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# Gel transformations in silicas: a combined NMR and SAXS study

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## Abstract

^{1}H NMR transverse spin–spin relaxation times ($T_2$) of water have been measured to monitor the aggregation and aging processes of low concentration silica gels. Along with ^{1}H NMR, small-angle X-ray scattering (SAXS) and physisorption measurements were used to obtain additional information on aging.

After acidification of water-glass (silica solution) the primary building units combine to form aggregates with fractal dimensionalities (decreasing $T_2$). Gelation occurs when these growing aggregates form a percolating network, resulting in a minimum value of the $T_2$ relaxation time. During and after these processes, rearrangements of silica take place (aging), a crucial step in the formation of pores. The aging of silica gel can be monitored by changing the relaxation behaviour (increasing $T_2$). With SAXS a densification of the structure is indicated by an observed decrease in fractal dimensionalities and an increase in the radius of the primary building units, indicating a migration of silica from the tips of the aggregates towards the centre of the aggregates. Aging is a slow process compared with the aggregation of the primary particles, but it can be accelerated by adding catalytic quantities of fluorine or by preparation at higher pH or at higher temperatures.

By using spin-spin relaxation measurements, reacting aqueous silica systems with a low solid content could be studied in situ. It is shown that hydroxyl and fluoride ions have different impacts on the silica systems, leading to different mechanisms. For aggregation and aging we observed (different) optimal fluorine concentrations.

*Keywords:* NMR; silica gels; small-angle X-ray scattering.

## Introduction

Silica gels and powders exhibit a large diversity in structural properties, making these amorphous materials useful for many domestic and industrial applications. The structural properties of silica are of major importance in heterogeneous catalysis.

In the preparation of porous silica, the reaction conditions during gelation and aging are impor-

tant. In order to study the influence of temperature, pH, concentration and the addition of cations or templates during the growth and aging of the aggregates, only a few techniques which preserve the ramified and fragile structure during analysis may be used. Therefore methods requiring the removal of pore fluids prior to analysis often cannot be used (e.g. physisorption, mercury porosimetry, transmission electron microscopy), and in situ spectroscopic techniques, e.g. small-angle X-ray scattering (SAXS) [1], ^{29}Si NMR [2,3] and ^{1}H NMR, have to be applied. The use of NMR

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spin–lattice relaxation experiments to study pore fluids is very informative, as was recently demonstrated by several investigators [4]. The advantages of this technique include the possibilities for in situ measurements on reacting systems, the analysis of wet solids [5], and especially the study of gels with a low concentration of silica where water is in rapid equilibrium between the bulk and the surface layer.

The present study describes systems with approximately 4 wt% solid in water. As far as we are aware, this is the first case of measurements of this kind on systems with such a low solid content. Spin–spin relaxation ($T_2$) was used rather than spin–lattice relaxation ($T_1$) because of the higher sensitivity of spin–spin relaxation at low silica concentrations [6].

Owing to the restricted movements and hence increased correlation times of the water molecules near the silica–water interface, the protons of water included in a porous solid have a larger relaxation rate than those of water in the bulk. This increase is caused by hydrogen bonding to the silica surface. The diffusion of the individual water molecules between the surface and the bulk water is fast compared with relaxation. With the two-fraction, fast-exchange model [7], a relationship between the observed relaxation time, the relaxation time of the surface and bulk phases, and the respective volume of fluid in each phase may be formulated:

$$1/T_i = (1/T_{ib})\dot{\eta} + (1/T_{if})(1 - \dot{\eta}) \qquad i = 1, 2$$

where $T_{ib}$ is the relaxation time of the bound water phase, $T_{if}$ is the relaxation time of the free water phase and $\dot{\eta}$ is the fraction of water molecules in the silica–water surface phase.

A decrease in the relaxation time $T_i$ (increase in relaxation rate) can be interpreted as an increase in the number of water molecules restricted in their movements owing to the proximity of the silica structure, assuming that correlation times of individual water molecules are not severely influenced by the thickness of the boundary layer.

When alkaline silica solutions (water-glass) are acidified, polycondensation reactions occur between the dissolved oligomeric species, resulting in (sub)colloidal particles. At pH values above the isoelectric point of silica (IEP = 2.3 [8]), the silica particles carry negative charges due to ionization of surface silanol groups; stabilization caused by these surface charges is negligible owing to the presence of alkali metal cations acting as a bridging agent between the negatively charged silica particles [9]. Subsequently, aggregates, networks or dense sediments are formed, depending on the conditions applied during preparation [8,10]. At pH 2–6 the silica particles in the aggregates may be arranged with a power-law-dependent density and are fractal objects exposing a non-integer or broken dimensionality with a non-Euclidian behaviour [11].

Recently, fractal objects have attracted much attention [11]. Computer simulations [12] have provided much information on the aggregation processes of primary particles and the role of the relative rate of diffusion and reaction herein. In a first approximation, there are two limiting cases concerning aggregation of particles into ramified fractal clusters. Either diffusion [13,14] or reaction [15] can be limiting, resulting in diffusion-limited cluster–cluster aggregation with fractal dimension $D_{DLCCA} = 1.75$ and reaction-limited cluster–cluster aggregation with fractal dimension $D_{RLCCA} = 2.1$ respectively. Both processes are accompanied and followed by rearrangements (aging) which are slow relative to aggregation, ultimately resulting in structures with fractal dimensionalities that are higher than those obtained from fractal structures that did not undergo any rearrangements [12,16].

Transformations of a gel during drying are strongly influenced by the structure of the aggregates. During drying, large forces are applied on the aggregates in the gels, owing to the high capillary stress and to the resistance of the fluid to flow in the very small pores of the gel [17]. This can result in the collapse of the tenuous networks of fractal aggregates, destroying the structure initially formed by aggregation of silica particles. During aging, the fragile aggregates in the gel can be strengthened, for instance, by treating the wet

network thermally [8] to preserve this structure during drying. The solubility of silica will increase upon heating, causing a net migration of silica from the more soluble convex surfaces to the less soluble concave surfaces. This means that the dissolved silica will tend to condense in the necks between the particles and a reinforcement of the interparticle connections within the aggregate will result [8,17], characterized by a change in fractal dimension.

Similar gel transformations are also to be expected in the precursor gels during zeolite synthesis. A good understanding of the underlying mechanisms of these transformation processes is of major importance for zeolite synthesis, since very small variations in reaction conditions are known to yield completely different products [18]. Of particular interest is the presence of $OH^-$ in the reaction mixture, determining the solubility of the reactants. With increasing pH and increasing concentration of dissolved reactants, the rate of crystal growth is enhanced [19,20]. However, replacement of $OH^-$ by $F^-$ also succeeded in the preparation of some zeolites [21,22]. This replacement has several advantages in zeolite preparation, e.g. the absence of alkaline cations, highly crystalline materials and working under milder conditions.

In this study we report on the aggregation and subsequent aging processes in low concentration silica solutions and gels. By measuring the $T_2$ of water in the liquids and subsequently formed gels it is possible to monitor the development of structure and differences in structure occurring in various systems. The influence of both pH and the addition of $F^-$ is described. In view of the higher reported sensitivities of $T_i$ measurements at lower NMR field frequencies and the low amount of surface water in the present systems, spin-echo measurements of the Hahn type were performed at 20 MHz.

## Experimental

Aqueous alkali silica (water-glass) was prepared by dissolving silica (aerosil 380, Degussa AG) and potassium hydroxide (Merck p.a.) in the appropriate ratio in distilled 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 pH was reached. In cases where the effect of fluorine was to be investigated, potassium fluoride was added to the hydrochloric acid before addition of the aqueous alkali silica solution. All gels contained the same silica concentration after preparation. Gelation was detected when no meniscus deformation was observed on twisting the container.

The spin–spin relaxation times have been determined by the Carr–Purcell–Meiboom–Gill $90°-[(180°)_x-echo]_n$ sequence at a frequency of 20 MHz using a Bruker Minispec pc100 at a field strength of 0.47 T. The operational temperature was 40°C in order to prevent temperature changes due to external influences. All samples were stored at 40°C. The magnetization decay curve was analysed using a monoexponential fit. A multiexponential technique yielded no perceivable improvement in the quality of the fit.

Physisorption measurements were performed on a Carlo Erba Strumentazione Sorptomatic 1900 using liquid nitrogen as sorbent. Before drying, the gels were frozen at −35°C for at least 3 h. The samples were freeze-dried using a Labconco Labtop freeze dryer operating at 900 Pa and at a −75°C condenser temperature for 24 h. Prior to the physisorption experiments the samples were outgassed for 16 h at 180°C.

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 0.2–3.0 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 [23].

## Results and discussion

Figure 1 shows spin–spin relaxation ($T_2$) for a silica system as a function of reaction time. The small increase in $T_2$ initially observed was caused by the warming of the sample in the Minispec after preparation at room temperature.

After 20 min of reaction the decrease in $T_2$ indicates the formation of a silica surface interacting with water molecules. This surface formation is due to the polymerization of silica monomers and oligomers present in the water-glass after acidification and the subsequent aggregation of the formed particles into clusters with fractal properties. This decrease in $T_2$ is due to the restricted motion of water molecules in the proximity of the larger silica particles compared with water molecules bonded to monomers and oligomers. The water molecules form hydrogen bonds at the surface of the silica particles.

When the minimum value of $T_2$ is reached, the beginning of gelation is observed (no meniscus deformation), in contrast to SAXS and $^{29}$Si NMR results, where no significant signals related to the transition from the liquid to the gel state were observed [24,25]. Besides turbidity or viscosity measurements, spin–spin relaxation might be an alternative and very effective way of detecting the cross-over from the fluid to the gel phase.
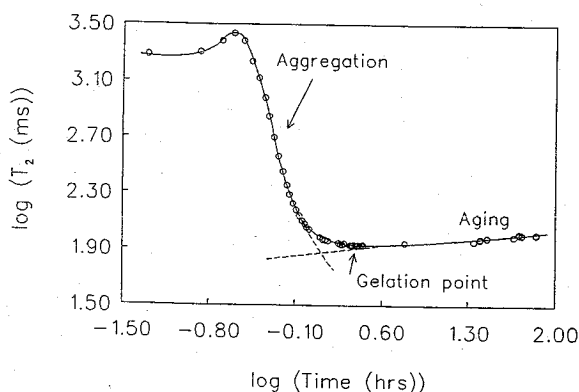
After gelation, aging processes become dominant. Owing to silica dissolution from soluble surfaces (convex) and redeposition of this material in the crevices and necks (concave surfaces) the specific surface area decreases [26] but not the average correlation time of the interacting water molecules. Because the number of water molecules interacting with the silica surface will decrease, an increase in $T_2$ as a function of reaction time is observed during aging.

The catalytic influence of fluorine on the rate of particle growth, aggregation, gelation and aging is attributed to the acceleration of the condensation reaction [27,28]. Adding fluorine to our systems gives a qualitatively similar development of $T_2$ to that observed for the non-fluorinated sample (Fig. 2). Moreover, the initial decrease and the minimum of $T_2$ both occur after shorter reaction times, and the increase in $T_2$ during aging (after the minimum) is faster compared with that for the non-fluorinated sample.

Apart from the faster gelation due to fluoride, Winter et al. [29] reported that for a silica system at pH 6.4, at the gelation point, 70% of the silica was incorporated in the gel whereas only 40% was incorporated when fluoride was added to the precursor solution. At this pH or lower, all fluoride ions are located on the silica structure in contrast to the situation at higher pH [30]. The presence
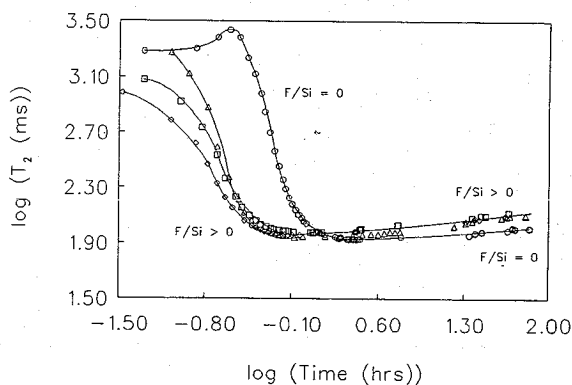
Fig. 1. Spin–spin relaxation behaviour as a function of reaction time for a silica system (silica concentration $C_{SiO_2} = 0.73\ M$; pH 4; temp., 40°C): ○, fluorine to silica ratio F/Si = 0. The drawn line is a visual guide, not a fit.

Fig. 2. Spin–spin relaxation behaviour as a function of reaction time for different fluorine to silica ratios ($C_{SiO_2} = 0.73\ M$; pH 4; temp., 40°C): ○, F/Si = 0; △, F/Si = 0.01; ◇, F/Si = 0.03; □, F/Si = 0.1. The drawn lines are a visual guide, not a fit.

of catalytic quantities of fluorine on the silica oligomers is assumed to lead to the formation of more diffuse and strongly anisotropic aggregates, resulting in faster gelation [31]. In agreement with this hypothesis we observed smaller $T_2$ values in the case where fluorine is added to the system, owing to the rapid growth of anisotropic aggregates. When these clusters achieve small intercluster distances, cages will be formed with a relatively large silica surface influence on the water molecules. Because of the anisotropy and the more tenuous character of the aggregates, water molecules will be influenced more strongly and the water structure will be distorted more compared with the non-fluorinated system. At higher fluorine concentrations, the fluoride ions are bonded on many sites on the aggregates, resulting in a fast growth of isotropic aggregates and longer gelation times [31].

Also, retarding effects have been observed after the addition of fluoride [30,31], as shown in Fig. 3, although condensation and hydrolysis reactions are assumed to be also accelerated at higher fluorine concentrations. This retardation of aggregation and gelation indicates a more random (isotropic) distribution of fluorine atoms on the silica structure, resulting in more active but also more dense and less elongated aggregates, and thus more similar to the system without fluorine.
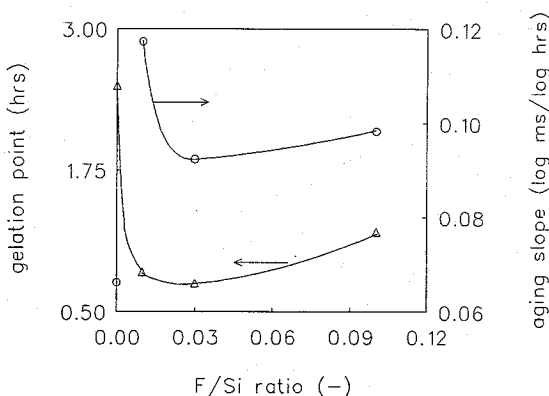
After the system has passed the gelation point (the $T_2$ minimum value), aging is the dominant process (Fig. 1) and we can observe the accelerating influence of the fluoride ions. However, the fastest aging rate is observed for the system with the lowest fluorine-to-silicon ratio (F/Si = 0.01). Clearly, the different mechanisms for the aggregation and the aging process require different optimal fluorine concentrations.

At higher pH (pH 5–6) a different type of behaviour is observed. Increasing the pH to pH 5 results in larger elementary particles, corresponding to a smaller silica surface area and resulting in a smaller rate of aggregation and aging, though gelation occurs already after 0.27 h of reaction (Fig. 4). At pH 6, gelation occurs within seconds and results in a $T_2$ curve with a very noisy pattern.

As can be seen from the results obtained by in situ spin–spin relaxation measurements of reacting silica systems, the influence of $F^-$ is different from the influence of $OH^-$. Although both are expected to accelerate the condensation reaction, the structures of the aggregates formed are different (elongated and dense respectively), probably due to the size of the elementary particles. This result can be of importance when preparing zeolites according to the "fluorine route". When using $F^-$ instead of $OH^-$, different synthetic gels will be formed which can give rise to different products.
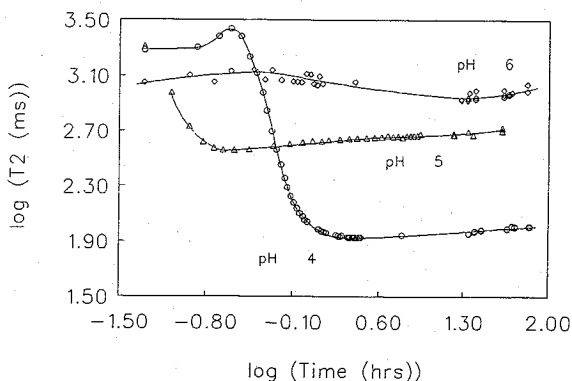


Fig. 3. Gelation time and aging speed (from $T_2$) as a function of the fluorine to silica ratio ($C_{SiO_2}$ = 0.73 $M$; pH 4): △, aggregation; ○, aging.



Fig. 4. pH dependence of the course of the spin–spin relaxation behaviour as a function of reaction time ($C_{SiO_2}$ = 0.73 $M$; pH 4; F/Si = 0): △, pH 4; ○, pH 5; ◇, pH 6. The drawn lines are a visual guide, not a fit.

The aging processes have also been followed by SAXS and physisorption (BET). With SAXS it is possible to study in situ particle growth and aggregation without disturbing the structure. Information is obtained about the average values of structural parameters. In Fig. 5 the spectra are shown for an aging silica system catalysed by fluorine. The straight lines in the log–log plots of the spectra cover a $Q$ range of more than a decade and are representative of fractal growth. After 32 min of reaction, before gelation, a fractal dimension $D$ of 1.7 is observed (Fig. 5), indicating the presence of ramified and elongated silica aggregates [14]. After the cross-over to gelation and aging, higher dimensionalities are observed (Fig. 5). The observed fractal dimensions are representative for structures grown by diffusion-limited cluster–cluster aggregation. After 41 h, both a Porod area (scattering slope −4) and a small decrease in the fractal dimension are observed. This corresponds to a growth of the average primary particle radius and a higher density gradient (decreasing $D$) respectively, caused by hydrolysis of silica particles at the peripheries of the aggregates, followed by a migration and condensation on the backbones of the aggregates. During this process both larger "elementary" particles in the centre and a higher density gradient from the centre to the periphery of the aggregates are created.

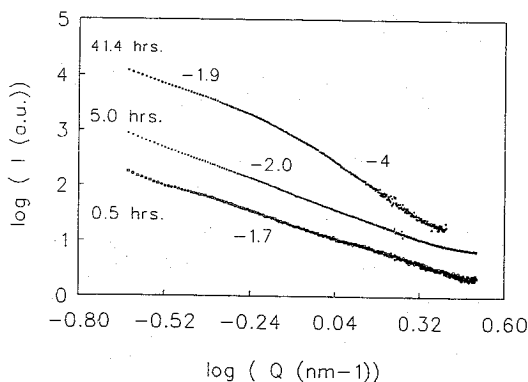The development of structure in the silica systems was also indicated by physisorption measurements that indicate an increase, followed by a decrease in the specific surface area (Fig. 6). Without or with only short aging times, the structures formed are unable to resist the large capillary forces to which they are subjected during drying, and a collapse will take place resulting in small specific surface areas and microporosity. The same features were observed when fluorine was added to the systems. After longer aging times the silica structures are reinforced and are able to preserve their structure during drying, causing the specific surface area to increase. The observed decrease is due to prolonged aging causing a reinforcement of the backbone and resulting in both a development of wider pores and a smaller specific surface area.

## Conclusion

In this study, ^{1}H NMR and SAXS were combined to study transformations occurring in colloidal silica systems. This combination of techniques proves to be very useful, because processes on a molecular scale (monitored by ^{1}H NMR) could be related to processes on a colloidal scale (examined by SAXS). The aggregation and aging processes taking place in various silica systems could clearly be distinguished and interpreted.
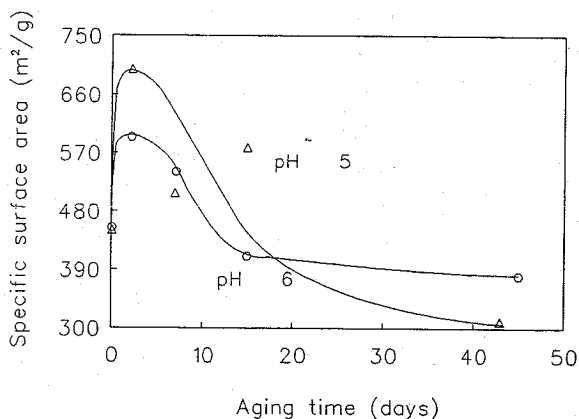


Fig. 5. SAXS spectra of a silica system aged with fluorine ($C_{SiO_2} = 0.73$ $M$; pH 4; F/Si = 0.01) at various times.



Fig. 6. Specific surface area (BET) as a function of aging time ($C_{SiO_2} = 0.73$ $M$; pH 4; F/Si = 0.01): △, pH 5; ○, pH 6. The drawn lines are a visual guide, not a fit.

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## References

1   P.W.J.G. Wijnen, T.P.M. Beelen, C.P.J. Rummens, H.C.P.L. Saeijs and R.A. van Santen, J. Appl. Crystallogr., 24 (1991) 759.
2   W.M. Hendricks, A.T. Bell and C.J. Radke, J. Phys. Chem., 95 (1991) 9519.
3   P.W.J.G. Wijnen, T.P.M. Beelen, J.W. de Haan, L.J.M. van de Ven and R.A. van Santen, Colloids Surfaces, 45 (1990) 255.
4   D.P. Gallegos, D.M. Smith and C.J. Brinker, J. Colloid Interface Sci., 124(1) (1988) 186, and references cited therein.
5   C.L. Glaves, C.J. Brinker, D.M. Smith and P.J. Davis, Chem. Mater., 1(1) (1989) 34.
6   F. Delville, Application of NMR Spectroscopy to Cement Science, Technodes International Workshop, Guerville, France, 1992.
7   J.R. Zimmerman and W.E. Brittin, J. Phys. Chem., 61 (1957) 1328.
8   R.K. Iler, The Chemistry of Silica, Wiley, New York, 1979, p. 92.
9   E.J.W. Verwey and J.Th.G. Overbeek, Theory of Stability of Lyophobic Colloids, Elsevier, Amsterdam, 1948.
10  M. Kallala, R. Jullien and B. Cabane, J. Phys. II, 2 (1992) 7.
11  B.B. Mandelbrot, The Fractal Geometry of Nature, Freeman, San Francisco, CA, 1979.
12  R. Jullien and R. Botet, Aggregation and Fractal Aggregates, World Scientific, Singapore, 1987.
13  P. Meakin, Phys. Rev. Lett., 51 (1983) 1119.
14  M. Kolb, R. Botet and R. Jullien, Phys. Rev. Lett., 51 (1983) 1123.
15  R. Jullien and M. Kolb, J. Phys. A, 17 (1984) L639.
16  M. Kolb, R. Botet, R. Jullien and H.J. Hermann, in H.E. Stanley and N. Ostrowski (Eds), On Growth and Form, NATO ASI Ser. E100, Martinus Nijhof, Dordrecht, 1986.
17  G.W. Scherer, J. Non-Cryst. Solids, 100 (1988) 77.
18  J.C. Jansen, in H. van Bekkum, E.M. Flanigan and J.C. Jansen (Eds), Introduction to Zeolite Science and Practice, Elsevier, Amsterdam, 1991, p. 77.
19  W. Meise and F.E. Schwochow, in W. Meier and J.B. Uytterhoeven (Eds), Molecular Sieves, Proc. 3rd Int. Conf. on Zeolites, Zurich, 3–7 September 1973, ACS Symp. Ser. 121, American Chemical Society, Washington, DC, 1973, p. 169.
20  D.T. Hayhurst, A. Nastro, R. Aiello, F. Crea and G. Giordano, Zeolites, 8 (1989) 416.
21  J.L. Guth, H. Kessler, J.M. Higel, J.M. Lamblin, J. Patarin, A. Seive, J.M. Chezeau and R. Wey, in M.L. Occeli and H.E. Robson (Eds), Zeolite Synthesis, ACS Symp. Ser. 398, American Chemical Society, Washington, DC, 1989, p. 176.
22  J.L. Guth, H. Kessler and R. Wey, in Y. Murikami, A. Iijima and J.W. Ward (Eds), New Developments in Zeolite Science and Technology, Proc. 7th Int. Conf. on Zeolites, Tokyo, 17–22 August 1986, Kodansha, Tokyo and Elsevier, Amsterdam, 1986, p. 121.
23  C.G. Vonk, J. Appl. Crystallogr., 6 (1973) 81.
24  R. Winter, D.W. Hua, X. Song, W. Mantulin and J. Jonas, J. Phys. Chem., 94 (1990) 2706.
25  P.W.J.G. Wijnen, T.P.M. Beelen, C.P.J. Rummens, H.C.P.L. Saeijs, J.W. de Haan, L.J.M. de Ven and R.A. van Santen, J. Colloid Interface Sci., 145(1) (1991) 17.
26  G.W. Scherer, J. Non-Cryst. Solids, 100 (1988) 77.
27  R. Winter, D.W. Hua, P. Thiyagarajan and J. Jonas, J. Non-Cryst. Solids, 108 (1989) 137.
28  E.J.A. Pope and J.D. Mackenzie, J. Non-Cryst. Solids, 87 (1986) 185.
29  R. Winter, J.B. Chan, R. Frattini and J. Jonas, J. Non-Cryst. Solids, 105 (1988) 214.
30  A.P. Tai and Y.S. Chen, Hua Hsueh Hsueh Pao, 29 (1963) 384 (in Japanese), Chem. Abstr., 60 (1964) 12865b.
31  L.R.T. de Bruyn, P.W.J. van den Heuvel, W.H. Dokter, P.W.J.G. Wijnen, T.P.M. Beelen and R.A. van Santen, to be published.