

## Growth and aging phenomena in silica gels

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## Growth and Aging Phenomena in Silica Gels

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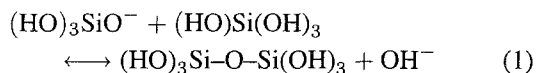
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**Abstract.** Growth and aging of silica aggregates are influenced both by temperature and by catalyzing fluorine ions as shown by SAXS and BET. It was found that both fluorine and increased temperature slightly increased the fractal dimension  $D_f$  during aging, but the fluorine catalyzed system showed a lower BET surface area.

To understand the effect of fluorine and increased temperature on the aggregates, 2D aggregations and SAXS simulations were carried out using two new programs GRASP and DALAI. In agreement with experiments it was found that binary RLCCA aggregates have a slightly higher  $D_f$  value compared to DLCCA aggregates and that branch-flexibility during aging increases  $D_f$  even further.

**Keywords:** aging in silica gels, growth, aggregation, X-ray scattering

Waterglass, a solution of silica in water at high pH, is the main source for large scale manufacturing of silica gels. Apart from monomers, many oligomeric species are present in water glass [1] due to the condensation/hydrolysis equilibria between  $\text{SiO}^-$  and  $\text{SiOH}$  groups formed by reactions like



The Si–O–Si angle can be very easily varied between  $90^\circ$  and  $150^\circ$ , leading to the formation of rings that are precursors to three dimensional structures, such as the prismatic hexamer, of which more than 20 different species have been identified using  $^{29}\text{Si}$ -NMR [2]. The equilibria between these species strongly depend on concentration, temperature, pH and the presence of cations. By decreasing the pH of a waterglass solution condensation is favoured over hydrolysis resulting in the formation of bigger oligomers. The ring formation and cross-linking form nearly spherical particles whose radii are determined by the negative charge on the surface (ratio of  $\text{SiO}^-/\text{SiOH}$  groups) and are there-

fore strongly pH dependent (1–2 nm at  $\text{pH} = 2\text{--}4$ , 100 nm at  $\text{pH} = 8\text{--}10$ ) [1].

Condensation reactions between groups of different particles lead to interparticle bonds. The stochastic distribution of the reactive groups on the surfaces of the particles causes the directions of the bonds to be arbitrary and the particle–particle interactions result in aggregates with no obvious, well defined structure. Interactions between aggregates are also possible, leading to highly ramified and extended aggregates. Ultimately, the growing aggregates contact each other forming a percolating system, the gel. The gel can be visualised as a network of interconnected aggregates, especially at low pH (small particles). Voids between aggregates or within their branches are still filled with a solution containing precursors, particles and small aggregates that are added gradually to the thin threads reinforcing the weak gelatinous system and extending the network.

The difference in surface energy causes silica particles at convex surfaces to dissolve relatively easily and to recondensate preferentially at low surface energy places, such as “necks” or crevices. This “Ostwald ripening” process is the main contribution to aging [1], the number of small particles decreases and the surfaces of the gel network are smoothed out, resulting in the strengthening of the network. This reinforce-

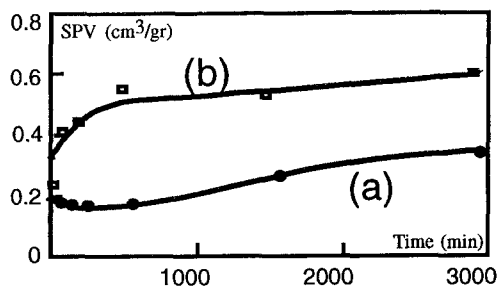


Fig. 1. Specific pore volume of silica prepared at different aging times. pH = 4, 4 wt% SiO<sub>2</sub>. (a) F<sup>-</sup>-catalyzed system (F/Si = 0.01), T = 23°C and (b) No catalyst, T = 80°C.

ment is necessary to withstand capillary forces during drying, without sufficient aging the weak gel structure collapses during drying and no porous structure is obtained [3, 4].

The study of the complicated aggregation, gelation and aging processes by “classical” physico-chemical methods is difficult because such methods disturb or even destroy the vulnerable structures. The best results have been obtained by scattering techniques (SAXS, SANS) using fractal concepts to describe the morphology [5, 6, 7], nondestructive techniques such as NMR and physisorption of N<sub>2</sub> (BET) on carefully freeze-dried samples [4, 8, 9]. We have studied aggregation, gelation and aging of acidified water glass at pH = 4 using synchrotron radiation (Daresbury Laboratory, UK). The interpretation of scattering data is often difficult and for this reason simulations of aggregation were carried out using program GRASP, an efficient implementation of the off-lattice cluster-cluster aggregation approach [7], and DALAI, a program to calculate the SAXS spectrum from the coordinates of the particles forming the gel [10]. The GRASP-DALAI combination permits direct comparison between experiment and simulation monitoring directly the influence of parameters on the SAXS spectra.

## 1. Results and Discussion

To study the influence of aggregation and aging on pore formation, silica gels were prepared by controlled addition of water glass (4 wt% SiO<sub>2</sub>) to a solution of hydrochloric acid until pH = 4 is reached. In one experiment a catalytic quantity of NaF (F/Si = 0.01) was added to accelerate condensation/hydrolysis reactions. After gelation the catalytic aging process was left to proceed at room temperature. Samples were taken at set times during aging and, after freeze-drying (to avoid

capillary effects), the specific pore volume (SPV) was determined by BET.

Acceleration of aging can also be achieved by increasing the temperature. To compare this last effect with the catalytic influence of F<sup>-</sup>, a silica gel without NaF was aged at 80°C. Again samples were freeze-dried at set times and the specific pore volume was determined. An appreciable difference between the two systems exists, as shown in Fig. 1.

To understand the difference in pore formation in Fig. 1 we have to realise that in system (a) the condensation/hydrolysis reactions are accelerated (F<sup>-</sup>-catalysed system), while raising the temperature in system (b) increases both the diffusion rates and the degree of internal movements (branch flexibility). This last effect would be a very important mechanism in the formation of aggregates composed of sub-nanometer particles [4] resulting in the reinforcement of the fragile network by ring formation and cross-linking. In contrast fluorine is believed to create active sites on the exposed tips of the aggregates causing rapid condensation and leading to the creation of elongated structures. This is confirmed by observed differences in the fractal dimension (Df) of aggregates in pre-gel systems [9]. Fluorine catalysed aggregation results in a rather low pre-gelation Df value (1.7), compared to 1.8 for non-catalysed systems and a higher post-gelation Df value of 1.9. Temperature aging leads to Df = 2. From this and from the difference in SPV (Fig. 1) we conclude that the aging processes prevailing in the two systems are not the same.

To study the role of condensation-activating agents (fluorine) and temperature aging (branch flexibility), simulations with the GRASP-DALAI combination have been performed. Fig. 2 shows snapshots of 2D simulations of a binary system with two types of particles called A and B. Particles A represent silica particles and particles B are considered to be silica particles with a fluorine attached to it. To simulate the catalytic influence of fluorine the sticking coefficient for AB bond formation is set to 1.0 while for AA sticking it is set to 0.001. It is believed that the charge of a fluorine atom causes it to repel other fluorine atoms. The sticking coefficient BB is set to 0.001 because the fluorines will tend to maximize their mutual distances and move to branch extremities, the “tips” of the aggregates [7]. This way the “catalytical” B particles caused a very effective screening of the aggregate “core” leading to fast growth of larger but more tenuous aggregates. The

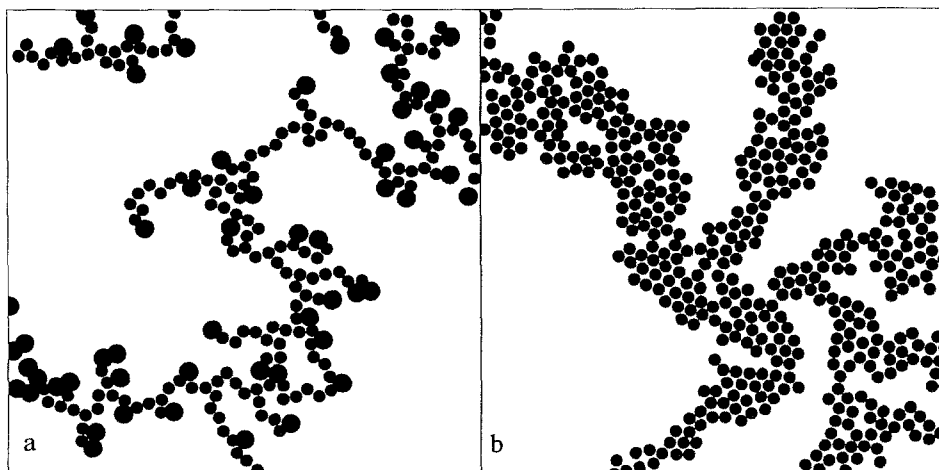


Fig. 2. a) Model for catalytic system: Binary system at the gelation point. The larger sphere are the active B particles. b) Model for temperature increase: Gelated system without fluorine after 20000 cycles of branch flexibility.

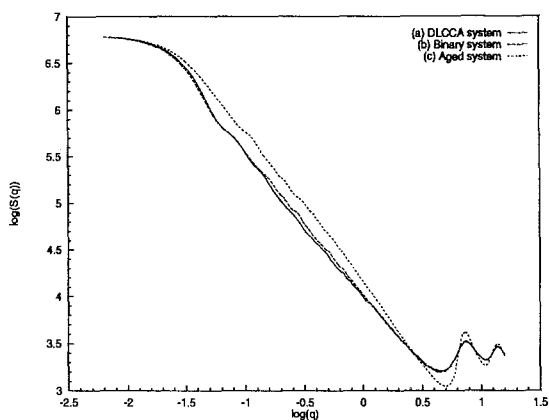


Fig. 3. Simulated structure factor profiles for 2D systems of 2500 particles at 10% volume conc. a) DLCCA single aggregate,  $D_f = 1.54$ . b) Binary system single aggregate with 30% B. Sticking coefficients  $AA = 0.001$ ,  $AB = 1.0$ ,  $BB = 0.001$ .  $D_f = 1.59$ . c) (a) after 20000 cycles branch flexibility.  $D_f = 1.64$ .

larger aggregates cause a decrease in gelation time and will have a rather low fractal dimension before gelation.

When gelation is reached, the active fluorine species will sustain rapid restructuring of the network and finally lead to a higher fractal dimension. The preliminary simulations presented here reproduce the decrease in gelation time observed experimentally [9]. Fig. 2b shows that branch flexibility in the gelated system causes densification and an expected increase in  $D_f$ . To calculate  $D_f$  for the aggregates shown in Fig. 2 DALAI has been used and the results are presented in Fig. 3.

It is known that in the zero concentration limit the fractal dimension for DLCCA aggregation (all bonds

formed at first contact) in 2D is 1.44 [7]. For higher concentration this value increases [10] and at the concentration we have used for these simulations (10 volume%) it is  $\sim 1.54$ , as shown in curve a). In the binary system of curve b) the changes compared to a) are small but discernible. The gelation time and the fractal dimension (1.59) are a function of the B/A mixing ratio, the concentration and the sticking coefficients, and it is therefore not surprising that the parameters used here lead to an optimum around  $B/A = 0.30$ , while the fractal dimension is hardly influenced by the modest reaction limitations we introduced. Curve 3c, where branch flexibility is activated (see Fig. 2b), shows that rings and thicker branches are formed and  $D_f$  increases to 1.63.

Furthermore, a striking change in Fig. 3 is the deep minimum appearing around  $q = 0.7$ , corresponding to the structure factor minimum of the new, composite, "primary" particles. The reaction limitations in the binary system give rise to a small dip, but the extensive branch flexing causes the minimum to develop further.

It is tempting to correlate gelation and aging according to Fig. 2 and Fig. 3 with the type of processes taking place in the system presented in Fig. 1. Physisorption experiments indicate the presence of slit-like pores in the catalysed aged gels suggesting the existence of elongated and weak aggregates [11]. On the other hand, thermal aging of non-catalysed systems seems to result in a greater degree of mass redistribution and structural reorganisation leading to more dense structures. The preliminary simulation (2D) results have to be confirmed by systematic calculations in larger (3D) systems including bond breaking, the effect

of which is determined by the values of a dissociation kernel in analogy to the association kernel employed by Kallala et al. [12]. It is clear though that conventional DLCCA or RLCCA models are not sufficient on their own in describing the complicated processes determining the final morphology. Similarly, SAXS is not sufficiently sensitive to small scale differences and other experimental techniques need to be employed in parallel. Therefore combination of experimental data and simulations is a powerful tool for the interpretation of data.

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