expected for reaction-limited cluster-cluster aggregates. During ageing silicic ions dissolve from the more soluble peripheral primary particles and condense in the crevices of the core of the aggregates. This process results in an increase in the size of the scattering primary particles and in a decrease in the fractal dimensionality of the silica aggregates from $D = 2.25$ to $D = 2.0$ or $D = 1.85$. The ageing processes are strongly enhanced by a slight increase in the pH of the solution, addition of fluorine anions and a rise in temperature. The aged silica gel is constructed of an ensemble of densified aggregates of which the density variation within the aggregates is larger than that of the freshly prepared aggregates. The primary particles of which the aggregates are built grow during ageing from molecular size to dense particles in the nanometer range, the ultimate radius depending on the type and duration of the ageing process.

1. Introduction

Recent developments in the sol-gel processing of silica (Brinker & Scherer, 1990) have stimulated fundamental research on the aggregation reactions of sols. Many new insights have been seen, especially concerning the fractal properties of the aggregates and the underlying mechanism of formation.

To obtain silicas suitable for sol-gel processing, silicon alkoxides were used as the source of silica. Controlled hydrolysis of silicon alkoxides resulted in tailor-made silica sols. However, using water glass as starting material, primary silica particles are relatively small (almost molecular sizes) and are strongly

dependent on the composition of the water glass (pH, cation, silica concentration); often one is dealing with a complicated mixture of monomeric and oligomeric ions of silicic acid (Wijnen, Beelen, de Haan, Rummens, van de Ven & van Santen, 1989; Wijnen, Beelen, de Haan, van de Ven & van Santen, 1990). Acidification of water glass results in the growth of particles as well as in the combination of particles in clusters and aggregates. In both processes Si—O—Si bonds are formed by the (OH^- -catalyzed) condensation reaction between SiOH and SiO^- groups of different monomers, oligomers or particles (Iler, 1979). At high pH (> 8.5), we have observed (Wijnen *et al.*, 1990) that reactions leading to cyclic and cage-like and other highly condensed structures are predominant. Under suitable conditions even precipitates of (sub-)colloidal silica particles are formed. At lower pH (4–6), the growth of primary silica particles is retarded. Since in aqueous silicate solutions no stabilization of particles by charge or steric effects occurs, very tenuous and fractal structures of aggregated particles are observed (Beelen, Wijnen, Vonk & van Santen, 1989).

Large-scale computer simulations have proven useful in the development of a new approach in the study of the aggregation processes of primary particles (Meakin, 1988; Jullien & Botet, 1987). In the limiting cases of either diffusion-controlled or reaction-limited cluster-cluster aggregation (DLCA and RLCA, respectively), different values for the fractal dimensionality have been observed: $D_{DLCA} = 1.75$ and $D_{RLCA} = 2.08$. Experimentally, dimensionalities are found ranging from $D = 1.7$, indicating diffusion-limited cluster aggregation, to $D = 2.4$, indicating reaction-limited cluster aggregation with rearrangements. Furthermore, it has been found experimentally that, when the kinetics are dominated by diffusion limitations ($D = 1.75$), the structures formed may reorganize into structures with higher dimensionalities, approaching values obtained from RLCA simulations (Aubert & Cannell, 1986; Wijnen,

1990). These experiments all report an increase in fractal dimensionality as a consequence of ageing of the structure.

In many applications of silica gels a thermally stable structure is required. Formation of aqueous silica gels from water glass implies that very small silica particles (often of molecular size) are coagulated into very tenuous and fragile networks of fractal aggregates. Unless some form of structure reinforcement is applied, these fragile aggregates are submitted to very strong capillary forces during drying of the structure (Iler, 1979), causing severe damage to the structure of the silica gel and the pores. Alexander, Broge & Iler (1956) have proposed a way to reinforce the silica-gel skeleton by thermal treatment of the aqueous gel network. Interparticle connections are reinforced through dissolution of silica from small particles (small surface curvature) and subsequent deposition of dissolved silica at places with large or even negative surface curvature, *i.e.* in the necks between two neighboring particles (Ostwald ripening) (De Groot & Mazur, 1964; Iler, 1979; van Santen, 1984; Casey, 1988). In the present paper we wish to discuss the molecular chemical aspects of transformations of aggregates grown by reaction-limited cluster-cluster aggregation. During the transformations, a decrease in fractal dimensionality is observed.

2. Experimental details

Water glass solutions were prepared by dissolution of amorphous silica gel (Wijnen *et al.*, 1989). The composition of the 10 wt% SiO_2 solutions was $\text{SiO}_2/M_2\text{O} = 3$ with $M = \text{Li, Na, K, Rb, Cs}$ and TMA (tetramethylammonium hydroxide). Silica gels were prepared by acidification of aqueous silicate solutions: water glass was carefully added to a 1.0 M solution of hydrochloric acid under vigorous stirring until a pH value of 6.0 or 4.0 was obtained. To study the influence of F^- appropriate quantities of NaF were added to the hydrochloric acid.

SAXS measurements were performed at the Synchrotron Radiation Source at Daresbury Laboratory, England (station 8.2). To obtain spectra with a fractal Porod plot over more than two decades, measurements at different lengths of the camera were combined, resulting in a Q range of $0.013\text{--}3.6\text{ nm}^{-1}$ [$Q = (4\pi/\lambda)\sin\theta$, $2\theta = \text{scattering angle}$, $\lambda = \text{wavelength of the incident X-rays}$]. Subtraction of parasitic (slits) and background (water solution and mylar window material) scattering was performed using standard procedures (Vonk, 1973). Accurate and reproducible results were obtained by digitation of the scattered intensities to up to 400 data points per measured spectrum. Growth of fractal aggregates and ageing of the gel were studied by *in situ* measure-

ments in a SAXS cell positioned in the X-ray beam. Consecutive recording yielded time-resolved (1 min acquisition) spectra. The fractal dimensionality, the size of fractal aggregates and the size of primary silica particles were determined by fitting of the experimental SAXS curves applying the scattering function (structure factor for fractal aggregates) given by Teixeira (1986). The form factor of spherical particles was used (Guinier & Fournet, 1955).

3. Results and discussion

3.1. Ageing of gels prepared at low pH values

Owing to the finite size of both fractal aggregates and primary particles, a finite linear region is to be expected in the double log plots of the SAXS spectra. The left and right extremities of the linear region are indicative of the size of the aggregates and the size of the primary particles, respectively. Accurate values are obtained by the procedure of Teixeira (1986).

Fig. 1 shows SAXS spectra of a reacting silica at pH = 3.9. After 10 min a short but distinct linear region can be discerned, corresponding with small fractal aggregates (approximately 1.8 nm). After 40 min of reaction the linear region has grown considerably in the direction of small Q values due to the growth of the aggregates to 8.2 nm. The fractal dimensionality obtained from both experiments is $D_{\text{exp}} = 2.2$, a value comparable to dimensionalities obtained from analogous experiments (Martin & Hurd, 1987) and from aggregation simulations employing reaction-limited cluster-cluster aggregation ($D_{\text{lit}} \geq 2.05$).

Fig. 1. SAXS spectra recorded (a) 10 min, (b) 40 min, (c) 60 min, (d) 2 d after acidification of aqueous potassium silicate solutions ($\text{K}_2\text{O} \cdot 3\text{SiO}_2$). pH = 3.9, $T = 297\text{ K}$, 1 min acquisition time. For clarification, the intensities are multiplied by 1, 3, 8 and 10 respectively.

No deviation from fractal power-law scattering is observed up to Q values of $Q \approx 2.5 \text{ nm}^{-1}$, indicating that the primary particles forming the fractal aggregates are monomers or small oligomers of silicic acid. In this Q region no change is observed in the spectrum during the process of aggregation, indicating that the size of the primary particles is constant during aggregation. Moreover, all of the primary particles have to be present in small clusters or aggregates and the growth of the aggregates has to be realized by the addition of these small clusters (cluster-cluster aggregation). The sharp decrease in scattered intensities at $Q > 2.5 \text{ nm}^{-1}$ should be interpreted as an instrumental artifact arising from camera width limitations (scattering angles become so large that scattered X-rays are captured by the camera).

A gel is formed after approximately 60 min from initial mixing. As reported for analogous systems (Cabane, Dubois & Duplessix, 1987), no change in fractal dimensionality is observed at the gelation point. Spectra of the silicate mixture after gel formation (Figs. 1c, d) show a continuous expanding linear region, indicating ongoing growth of fractal aggregates, even after formation of a continuous network took place. Moreover, preliminary USAXS (ultra-small-angle X-ray spectroscopy) results (Beelen, Wijnen & van Santen, to be published) indicate a cut-off size of approximately 100 nm in a gel after several days. These observations are not fully in line with the classical concept of gel formation (Iler, 1979), corresponding with an infinite percolating structure of aggregated particles. However, structures grown under reaction-limited conditions of cluster-cluster aggregation are anisotropic (Botet & Jullien, 1986). After gelation, the prolonged

observed increase in the size of the aggregates can be ascribed to growth in a tangential direction of the thread-like aggregates (Beelen, Wijnen & van Santen, 1990).

However, ageing of the silica gel (one year) gives a completely different SAXS spectrum as can be seen in Fig. 2. Care has been taken to prevent dehydration of the tenuous and highly fragile fractal gels. One now observes a second almost linear region in the double log plot (corresponding to the classical Porod scattering of non-fractal particles) indicating the presence of particles with a radius of 3 nm in the aged gel (Hurd, Schaefer & Martin, 1987).

Determination of the fractal dimensionality of the aged structures gives a value slightly larger than 2.0, distinctly different from the fractal dimensionality of freshly prepared silica gels. This deviation in fractal dimensionality is significant since dimensionalities obtained from experiments dealing with aqueous non-aged silica gels always gave dimensionalities in the range 2.22–2.26 (Beelen *et al.*, 1989, 1990). The dotted line in Fig. 2 presents the linear least-squares fit of the data set yielding a slope of -2.00 (5). Thus we may conclude that ageing of the gel structure leads to structures with a larger fall off in the density of the aggregates compared to freshly prepared gels: as such there is a larger variance in density within aged aggregates compared to freshly prepared silica aggregates ($\rho \propto r^{D-3}$). This can be interpreted as a densification of the core of the silica aggregates at the expense of the peripheral sites of the aggregates, due to migration of silica from the boundaries of the aggregate towards the center of the aggregates. The driving force for this migration is the difference in the Ostwald ripening process between the periphery and the core of the aggregates. Owing to the smaller and less tightly connected particles in the periphery the dissolution is here the dominating reaction. Contrarily, in the denser core most of the silica is deposited in the necks or crevices between particles. Moreover, dissolution of peripheral particles is expected to decrease the fractal cut-off size, as is reflected in a shrinkage of the aqueous silica gels as a function of time. Fractal behavior will thus extend over smaller length scales in case the gel has been aged as compared to the non-aged gels. ^{29}Si NMR spectroscopy confirms this picture (Wijnen, 1990); during ageing the local environment of Si atoms in the aggregate shows a decrease in SiOH groups in favor of $\text{Si}(\text{—O—Si})_4$ groups.

Fig. 2. SAXS spectrum of silica gel prepared at pH = 3.9 from potassium water glass one year after preparation. The dotted line gives a linear least-squares fit, yielding $D = 2.0$ and the Porod law (slope = -4) is shown by the dashed line.

3.2. Ageing of gels prepared at intermediate pH values

SAXS measurements on silicas prepared at intermediate pH values (pH = 6–8) are presented in Fig. 3. A more accurate value for the pH cannot be given

since aqueous silica solutions at $\text{pH} > 6$ form gels almost instantaneously during addition of the last drops of water glass to the reaction mixture. The spectrum in the high- Q region indicates that again the primary particles are of molecular size. Primarily, the size of silicate anions or oligomers in the starting water glass solutions appear to control the sizes of the primary particles constructing freshly prepared silica aggregates and gels. Growth of primary particles is, at these intermediate pH values also, a slow process compared to aggregation.

However, in contrast with the gels prepared at $\text{pH} = 4$, ageing of the intermediate pH gel for 2 d clearly shows an increase in elementary particle size (Fig. 3b). Moreover, the fractal dimensionality of the system decreases just as in the case of long-term ageing of low-pH silica gels as can be conducted from the fractal regime in Fig. 3(b). The dimensionality of aggregates in the gel after 2 d of ageing has decreased to $D = 2.0$. Even after a month of ageing, the size of elementary particles increases steadily, whereas fractal dimensionality shows a decrease from 2.2 (initial gel) to 1.8. Apparently, the rate at which reorganizations occur in the silica gels is strongly dependent on the pH of the enclosing aqueous solution. Increasing the pH yields an increase in the rate of restructuring of the silica gels.

An interesting observation was made after changing the cation in water glass. Earlier we concluded from NMR experiments describing the dissolution of amorphous silica gel (Wijnen *et al.*, 1989, 1990) that substitution of potassium cations in the water glass solution by other cations (TMA, lithium, sodium, rubidium or caesium) causes retardation of dissolution rates due to differences in cation-(silica)anion interactions. In Fig. 4, SAXS spectra are presented

Fig. 3. SAXS spectra of a silica gel prepared at $\text{pH} = 7-8$ (lithium water glass). (a) 15 min; (b) 2 d; (c) one month after preparation.

taken one month after preparation of silica gels and prepared from different alkali-metal silicate solutions. From this figure it is clear that at intermediate pH TMA and caesium cations behave considerably differently compared to potassium cations: the larger negative slope in the double logarithmic Porod plot corresponds to a fractal dimensionality $D = 2.85$. This indicates that at $\text{pH} = 6-8$ we are dealing with a different aggregation process and this was confirmed by the observation that, during addition of TMA or Cs water glass to the hydrogen chloride solution above $\text{pH} = 6$, flocculation of silica occurred. This suggests that specific ionic interactions between negatively charged silicate oligomers and TMA or caesium cations cause rapid aggregation into a dense silica network. Fast reorganizations due to the strong ionic interactions might lead to higher dimensionalities compared to the other alkali metals. This may suggest that the size of the cations present in the solution and thus adsorbed on the silica oligomer surface groups ($\text{Si}-\text{O}^-$) are very important for the mechanism of the aggregation of the silica particles. At intermediate pH most of the silanol groups are ionized, resulting in strong interactions between cations and anions.

SAXS spectra of the other alkali-metal silicates (*i.e.* Li, Na, Rb) clearly show large similarities with silica gels obtained from potassium silicate solutions, suggesting strongly that, for lithium, sodium, potassium and rubidium, fundamentally the same processes occur in the restructuring of aqueous silica gels prepared at low and intermediate pH. Since the only difference between the procedures described for gel formation and for ageing can be found in terms of the alkalinity of the solution, we have to conclude

Fig. 4. SAXS spectra of silica gels prepared at $\text{pH} = 7-8$, using different alkali-metal hydroxides and tetramethylammonium (TMA) silicate. (a) Li; (b) Na; (c) K; (d) Rb; (e) Cs; (f) TMA. The peaks in the spectrum are instrumental artifacts.

that the rate of ageing of aqueous silica gel is a process mainly dominated by the pH or the concentration of OH^- ions. Because OH^- ions are a catalyst for both the formation and the hydrolysis of the Si—O—Si bonds, we may expect that by increasing the pH the rate of reorganization of the silica network will also increase.

In the silica aggregates differences in solubility occur as a consequence of differences in radius of curvature of the primary particles: small particles with small radius of curvature dissolve and larger particles with large radius of curvature grow (Ostwald ripening). Moreover, solubility is extremely low at places with negative radius of curvature, *i.e.* at the interparticle connections or necks between particles. Dense parts within the aggregate also show poor solubility whereas the very tenuous parts of aggregates (at the peripheral positions within the aggregate) show very high solubility.

3.3. Preparation of silica gels in the presence of fluorine anions

Since it is known (Iler, 1979) that at low pH even minor concentrations of fluorine anions give rise to a substantial increase in the rate of polymerization of silicate solutions (fluorine acts as a catalyst), a SAXS study on the effect of fluorine anions on the polymerization of aqueous silicate solutions was performed. Fig. 5 shows SAXS spectra of silica gels with 0, 0.01 and 0.1 mol sodium fluoride per mol silica present in solution. Clearly, it can be seen that, one month after preparation, fluorine has had a profound influence on the growth and arrangement of the elementary silica particles. In the case no fluorine

was added, primary silica particles constructing the silica gel are again of molecular dimensions and the fractal dimensionality of the aggregates is 2.2. Adding 0.01 mol NaF per mol silica to the solution and ageing for one month causes the classical Porod scattering to appear. The size of the elementary particles is approximately 6–7 nm, a value comparable with the sizes of primary particles of the low-pH gels aged for one year and of the intermediate-pH gels aged for one month. Again, a decrease in the fractal dimensionality is observed. Addition of fluorine to the reacting silicate solutions at low pH gives rise to a substantial increase in the rate of restructuring processes. A deviation from Porod's law may be discerned, which might be attributable to surface fractality; however, the experimental data in this region of the SAXS curve show a rather poor signal-to-noise ratio. Future experiments will be focused on the phenomenon of Porod deviation for these systems.

3.4. Influence of temperature on formation and ageing of aggregates

Aggregates and gels of silica, prepared as described in this paper, can be considered as systems far from equilibrium. From this point of view ageing is a (slow) reaction towards equilibrium and catalysts such as hydroxide or fluoride ions enhance the rate of this reaction. The same effect may be expected from a (moderate) increase in the temperature of the gelation and ageing reaction.

At pH = 4 a silica gel was prepared from potassium water glass. After standing for 2 h the reaction mixture was placed in a thermostat at 353 K. In the SAXS spectra in Fig. 6 it is shown that again the

Fig. 5. Influence of fluorine. SAXS spectra of (a) 0.0, (b) 0.01, (c) 0.1 mol NaF per mol silica. Spectra taken one month after preparation. pH = 4.0 and potassium waterglass.

Fig. 6. Influence of temperature. (a) No high-temperature ageing; (b) 24 h ageing at 353 K.

ageing process is accelerated: after heating for 24 h at 353 K the elementary particles have grown from molecular dimensions to approximately 7 nm. Also a considerable decrease in fractal dimensionality (from 2.2 to 1.8) is observed.

These considerations have led us to postulate a new description of the process of aqueous silica gels, which may be visualized as in Fig. 7. Ageing of silica gels prepared at pH = 4–8 can be seen as a densification of the aggregate kernel, accomplished by dissolution of the small silica particle at the periphery of the ramified fractal aggregates and precipitation in crevices and 'necks' in the center, ultimately resulting in a decrease of the fractal dimensionality of the aggregates.

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Fig. 7. Visualization of the ageing process.

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