SAXS STUDY OF SILICA GEL FORMATION FROM AQUEOUS SILICATE SOLUTIONS

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In situ SAXS measurements of silica gel formation in the presence of different cations are presented as a function of reaction time. Conditions used are similar to those applied to prepare catalyst supports. The data can be interpreted in terms of aggregation of elementary silica particles with sizes of approximately 1 nm, thus finally forming a continuous silica gel network. The aggregates are fractal with respect to their masses, in the range 2–10 nm. The dimensionality of the fractals can be determined from the SAXS curves; it increases from 1.8 to 2.5 during gelformation, corresponding with a diffusion limited aggregation process (DLA) of gel formation followed by densification of the silica gel network. The finding that the rate of change in fractal dimensionality does not change as a function of cation, indicates strongly that gelformation is a diffusion limited aggregation process.

1. Introduction

The formation of silica gels and silica powders has been of interest since many years. Recently, the application of fractal theory [1] to physical systems brought new light in the study of silica gel structures. During gelformation structures with fractal dimensionalities may be formed. Since silica gels are often used as catalyst supports, they can be used to investigate the effect of the fractal silica gel dimensionality on the catalytic reaction kinetics [2]. However, only few studies on the preparation of silica gels with particular fractal dimensionality and structure have been reported. Especially the influence of differences in mother liquid composition on the final structure of silica gels have not yet been investigated.

In a former study [3], by using ^{29}Si -NMR we encountered a profound effect of alkali metal cations on the dissolution rate of amorphous silica gel in aqueous solutions. Since ^{29}Si -NMR is not very informative concerning the structure of aggregates and gels in the size range 1–100 nm, small angle X-ray scattering is used to investigate gel structures in solution. According to recent reports [4–7] SAXS enables the characterization of silica systems that have fractal dimensional-

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ity. Notably, studies on silica gel formation by hydrolysis of tetra alkyl orthosilicates have demonstrated the fractal behaviour of gels formed through this route [4].

Present research has been undertaken to investigate the feasibility of small angle X-ray scattering (SAXS) in determining differences in gel structure starting from aqueous water glass solutions [3]. In this report, we show that also gels formed by acidification of aqueous alkali metal silicate solutions exhibit fractal behaviour in SAXS curves as well; the gelation and subsequent densification (aging) processes can be followed in time and are characterized by the increasing (mass) fractal dimensionality and the size of the fractal aggregates.

2. Experimental section

Water glass solutions have been prepared by dissolution of pure pyrogenic silica gel (Aerosil 380, ex Degussa) in *pro analysi* KOH (Merck, Darmstadt). PTFE (Teflon) containers were used to minimise contamination of the reaction mixture with metal ions, leached out from the container wall. The molar composition of the silicate solutions was 2 KOH : 3 SiO₂ : 108 H₂O, a composition comparable with commercial water glass solutions. The gelation of silica gel was initialised by adding appropriate amounts of silicate solution to 4N HCl (Merck p.a.) solutions to which small (1 mol% with respect to the silica gel) amounts of polyvalent cation salts were added (CaCl₂, MgCl₂, Al₂(SO₄)₃ Merck p.a.). The slowly gelating reaction mixture (*pH* = 2.0 or *pH* = 3.45) was introduced in a SAXS cel with thin mica or mylar windows and a spacing of approximately 1 mm. The SAXS measurements were carried out on the gelating reaction mixture at room temperature (± 295 K). The intense monochromatic X-ray beam ($\lambda = 0.1542$ nm) at the Synchrotron Radiation Source at Daresbury Laboratory (U.K.) had a point like cross section (no desmearing of data was necessary to correct for slit height/width effects) and the scattered X-rays were detected by a 1-dimensional position sensitive detector carrying 512 ionisation chambers. The sample to detector distance was chosen to be 205 and 160 cm, whereas acquisition times were chosen 10 or 20 minutes (indicated in text).

3. Results and discussion

Figure 1 shows SAXS curves of gelating silicate solutions measured at 85, 210 and 650 minutes after acidification of the water glass at *pH* = 2.0. The intensity of the scattered radiation is given in arbitrary units. During gelation a slow but significant increase in the intensity of the scattered X-rays could be detected; a threefold increase at $h = 0.1 \text{ nm}^{-1}$ from $t = 85$ to $t = 650$ min was observed. This increase is ascribed to the growth of surface area of the silica aggregates by the

Fig. 1. Small angle scattering curves of gelating aqueous silicate solutions ($pH = 2.0$) at 85, 210 and 650 minutes. Acquisition time per curve: 10 min.

addition of silicate monomers, oligomers and small clusters to the aggregates resulting in enhancement of scattering at smaller angles.

Each curve exhibits a linear region approximately between $h = 2 \text{ nm}^{-1}$ and 0.5 nm^{-1} ($t = 85$ minutes) or 0.2 nm^{-1} ($t = 210$ min and 650 min) ($h = 4\pi(\sin 2\theta)/\lambda$) when $\log(I)$ versus $\log(h)$ is plotted (fig. 1). Analysis in terms of a power law

$$I(h) = a \cdot h^{-D}$$

yields a value of the fractal dimension D from 1.8 to 2.5. Similar observations have been made on samples at $pH = 3.45$. The exponent D relates to the fractal dimensionality for a certain range of length scale, which for aggregates will be approximately between the diameter of the individual particles and the overall size of the aggregate. The extension of this scale may be estimated from the h -interval over which the corresponding power law is obeyed. The deviation from Porod's law ($I(h) = b \cdot h^{-4}$) have been observed by many authors for different types of silica (for example aerogels [5], colloidal aggregates [6], silica gels formed by controlled hydrolysis of tetra ethyl orthosilicates [7]). Especially the excellent

review articles of Martin and Hurt [8] and Ramsay [9] give a good overall picture of the fractal properties of silica gels derived from SAXS or SANS spectra in the Porod region.

The present study shows that also silica gels prepared from water glass solutions, consisting of a mixture of monomers, oligomers and even sub-colloidal particles of silicic acid, at $pH = 2.0$ and 3.45 also give rise to deviations from the Porod law.

According to Iler [10] the polymerization reactions at low pH are slow compared to polymerizations at higher pH values. Moreover, dissolution of small particles in favour of formation of larger spherical silica particles is negligible. This is consistent with our finding, that the elementary silica particles, forming the primary building blocks of the silica gel, are smaller than 1 nm and not growing. This results in an exceptional high upper limit of h in the range of self similarity.

The low initial value of the fractal dimension ($D = 1.8$ at $t = 85\text{ min}$ for gel formation at $pH = 2.0$) indicates that the aggregates have a very open structure. This value of D is similar to the value of 1.75 which has been predicted by a computer simulation for cluster-cluster aggregation [8]. In this process an assembly of Brownian particles stick together upon contact to form clusters. The newly formed clusters diffuse along with the particles and continue to grow when they meet other particles or clusters, the growth process resembling diffusion limited aggregation. However, the gels formed by cluster-cluster aggregation are much more ramified than the aggregates in DLA (Diffusion Limited Aggregation) models [11].

Figure 2 shows the increase of fractal dimension at $pH = 3.45$ in relation to the reaction time. From this figure it may be concluded that initially very tenuous or even linear clusters are being formed which aggregate in a cluster-cluster aggregation-way to more dense particles with larger values for the fractal dimension D .

Further, the increase in fractal dimension as a function of reaction time appears not to be dependent on polyvalent cations, present in $1\text{ mol\%}$ concentration. This observation confirms the assumption that the aggregation is limited by diffusion of Brownian particles or clusters to other aggregates and is not limited by the kinetics of the corresponding chemical reaction. Densification of the core of the aggregate also leads to increase in fractal dimensionality. Parallel with the increase of fractal dimensionality, the size of the fractal units, as estimated from the lower h -limit, increases as well (see fig. 3). This seems to indicate growth of the ramified structures. In contrast with the observation that fractal dimensionality is not influenced by different cations, the size of the aggregates formed in the presence of additional polyvalent cations depends on the cations. Growth of the aggregate is retarded by trivalent aluminum cations. Adsorption of these cations increases the positive charge of the silica gel particle surface thus decreasing the amount of reactive anionic surface sites.

Fig. 2. The increase of fractal dimensionality as a function of reaction time and additional polyvalent cations. Δ : Al; $\circ$: Ca; ∇ : Mg; $+$: K. pH of the solutions: 3.45. 1 mol% cations with respect to SiO_2 . Acquisition time: 20 min.

Non-fractal behaviour is encountered when a silica sol of monodisperse particles prepared at high pH values is studied. This is illustrated in fig. 4. The slope in the $\log(I)$ vs $\log(h)$ plot is approximately -4.0 , a value to be expected for non-fractal systems.

Our results indicate that silica gel formation in aqueous silicate solutions can be followed as a function of time by small angle (X-ray) scattering and the

Fig. 3. The increase of fractal sizes as a function of reaction time and additional polyvalent cations. Δ : Al; $\circ$: Ca; ∇ : Mg; $+$: K. pH of the solutions: 3.45. 1 mol% cations with respect to SiO_2 . Acquisition time: 20 min.

Fig. 4. Small angle scattering curve of a 0.4 wt% silica sol (Ludox AS 40). Acquisition time: 10 min.

intermediates in the catalyst support preparation process can be analysed and identified with respect to the dimensionality and size of the gel aggregates.

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