

Structural development in silica systems

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STRUCTURAL DEVELOPMENT IN SILICA SYSTEMS

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ABSTRACT

Results obtained with small angle neutron and X-ray scattering will be presented of systems with various silica concentrations. Silica gels with low silica concentration exhibit uniform mass fractal behaviour and after prolonged aging, dual mass fractal behaviour. A zeolite (silicalite) synthesis precursor gel with a high silica concentration was also investigated and was found to exhibit surface fractal behaviour. A model is presented, explaining the occurrence of dual fractality after prolonged aging. The change-over from mass fractal behaviour to surface fractal behaviour is explained, supported by scattering spectra calculated from simulated aggregate structures.

INTRODUCTION

Silicas are used for many different applications, which is due to the wide structural and morphological diversity of these materials. They are used as filling agents, filter materials, in ceramics and also as support for heterogenous catalysts. Furthermore silica is the main component in most of the zeolites, form selective and possibly bicatalytic (redox and acid) crystalline catalysts [3].

During the preparation of silica several reaction steps occur after acidification of an alkali silica solution (waterglas). First the monomers and oligomers will combine into particles, which will aggregate depending on reaction parameters. After aggregation and possibly gelation, aging or reorganisation reactions will become the dominant reactions in the system.

During aging, through several reorganisation reactions [2,4], the pore structure is formed in the silica gels. Reinforcement of the structure in the wet phase is desired, because during drying a collapse of the structure may occur due to the very high capillary forces which will work on the pore walls of the silica structure [4].

Aging steps also play a very important role in zeolite synthesis. In the induction period, before crystallisation, one or more gel transformations occur [7] until a phase is formed from which the last transformation, nucleation and subsequent crystallization, can occur. These phase transitions might be based on related molecular principles as the aging processes occurring in the wet silica systems.

Characterization of amorphous phases, without alteration of the structure present in the wet gel phase, can be performed with suited spectroscopic techniques. ^{29}Si -NMR [8] is a non-destructive technique, limited however to the direct surroundings of the silicon atom. Furthermore application of ^{29}Si -NMR is limited to concentrated wet gels, due to the low natural abundance of ^{29}Si . Small angle scattering of X-rays (SAXS) or neutrons (SANS) can provide information on length scales from 1 nm up to 100 nm.

The concept of the fractal dimension [9] is very useful in interpreting the small angle scattering data [10,11]. Mass fractal structures exhibit a mass gradient in the aggregates according to: $M \sim R^{D_f}$, with M the mass, R the radius and D_f the mass fractal dimension of the aggregate. Surface fractal structures also show a power law behaviour, but in the

development of the surface area (S) as a function of the radius (R): $S \sim R^{D_s}$, with D_s being the surface fractal dimension [12]. These power law exponents and the sizes of the aggregates and constituting particles can be easily deduced from a log-log presentation of the scattering spectra.

Computer simulations provided useful information about aggregation processes and the relative roles of diffusion and reaction herein [13,14,15]. Recently also processes accompanied and followed by rearrangements have been studied by simulation [16,17,18]. In this study the structure of silica gel as a function of aging and the effect of concentration on the structure is studied with small angle scattering. The results will be discussed and the proposed model for the concentration effect is supported by computer simulations.

EXPERIMENTAL SECTION

Small angle scattering

SAXS experiments were performed at the synchrotron radiation source at Daresbury Laboratories, United Kingdom, using beam line NCD 8.2. The Q -range covered in the experiments was 0.035 - 0.28 nm^{-1} . Typical acquisition times are 5 min. of X-ray exposure. Accurate and reproducible results are obtained by digitization of the scattered intensities up to 400 data points per measured spectrum. Corrections for background scattering and solvent were performed using the procedure introduced by Vonk [19].

SANS experiments were performed at the Rutherford Appleton Laboratory, ISIS facility, Abingdon, United Kingdom. Pulsed neutrons with wavelengths in the region 2.2 - 10 \AA were used in the LOQ diffractometer and were recorded on a 64 cm diameter position sensitive detector at 4.3 m from the sample. Scattering vectors between 0.005 and 0.23 \AA^{-1} were obtained, providing information on distance scales from roughly 20 to 1000 \AA in a single measurement. Wavelength dependent corrections for sample transmission and detector efficiency have been included in the data reduction procedure to obtain a composite cross section in absolute units. Corrections have been made for the incoherent scattering of the hydrogen atoms of the template molecule used in zeolite synthesis.

Materials

Aqueous alkali silica (water glass) was prepared by dissolving silica (Aerosil 380, Degussa AG) and sodium hydroxide (Merck p.a.) in the appropriate ratio in demineralised water. Gels were prepared by the addition of water glass to a solution of hydrochloric acid in polyethylene containers under vigorous stirring at room temperature until the desired $\text{pH}=4$ was reached. The concentration of silica in the prepared reaction mixture is approximately 4 wt\% . Gelation was detected when no meniscus deformation was observed on twisting the container. No detectable shrinkage of the silica gel was observed during aging.

Zeolite precursors were prepared using Aerosil 380 (Degussa AG) as a silica source. Appropriate amounts of sodium hydroxide (Merck p.a.) and D_2O (demineralized) were added as well as the template tetrapropylammonium bromide (Aldrich Chemie 98%), in the following molar ratios: $\text{SiO}_2/\text{TPA}=6.25$, $\text{SiO}_2/\text{NaOH}=12.8$ and $\text{D}_2\text{O}/\text{SiO}_2=13.8$ [20], resulting in a silica concentration of approximately 20 wt\% . (D_2O was used because ^2H has a negligible incoherent scattering contribution compared to ^1H).

RESULTS AND DISCUSSION

Silica systems are prepared by adding appropriate amounts of water glass to hydrochloric acid. The silica concentration present in the reaction mixture increases gradually during the addition of the water glass to the acid but never exceeds 4 wt%, the amount present at the reaction pH. From that moment on the species are allowed to react and will build primary particles and aggregates from these primary particles. If a cluster large enough to span the entire reaction vessel is formed, gelation will occur. From that moment on aging processes, not visible before due to the high rates observed for the aggregation process, will be the dominant process occurring in the wet gels.

The zeolite precursor gels are prepared by addition of Aerosil 380 to a template ion, sodium hydroxide and water. Compared to the silica gels this mixture has a higher concentration silica (approx. 20 wt%), a higher pH (13) and an organic structure-directing salt has been added. When this mixture is heated to reaction temperature (hydrothermal, 150°C), gel transformations will take place resulting in nucleation and crystal growth of silicalite.

In figure 1 the SAXS spectra are shown of a gel with 4 wt% silica at pH=4 aged for various times. The slopes exhibit power law behaviour over the entirely observed Q-range. The observed scattering slope α varies between approximately -2 and -2.35 indicative of mass fractal behaviour. After one week reaction (figure 1a), a mass fractal dimension of 2.2 is observed, indicating a reaction limited cluster cluster aggregation process (rlcca). Reaction limited indicates that the particles will not stick on every collision with another reactive particle, leading to more dense structures than diffusion limited aggregation processes.

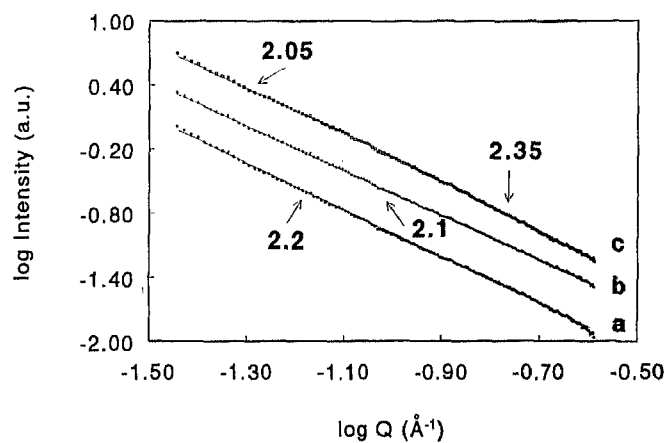


Figure 1: Small angle X-ray scattering curves of 4 wt%, pH=4 silica samples aged for various times: (a) 1 week, (b) 2.5 months and (c) 5 months.

After 2.5 months (figure 1b) aging a small decrease of the fractal dimension to 2.1 is observed, contrary to a densification normally expected to be caused by aging. After aging for 5 months (figure 1c), dual fractality is observed in the SAXS spectrum. At small Q (large R) the fractal dimension is decreased to 2.05 while at large Q (small R) the fractal dimension is increased to 2.35.

Curve a (figure 1) shows a slight deviation from power law behaviour at $\log Q \approx 0.8 \text{ \AA}^{-1}$, due to a hump (instrument artefact) superimposed on the scattering signal. This is not visible in curve b and c because of the higher intensity of the incoming (synchrotron) beam during these experiments.

After aggregation aging processes become dominant in the gel resulting in a reorganisation of silica particles possibly by transport of monomers. The initial decrease of the fractal dimension can be understood by the following internal reorganisation process of the aggregates. Silica particles will start to redissolve at high energy positions and will redeposit on low energy positions. Particles dissolving at large length scales or in the peripheries of the aggregates will be able to move to other branches. Particles dissolving in the cores of the aggregates will meet a lot of adjacent neighbours, resulting in a densification of the backbone without migration of silica over many monomer distances. This model will lead to a densification at small length scales (figure 2a) resulting in an increase of the fractal dimension. At larger length scales a decrease of the fractal dimension is expected due to the fact that small side branches will become part of the backbone, thus increasing the linearity of the structure resulting in a decrease of the fractal dimension (figure 2b). On even larger length scales (figure 2c) however, no change is expected because the basic structure of the aggregates is not altered by these local reorganisation processes.

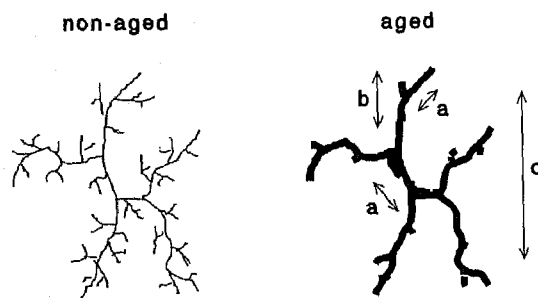


Figure 2: Effects of local reorganisations on structure on small (a), intermediate (b) and large length scales (c).

After 2.5 months aging a decrease of fractal dimension was observed over the whole Q -range, thus no dual fractality was observed at small length scale (high Q). The densification of the backbone has not proceeded enough to larger length scales ($Q < 0.28 \text{ \AA}^{-1}$) to be visible in the available Q -range.

The dual fractality observed after 5 months aging is in agreement with the aging mechanism proposed above. The fractal dimension of 2.35 observed at large Q (small length scale) is indicative for a densification of the cores of the aggregates. From the inflection point visible at $\log Q = -1.09 \text{ \AA}^{-1}$ it can be concluded that this densification occurs from 39 \AA downwards. The decrease of the fractal dimension expected at larger length scales due to the reduction of the number of small side branches, is also visible.

The zeolite precursor systems show a completely different behaviour. In principle two factors may be responsible for this behaviour namely the high silica concentration and the pH. The primary particle size of silica systems increases with increasing pH. The zeolite reaction mixture does however have a pH of 13 at which silica particles tend to dissolve. We therefore exclude the pH as a possible factor for causing the observed behaviour.

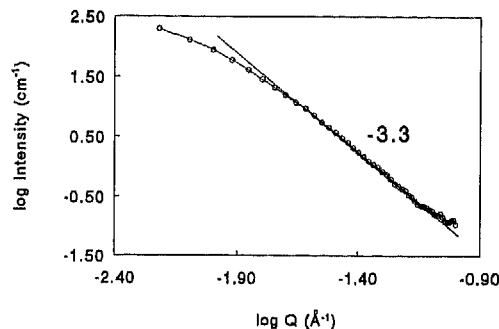


Figure 3: Small angle neutron scattering spectrum of a non-reacted silicalite precursor mixture

In figure 3 the small angle scattering spectrum of a non-reacted (room temperature) zeolite precursor gel is shown. In the spectrum power law behaviour can be observed with a deviation of this power law at small Q , large length scales. The slope of the scattering curve α appears to be 3.3, indicative for scattering from a fractal rough surface with a surface fractal dimension of 2.7, a very rough surface structure. The size of the surface scattering particles can be obtained from the deviation of power law scattering and appears to be 140 Å.

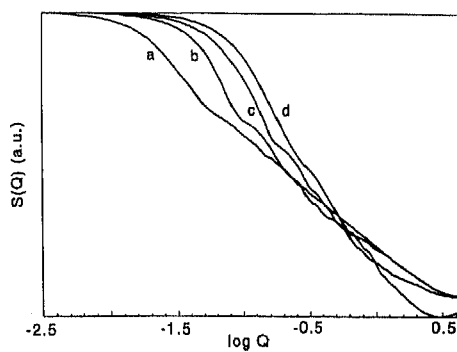


Figure 4: Structure factor (mass fractal dimension) as a function of concentration for various concentrations: (a) 0.25 vol%, (b) 5.0 vol%, (c) 15.0 vol% and (d) 30.0 vol%.

In figure 4 calculated structure factors of small angle scattering spectra are shown of diffusion limited cluster cluster aggregation simulations performed in 3 dimensional space with 27,000 primary particles. Increasing the concentration results in a shift of the mass-fractal behaviour ($D_f = 1.74$) first observed over the entire Q-range (0.25 vol%) to larger Q, while at smaller Q-values a homogeneous dense structure is observed. At 30.0 vol% this homogeneous dense structure ($D_f = 3.0$) is observed over the entire Q-range. Surface fractal behaviour will not be observed because the scattering form factor ($P(Q)$) has not been included in the simulation of the scattering spectrum.

These simulations show that the fractal dimension is dependent on the concentration. A similar behaviour is found for a low concentration wet silica gel and a high concentration zeolite precursor gel, exhibiting mass fractal and surface fractal behaviour respectively. Furthermore dual fractality has been found to occur in prolonged aged silica systems. Computer simulations describing the phenomenon of dual fractality will be published elsewhere.

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