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Aggregation and aging in silica gel

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Abstract

Aggregation and aging of silica gels, prepared by controlled addition of water glass to hydrochloric acid, and the transformation of an aged gel to a crystalline phase have been studied in-situ using high-brilliance synchrotron radiation.

Small angle X-ray scattering (SAXS) has proved to be very informative in readily detecting transformations in the silica gels which can be described using the concepts of mass and surface fractality.

The interpretation of SAXS spectra of aged silica gels has been accompanied by computer simulations of aggregation and aging based on a model for the aging mechanism and the calculation of the corresponding structure-factor patterns. Comparison with experimental spectra of aged silica highlights the important role of particle growth on the fractal dimension.

Gel transformations during the transition from an amorphous gel to the crystalline phase of silicalite have been successfully monitored, in-situ, both for heterogeneous and for homogeneous preparations, using the combination of small and wide angle X-ray scattering (SAXS–WAXS).

1. Introduction

1.1. Silica gels

The use of amorphous silica gels as a supporting agent in heterogeneous catalysis requires a high specific surface and high stability. Although silica gels exhibit a large diversity in structural properties for many applications in selective catalysis, a tailor-made porous structure is necessary or very desirable.

When silica is prepared by addition of water glass (alkali solution of silica in water) to hydrochloric acid (HCl), polycondensation reactions occur between dissolved oligomeric silica species, resulting in (sub)colloidal particles [1]. These primary particles combine into aggregates with power-law dependent density (fractals), a process described by diffusion or reaction limited cluster aggregation [2,3]. For sufficiently high concentration gelation occurs which preserves the fractal structure at sub-micrometer scale, while at larger scale Euclidean behaviour is observed.

These freshly prepared silica systems often appear to be microporous after drying because the fractal structures are too weak to resist capillary forces or even gravity and the fragile aggregates collapse during the drying process. For this reason, reinforcement of the weak and tenuous structures by aging processes is necessary [1,4].

It has been proposed that silica is redistributed in the gel during aging [1]. Although this redistribution is based on simple hydrolysis and (re)deposition reactions of silica

monomers, oligomers or particles, many transformations and structures may be formed depending on process parameters (temperature, concentration, pH, catalysts). This results in the preparation of a wide variety of porous structures.

1.2. Scattering and simulations

The investigation of aging mechanisms is quite challenging. Understanding of aging reactions is essential in preparing tailor-made porous silicas on a scientific basis. Only non-invasive techniques may be used because of the vulnerability of fresh silica systems. This limits the choice of appropriate investigation methods. In addition, the extended length scale (more than 4 decades from sub-nanometer to a few microns) requires a combination of techniques. For this reason, progress in this field has up to now been very slow despite the industrial relevance and high commercial interest [1].

Since the advent of synchrotron radiation as a high-brilliance X-ray source, small angle scattering (SAXS) has proved to be a very suitable non-invasive technique for the study of colloidal and amorphous wet gels. It has opened new possibilities for studying mass density distributions during aggregation and aging processes using fractal concepts in quantifying these transformations and mass distribution changes [5].

During the preparation of zeolites, aging of precursor gels is a prerequisite for crystallization. Similar to silicas, these precursor gels are very difficult to investigate with

standard physical or chemical methods. Only scattering techniques such as SAXS, SANS and light scattering can give information concerning mass transformations. To study the cross-over from an amorphous gel to the crystalline state, the combination of small and wide angle scattering (SAXS–WAXS) is a real advance for the in-situ study of zeolite preparations. Disturbance of the vulnerable gels during sample preparation for X-ray diffraction (XRD), needed to determine the relation between the amorphous species and the crystalline phase and the onset of crystallization, can thus be avoided.

Computer simulations are extremely helpful in the interpretation of experimental results. The combination of the computer programs GRASP [6] and DALAI [7] permit the simulation of the aggregation and aging processes as well as the computation of the corresponding scattering patterns. Comparison with experiment provides an immediate check of the validity of proposed process models.

2. Experimental

Silica gels were prepared by pH-controlled addition of water glass, an aqueous solution of silica in sodium hydroxide at high pH between 12 and 14, to hydrochloric acid (Merck p.a.) [4]. Aging of wet silica gels was carried out at room temperature [8]. Silicalite was prepared according to both heterogeneous [9] and homogeneous [10] preparation recipes.

SAXS experiments were performed at the synchrotron radiation source (SRS) at DRAL, Daresbury Laboratory (UK) at the NCD station 8.2. Wet gels and solutions were measured in closed cells with Mylar (DuPont) windows (spacing 0.2–0.5 mm). Dried gels were fixed on Scotch tape (3M). The Q -range between 0.05 and 2.5 nm⁻¹ was covered at a fixed wavelength of 0.15 nm ($\Delta\lambda/\lambda = 4 \times 10^{-3}$), and by varying the camera length (sample to detector distance) between 1.0 and 4.0 m.

A quadrant detector was used to enhance sensitivity at low Q . Satisfactory signal to noise ratios were obtained with acquisition times between 1 and 5 min. When determining the slope of the scattering curve two possible sources of error may be distinguished. The first is the natural noise being present in the data, which is however small compared to the error introduced during background subtraction. Subtraction of parasitic (slits) and background scattering (water solution, mylar windows, Scotch tape) was applied using the procedure introduced by Vonk, adapted for fractal systems [11]. The error introduced during this procedure is larger than all other errors ($D_f \pm 0.05$).

The Q -range covered with WAXS is $8 < Q < 34$ nm⁻¹. The WAXS detector is a curved knife-edge INEL detector [12] with a spatial resolution of 50 μ m that can handle up to 100 000 counts s⁻¹. It can cover 120° of arc at a radius of 0.2 m, but only 90° of arc is used in these experiments.

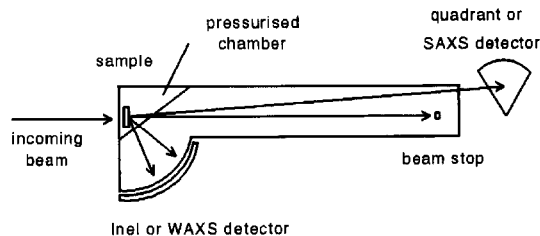


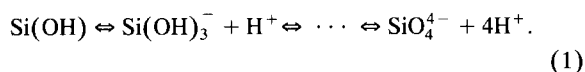
Fig. 1. Experimental set-up for SAXS–WAXS experiments.

More details concerning camera geometry and data collection were presented extensively elsewhere [13]. A fully crystallized specimen of zeolite A (NaA, Procter and Gamble) was used to calibrate the Q -axis of the WAXS pattern. The incident intensity was recorded by a parallel plate ionization detector. Appropriate attenuators were used in order not to exceed the data rates that both detectors can handle. The experimental data were corrected for background scattering, sample thickness and transmission and detector sensitivity. See Fig. 1 for the experimental set-up.

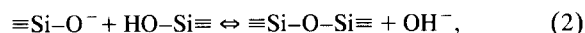
3. Results and discussion

3.1. Polymerization and aggregation of silica

In water glass, monomeric silica is present as a mixture of ions of silicic acid:



Condensation reactions lead to the formation of dimers as well as branched oligomers:



where three horizontal bars at Si represent bonds with OH, O⁻ or –O–Si≡ groups [1].

Because the Si–O–Si angle can be very easily varied between 90° and 150°, 3, 4, 5 or higher membered rings can also be formed, being precursors for three-dimensional structures [9].

Decreasing the pH of a water glass solution favors condensation over hydrolysis, resulting in bigger oligomers or polymers. This results in roughly spherical particles with only Si–OH and Si–O⁻ species at the surface. The pH and to a lesser extent concentration and temperature, control the Si–O⁻/Si–OH ratio and, therefore, the reactivity. These so called primary silica particles may form inter-particle bonds due to condensation reactions between SiOH and SiO⁻ groups on different primary particles. Because the distribution of reactive groups on the surface of the particles is stochastic, directions of particle–particle bonds are rather arbitrary. Interactions are not restricted to the formation of particle–particle or particle–aggregate

bonds. Interactions between aggregates are also possible resulting in tenuous, ramified aggregates with an extended amorphous structure.

If the silica sol contains sufficient silica, the growing aggregates ultimately contact each other forming a percolating system, the gel. In particular, at low pH (small particles) the gel can be visualized as a tenuous network of interconnected aggregates with the silica density mainly concentrated in the centers of the aggregates. The branches of the aggregates are relatively thin threads composed of chains of silica particles [14]. Voids between the aggregates or within the branches of the aggregates are still filled with a solution containing silica as monomers, oligomers, elementary particles and small aggregates. After the gelation point is reached, this silica is added gradually to the thin threads, reinforcing the weak gelatinous system (see also Section 3.4).

3.2. Fractals and small angle scattering

Fractal concepts are indispensable in the characterization of stochastic processes such as aggregation and the subsequent transformations during aging. Introduced to the scientific community rather recently (Mandelbrot's "The Fractal Geometry of Nature" was published in 1977 [15]), many phenomena in physics, chemistry and biology can be described using fractal principles, including aggregation [2,16].

In normal Euclidean geometry D the mass M of an object scales with its length scale R as:

$$M(R) \sim R^D \quad \text{where } D \text{ is } 2, 3, \dots \quad (3)$$

For a fractal structure the scaling of $M(R)$ is:

$$M(R) \sim R^{D_f} \quad \text{where } 1 < D_f < D. \quad (4)$$

In other words, the mass density of a fractal object is not a constant and the mass scaling with R (or any other representative length scale) is not an integer. As an example, in Fig. 2 a two-dimensional aggregate is shown with a mass density gradient. The aggregate is (in a statistical sense) self-similar. The same gradient in density distribution is observed on different length scales, resulting in a characteristic quantity or variable for the density gradient, the fractal dimension D_f .

Using the fractal concept, the D_f in Fig. 2 equals 1.45 [2,17]. The mass distribution in the center is distinctly different (higher average density) compared with the mass density in the periphery. This mass distribution and its gradient are determined by the physics of the aggregation process and therefore related to the process parameters. It should be noted, however, that for real systems the fractal region is normally restricted to length scales smaller than the size of the aggregate and larger than the size of the (non-fractal) primary particle.

A very important feature of SAXS is the direct infor-

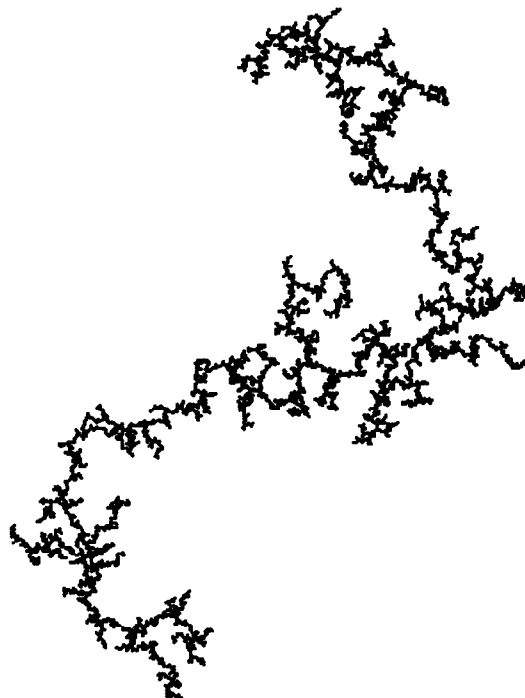


Fig. 2. Simulated fractal DLCA aggregate of 4900 monomers at $0.05v/v$ in 2D with $D_f = 1.45$.

mation concerning fractal properties. The number of elementary particles $N(R)$ in a fractal aggregate is given by:

$$N(R) \sim M(R) \sim \left(\frac{R}{R_0} \right)^{D_f}, \quad (5)$$

where R_0 is the radius of the primary particle. The scattering vector Q equals:

$$Q = \left(\frac{2\pi}{\lambda} \right) \sin 2\theta \sim \frac{1}{R}. \quad (6)$$

Combination of Eqs. (5) and (6) results in:

$$I(Q) \sim Q^{-D_f}, \quad (7)$$

i.e., the scattered intensity $I(Q)$ is proportional to D_f . The log-log plot of $\log I$ vs. $\log Q$ results in a straight line with slope $-D_f$ [18]. See Fig. 3.

Because in fractal aggregates the fractal region is restricted both by the size of the aggregate (upper size R_g) and the size of the primary particle (lower size R_0), the straight line in the log I -log Q plot has also a limited length. The cross-over at the low- Q limit represents the size (radius of gyration R_g) of the fractal aggregate. The cross-over at the high- Q limit represents the radius R_0 of the primary particle. The region $Q > Q(R_0)$ is called the Porod region whose slope is related to the (surface fractal) dimension of the surface of the primary particles.

$$\text{Slope} = D_s - 6, \quad (8)$$

where D_s is the (surface fractal) dimension. This D_s is a

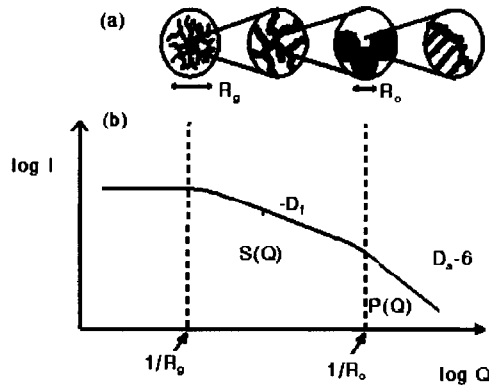


Fig. 3. (a) Logarithmic scaling of an aggregate, part of an aggregate, primary particle and part of a particle (surface). (b) Theoretical $\log I$ - $\log Q$ on the same scale and corresponding to (a).

measure of the “roughness” of the surface of the primary particles. In the case of monodisperse primary particles with a smooth surface, D_s equals 2 leading to a Porod slope of -4 [18,19]. Particles may also show a rough (fractal) surface. In these cases D_s lies between 2 and 3 leading to a Porod slope between 3 and 4.

3.3. Simulation

Since the pioneering work of Jullien et al. and Meakin in 1983, computer simulations of fractal growth have given an extremely important contribution to the development and understanding of fractal concepts in growing aggregates (for a review see Ref. [2] and [20]).

Up to now, the prediction of fractal dimensions or the position of the high- and low- Q limits of the fractal region can not be made using analytical methods. For example, it is rather difficult to predict a priori the change in fractal dimension due to hydrolysis and condensation or due to growth of primary particles by ring formation *without* hydrolysis effects [2,20]. For this reason large scale computer simulations have had to be employed. These have proved very useful in studying the transformation of a “solution” (sol) of particles into a continuous three-dimensional network (gel) and for examining relations between physical parameters and fractal properties during aggregation and aging of the systems.

The method of diffusion limited cluster aggregation (DLCA) has been applied in many simulations. In this type of simulation, particles are placed in a box and subjected to Brownian motion (random walk). Aggregation may occur when two or more particles contact, leading to bond formation. The combined aggregate continues the random walk and may form new bonds with other particles or aggregates. The simulation is stopped at the gelation point (percolating system) or when all particles are combined in one final aggregate. In 2D the D_f of DLCA aggregates is

1.45, while the predicted value for 3D is 1.77 in good agreement with the experimental value [2,20].

In the case when the reactivity is not limited by diffusion but by the rate of reaction between colliding particles or aggregates, the aggregation process becomes reaction limited (RLCA). Although the ramified aggregates appear to be rather similar to the DLCA aggregates, the fractal dimension increases to 2.1. This can be explained by the observation that during growth of a DLCA aggregate the majority of particles approaching the aggregate collide with the outermost particles or branches. In this way the inner part of the aggregate is screened rather effectively. However, if only a small percentage of the collisions is successful and results in the formation of a bond (as in reaction limited situations), particles may overcome the screening of outermost branches and react with branches nearer the core of the aggregate. This results in a more compact structure with a smaller mass gradient and higher D_f . Recent calculations [3] have shown that by varying the reactivity according to the local coordination, a continuous array of D values can be produced.

During aggregation and aging of silica a great variety of D_f values has been found using SAXS or SANS. Computer simulation can be usefully employed to interpret these observations. We developed, GRASP an off-lattice box program for the formation of aggregates using cluster-cluster aggregation, including DLCA and RLCA and several aging algorithms such as single and random bond breaking, internal aggregate flexibility and shrinking [6]. The aggregate coordinates obtained are passed to DALAI, a program to calculate SAXS or SANS patterns from particle coordinates [7]. The patterns produced by the GRASP/DALAI combination can be used to test the influence of physical parameters on the scattering pattern and to compare the simulated with the experimental profiles, as well as for the determination of fractal properties such as D_f , R_0 and R_g of a simulated aggregate.

3.4. Aging of silica gels

The silica gel that is formed during the gelation of the silica sol is still far from thermodynamic equilibrium. Aging processes modify the morphology of the network. One of these aging processes is the continuous hydrolysis and (re)condensation through the dynamic equilibria of Eqs. (1) and (2). Differences in surface energy cause silica at highly curved surfaces (convex surfaces) to dissolve relatively easily and to recondense preferentially in the “necks” between particles or in the crevices in the center of the aggregates (concave surfaces). This effect (Ostwald ripening) decreases the number of small particles and smooths the chains or surfaces of the gel network. It is believed to be the main contribution to the aging process [1]. During aging the gel network is reinforced considerably and can therefore better withstand the capillary forces

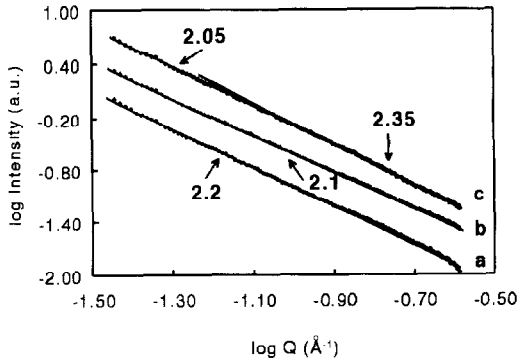


Fig. 4. SAXS curves of silica gels (4 wt.%) aged for various times at room temperature: (a) 1 week, (b) 2.5 months, (c) 5 months.

during drying, resulting in a porous structure after drying. Without sufficient aging the weak gel structure collapses during drying and microporous silica is produced [1,4].

The SAXS spectra confirm Ostwald ripening during aging. In Fig. 4 three SAXS curves in a $\log(I)$ – $\log(Q)$ plot are shown at various aging times.

The spectra in Fig. 4 are rather difficult to interpret. The straight line of curve (a) suggests that we are dealing with an extended fractal region. The SAXS “window” (Q -range) is too small to contain the cross-over points to non-fractal regions at both low and high Q [4]. Curve (b) shows that D_f decreases and curve (c) shows a split-up into two regions. D_f has increased at high Q and decreased at low Q .

Both aging experiments and SAXS spectra, indicate that aging is much more complicated and can not be described by Ostwald ripening alone. For example, in wet gels a considerable shrinking and discharge of water dur-

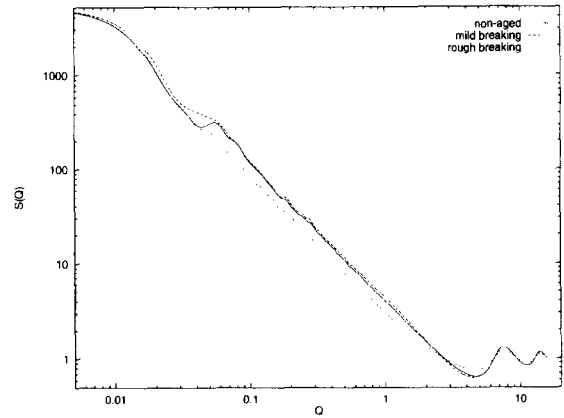


Fig. 5. Effect of mild and rough breaking of single connected monomers.

ing aging is observed. To explain these phenomena one has to assume changes in the structure at a relatively large scale compared to smoothing of branches. As mentioned before, in many experiments SAXS spectra show a decrease of the fractal dimension during aging, although both from intuition and from simulations [3,20] an increase would be expected during restructuring.

To explain the growth of primary particles and the (slight) decrease of the fractal dimension during aging, an aging mechanism has been postulated [4] based on a scheme whereby the hydrolysis of primary particles at the periphery of the aggregates (dissolution of the outermost branches), is followed by migration through diffusion towards the center of the aggregates and re-combination in the inner crevices. Preliminary simulations with the

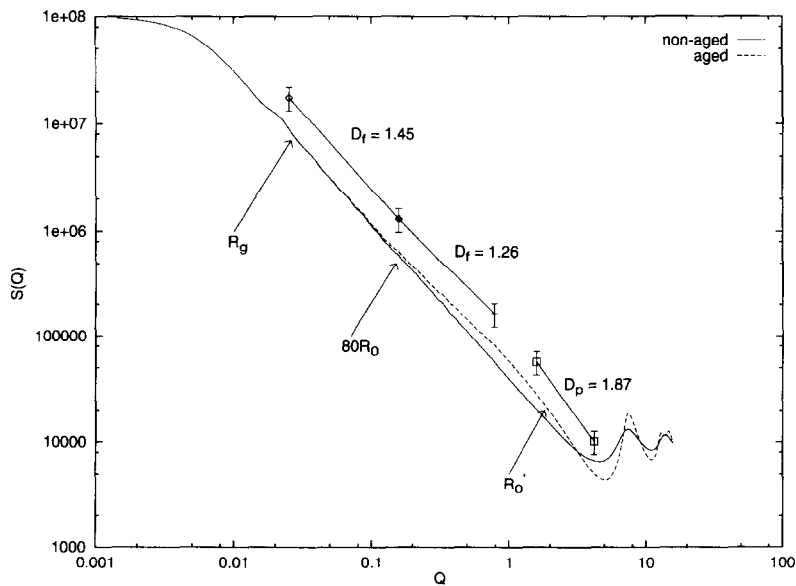


Fig. 6. Simulated SAXS patterns before and after aging by local reorganization.

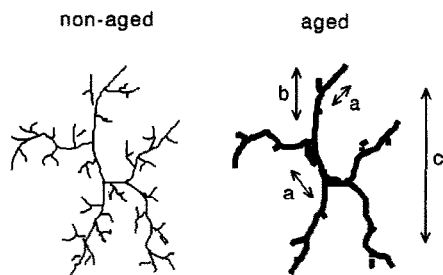


Fig. 7. Pictorial view of aging by local increase of density.

GRASP/DALAI combination, however, clearly showed that hydrolysis alone will not lead to a decrease in the fractal dimension with a concomitant particle growth. Two types of simulations were carried out, starting from a single aggregates of 4900 monomers in 2D at $0.05v/v$. 25 000 aging steps were performed.

For the first type, called mild breaking, 10% of all the single connected monomers that are bonded to other single or double connected monomers are hydrolyzed. This attempts to mimic the breaking-off from the periphery to allow for inward diffusion. For the second type, called rough breaking, 10% of *all* single connected monomers are hydrolyzed, making the breaking process connectivity independent.

In Fig. 5 the structure factors of the starting system and the systems after mild and rough breaking for 25 000 steps are shown. It is clear that mild breaking has a negligible effect on the morphology of the system. Rough breaking causes a decrease in D_f only at short length scales. Both simulation types show no decrease in D_f on longer length scales and no primary particle growth.

Much more successful were recent simulations based upon local reorganization of aggregates. In this model the monomers were allowed to perform small movements with respect to each other, a process called shaking [17]. Any overlap detected resulted in bond formation. This reinforces the thin branches. In Fig. 6 simulated (two-dimensional) patterns are shown, calculated from the simulated aggregates before and after aging by local reorganization.

The $D_f = 1.45$ value before aging has decreased to 1.26 at low Q (large scale effect) and increased to 1.87 at high Q (local effect). These 2D results agree very well with the experimental 3D spectra shown in Fig. 4, and can be explained by assuming different effects of local reorganizations at small and large length scales (see Fig. 7).

At small length scales (scale a) the density of silica has increased resulting in a lower density gradient and therefore an increase in fractal dimension. At large length scales (scale c), however, mass is even more concentrated in the ‘linear’ branches without changing the overall morphology and therefore resulting in an increase of the mass gradient and corresponding decrease of D_f . Although we do not believe local reorganization is the only aging

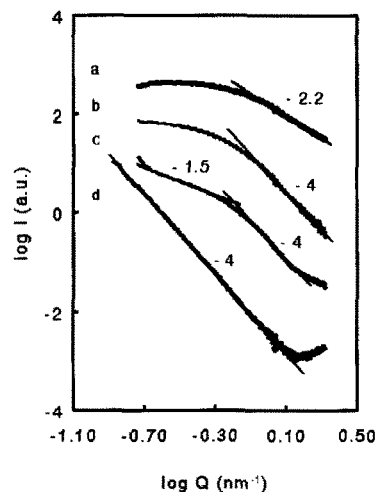


Fig. 8. SAXS curves during preparation of silicalite. (a) 5 minutes, (b) 35 minutes, (c) 75 minutes and (d) 105 minutes.

mechanism, the agreement with fractal properties of aged systems indicates that this type of aging probably makes an important contribution to aging.

4. SAXS–WAXS investigations on silicalite

Similarly to silica gels, precursors of zeolites and molecular sieves are also kinetically determined colloidal systems and far from thermodynamic equilibrium. However, unlike silica gels, special reaction conditions and templates transform zeolitic gels into crystalline species. In order to investigate the influence of reaction conditions on the aging and crystallization of zeolite precursors, in the amorphous and crystalline phase simultaneously, without disturbing the vulnerable structures by sample preparation,

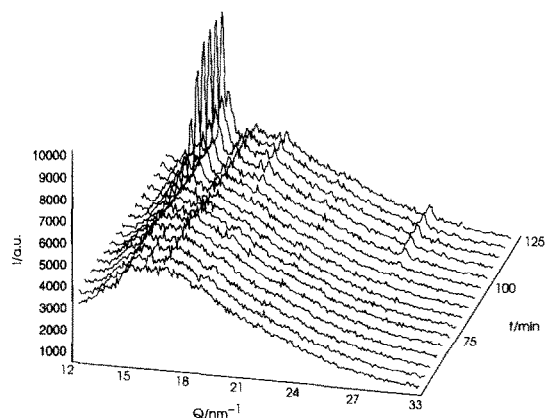


Fig. 9. WAXS curves during preparation of silicalite. Diffraction peaks start to develop after 50 minutes of reaction demonstrating the formation of micro-crystalline regions.

combined small and wide angle X-ray scattering experiments are necessary. This aim has been achieved with the recently developed SAXS–WAXS technique [13].

To obtain information concerning the nature of the precursor gel and whether nucleation occurs within the gel or from the mother liquid of the synthesis mixture, silicalite was prepared both heterogeneously from a gel [9] and homogeneously starting from solution [10]. Although reaction conditions were different (190°C and 120°C, respectively, and slightly different reaction mixtures), SAXS–WAXS spectra were very similar and are shown in Figs. 8 (SAXS) and 9 (WAXS) for the homogeneous preparation.

The SAXS spectra are characterized by the cross-over from a fractal (soluble) gel ($D_f = 2.2$) into growing non-fractal species with a smooth surface (slope = $-4 \rightarrow D_f = 2$). The onset of crystallization corresponds to the cross-over to the non-fractal particles. Therefore, it may be concluded that crystallization occurs within non-fractal precursor gels, transformed from primary species during aging.

5. Conclusions

In-situ X-ray scattering with synchrotron radiation has been successfully applied in the study of aggregation and aging of silica and zeolites. Transformations on colloidal scale in wet gels can be characterized using the fractal dimension parameter, D_f , easily extracted from the SAXS spectra.

We have shown that the combination of X-ray scattering techniques and computer simulations is a new and very promising approach to the study of transformations in colloidal systems and that it may be applied successfully in the investigation of the preparation of silicas and zeolites.

In zeolites, precursors of the crystalline phase are characterized by surface fractals. In-situ SAXS–WAXS experiments revealed the cross-over from amorphous to crystalline systems. The transformations occurring in the amorphous zeolite precursors can be directly related to the onset of crystallization.

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