

Aging and pore formation in silica gels

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Aging and Pore Formation in Silica Gels

W.H. Dokter, T.P.M. Beelen, H.F. van Garderen and R.A. van Santen

Schuit Institute of Catalysis, University of Technology Eindhoven, P.O. Box 513,
5600 MB Eindhoven, The Netherlands

1. ABSTRACT

Small angle neutron scattering (SANS) and physisorption (N_2) experiments have been used to study the influence of aging on the structure of dried gels. These gels were aged for various times at elevated temperature (80°C) or under the addition of catalytic quantities of fluorine. Both the porous kernel and the pores within the kernel grow during aging. However, addition of fluorine or aging at 80°C results in different pore structures, although the same ultimate particles size is reached in both cases. Owing to slit-like or isolated pores obtained in the fluorine aged sample, the physisorption and SANS results did not coincide while the 80°C aged gels showed reasonable agreement between both techniques. Although the structure of the porous silica was distorted by wetting, contrast variation experiments with a H_2O/D_2O mixture confirmed the scattering by pores. This scattering is replaced by scattering from the surface of the particles.

2. INTRODUCTION

Amorphous oxidic silica gels exhibit a large diversity in structural properties, making these materials useful for many different applications. It can be used as a filling material, filter material and as a supporting agent in heterogeneous catalysis, owing to its high possible specific surface area and high stability.

With sol-gel processing it is possible to obtain a large variety in materials [1] starting from alkoxy-silicate systems or water-glass (alkaline silica solution). Understanding of the underlying molecular mechanism is still very limited, but required [2] since small variations in preparation conditions or in precursor solution can result in different structural properties of the final material.

The present study describes systems prepared from water-glass. When water-glass is acidified, polycondensation reactions can occur between dissolved oligomeric silica species, resulting in (sub)colloidal particles. Subsequently, aggregates, networks or dense sediments are formed depending on the conditions applied during synthesis [3]. 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 [4].

Computer simulations [5] have provided much information on the aggregation

processes of primary particles into fractal objects and the role of diffusion and reaction herein, resulting in fractal dimensions between 1.75 and 3.0 [6-9]. These 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 [6,10].

A wide variety of chemical and physical changes are observed after gelation of the reaction mixture. An increase of the connectivity of the gel network can occur or an expulsion of the solvent (syneresis) or an increase of the pore size and decrease of specific surface area (coarsening) [11]. All these processes (aging) are resulting in a reinforced silica network structure and are strongly effecting the behaviour of the gels during subsequent processing like drying.

To avoid the occurrence of capillary stresses during drying other non-evaporative drying methods have been developed. Hypercritical drying [12,13] eliminates capillary pressure entirely like freeze-drying [14], the technique used for drying the samples that are investigated in this study.

The drying processes are of great importance because in most of the applications of the silica structures the dried version of the material is used. Besides characterisation of the wet gels also characterisation of the final dried product is of great importance for industry.

A large number of methods exist to characterize porous bodies but most of these methods are of little use due to their destructive interaction with the gels [3, 15] or the length scale they can enlighten. With small angle scattering (SANS, SAXS) it is possible to obtain nano-structural information about the scaling of the mass in the amorphous aggregates (fractal dimension) and particle sizes (aggregate size and building particles size) for both the wet gels and as is here the case, for dried silica bodies [16, 17]. Also, with dried materials the concept of contrast variation can be used to obtain additional information about the structure of the investigated silica materials.

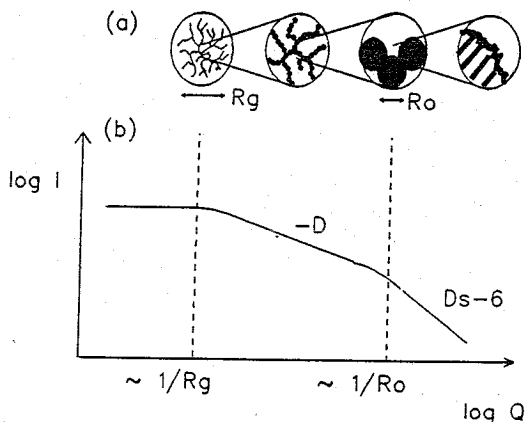


Figure 1: Schematic representation of (a) an aggregate with mass-fractal as well as surface-fractal properties and (b) its scattering spectrum.

The characteristics of the scattering pattern can be related to different structural features on different length scales as shown in figure 1. Three distinct

regions are distinguished in the log intensity versus log Q curve ($Q=2\pi/\lambda*\sin(2\theta)$, with λ being the wavelength and 2θ the scattering angle). At small Q -values the intensity is constant because at these large length scales no resolution of inhomogeneities in the sample is possible. In the intermediate area a power-law decrease of the intensity is observed according to $I\sim Q^{-D}$ [18], with D being the fractal dimension as mentioned above. The power-law behaviour at large scattering vectors according to $I\sim Q^{-D_s}$, can be attributed to the surface structure of the building particles [19]. D_s is the surface fractal dimension and for smooth surfaces $D_s=2$, leading to the well-known Porod relation ($I\sim Q^{-4}$) [20]. When the surface is irregular, D_s may range between 2 and 3, corresponding with power-law exponents smaller than 4. This has been observed for very small colloidal particles [21, 22] and porous surfaces [23].

In this study we report on a combined small angle neutron scattering and physisorption (BET) study to characterise dried silica gels after aging in the wet gel state using the complementary character of both techniques.

3. EXPERIMENTAL SECTION

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 (4) was reached. A number of gels was heated to 80°C directly after the desired pH was reached and aged for various times at this temperature. To investigate the effect of fluorine, potassium fluoride was added to the hydrochloric acid before addition of the aqueous alkali silica solution and aged for various times at room temperature. All gels contained the same silica concentration after preparation (4 wt%).

Before drying, the gels were frozen at -35°C for at least 4 hours. The samples were subsequently freeze-dried using a Labconco Labtop freeze dryer operating at 900 Pa. and at a -75°C condenser temperature for 24 hours.

The SANS experiments were performed at the Rutherford Appleton Laboratory, ISIS facility, Abingdon, U.K. Pulsed neutrons with wavelengths in the region between 2.2-10 Å 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 Å were obtained, providing information on distance scales from roughly 20 to 1000 Å 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.

In cases where contrast variation was used, the dried silica samples were impregnated with a H_2O/D_2O mixture (63 vol% D_2O) to obtain matching conditions. After impregnation the samples were partially dried.

Physisorption measurements were performed on a Carlo Erba Strumentazione Sorptomatic 1900 using liquid nitrogen as sorbate. Prior to the physisorption experiments the samples were outgassed for 16 hours at 180°C.

4. RESULTS AND DISCUSSION

A typical scattering spectrum of silica powder after aging at 80°C for 56 minutes in the wet gel phase before drying is shown in figure 2. Two different scattering regions can clearly be distinguished. A straight line (approximately one decade) in the $\log I(Q)$ versus $\log Q$ curve is observed, indicative for a fractal region with a rather low fractal dimension of 1.4. The dried silica systems may consist of a network of air-filled channels in a solid matrix [24] with an apparent density larger than unity. Following Babinet's principle that in case of a two phase system, scattering results from the phase that is not dominantly present in the structure, this low dimension is caused by scattering of neutrons by pores and thus at these length scales the scattering spectrum provides information about the pore structure present in dried silica particles.

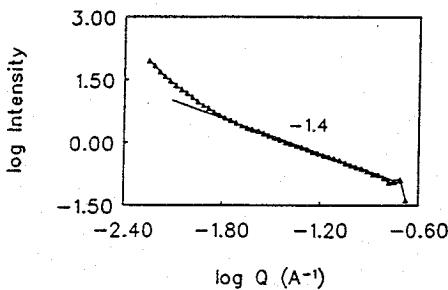


Figure 2: Small angle neutron scattering spectrum of dried gel after aging at 80°C in the wet gel state for 56 min.

If scattering results from aggregates of solid material present in solution, the mass scales with the radius of these aggregates according to: $M \sim R^D$, corresponding with ramified and fractal aggregates according to the second diagram of figure 1a. If scattering is caused by the pores, one can substitute the mass in the equation above by the volume of the pores causing the scattering, replacing the silica aggregate by an 'aggregate' composed of interconnected pores. However, pores might not be interconnected. For this case a schematic representation of the development of the number of pores as a function of the particle radius for three different fractal dimensions is shown in figure 3. For clarity reasons a two-dimensional plot is presented. It is obvious that at low fractal dimensions ($D \sim 1$) a high pore-density gradient, from the centre to the periphery, is observed. When $D \sim 1.5$ a lower density gradient is observed, while at $D \sim 2$ the number of pores is increasing linearly with the radius preceding to the periphery of the particle. In the three dimensional space all fractal dimensions between 3 and 0 resulting from pore scattering indicate a structure with a decreasing volume of pores from the core to the outer parts of the particle.

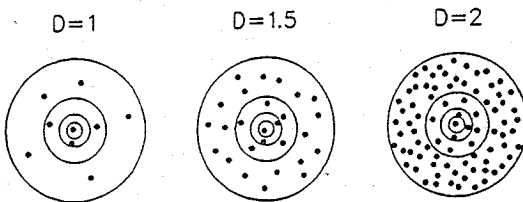


Figure 3: Two dimensional schematic representation of the distribution of pores as a function of the radius for various fractal dimensions

An increase in intensity at small scattering vectors (large length scale) is observed as well (figure 2). Probably, this deviation from the power-law behaviour is resulting from scattering structure at larger length scales compared to the size of the porous particles and might be indicative for cavities in the structure build from the particulate porous particles discussed above. The outer parts of the aggregates present in the wet gel phase are very brittle and will collapse during subsequent processing as indicated by the considerable shrinkage of the wet gels after freeze-drying. However, the range of scattering vectors is too small to obtain significant quantitative information related with the structure from this part of the scattering curve.

Summarising, the right part of the scattering (high Q) spectrum provides information about the intra-particle porous structure, while from the left part of the scattering spectrum information can be obtained about the inter-particle porous structure of the dried silica xerogel.

After prolonged aging in the wet gel state (1505, 2094, 3240 min.) both an increase in intensity and a deflection of the straight line at high Q -vectors can be observed (figure 4). Although an accurate measurement of the slope is difficult due to the short length of the region, probably we are dealing with the crossover to the Porod region of the pores. This crossover shifts to smaller Q -vectors as a function of aging, indicative for the growth of the pores. The size of the pores as a function of time is shown in figure 5. After 56 minutes aging no crossover was observed in the scattering curve. Therefore, for the pore radius plotted in figure 5 the high Q limit of the scattering curve is chosen indicating the maximum possible value of the pore radius at that moment. Clearly the pores are growing during aging due to a reorganisation of the silica in the wet gel phase. Moreover, the increase in intensity of the scattered spectrum is indicative for an increase of the scattering surface of the pores.

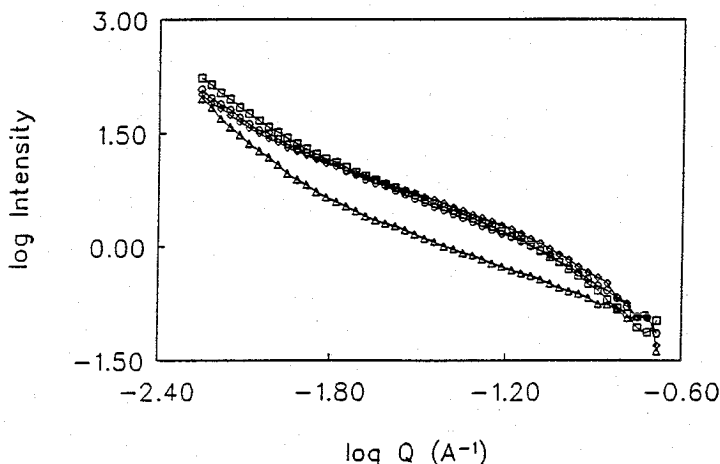


Figure 4: Small angle neutron scattering spectra of the dried gel aged at 80°C in the wet gel state for various times (Δ 56 min., \circ 1505 min., \diamond 2094 min., \square = 3240 min.)

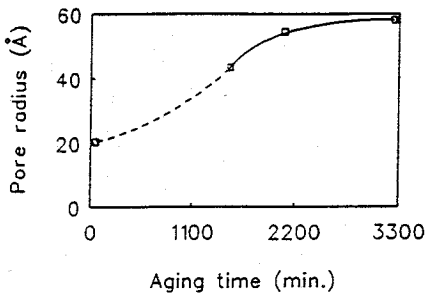


Figure 5: Pore size determined from small angle scattering spectra as a function of aging for the gel aged at 80°C in the wet gel state

The slope of the scattering curve after prolonged aging is rather difficult to determine accurately owing to the short power-law dependency observed. Significant is that for all samples the slopes are small (~ 1.5) and thus indicative for a porous particle with increasing density of silica from the core to the peripheries of the particles.

The size of the porous particles increases as a function of aging time as can be determined from the limit of the power-law dependency at small Q -vectors and is illustrated in figure 6. During aging the outer parts of the aggregates are reinforced as well as the kernels. Less collapse will occur when the materials are dried after prolonged aging, resulting in an increase of the porous kernel as a function of time, as observed in wet gels also [25,26].

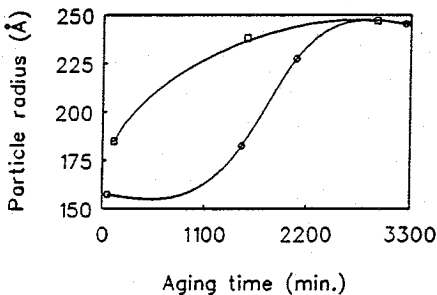


Figure 6: Particle radius as a function of aging for the dried gels aged at 80°C (O) and under addition of fluorine (□) in the wet gel state.

In case the gels in the wet phase have been aged at room temperature with catalytic additions of fluorine, similar scattering curves are observed (figure 7). Three distinct regions of different scattering modes are observed, indicating the presence of pores of 47Å already after 125 min. aging.

However, at prolonged aging times (1563, 2943 min.) a different scattering spectrum is obtained. Contrary to aging at 80°C, the slope of the scattering curve at intermediate Q -values is decreasing after prolonged aging, indicative for an increase of the pore-density gradient of the silica body as a function of aging.

At low Q -values, now a decrease of the intensity as a function of aging is observed resulting from the growth of the porous kernels combined with the

development of a less open structure. When the peripheries of the aggregates have not been reinforced sufficiently during the aging process, collapse of these outer parts will occur upon drying of the wet silica gel, resulting in a porous body with relatively large cavities between the separate particles. During prolonged aging the outer parts of the aggregates get reinforced more resulting in less collapse during the subsequent drying process and in smaller cavities between the porous kernels.

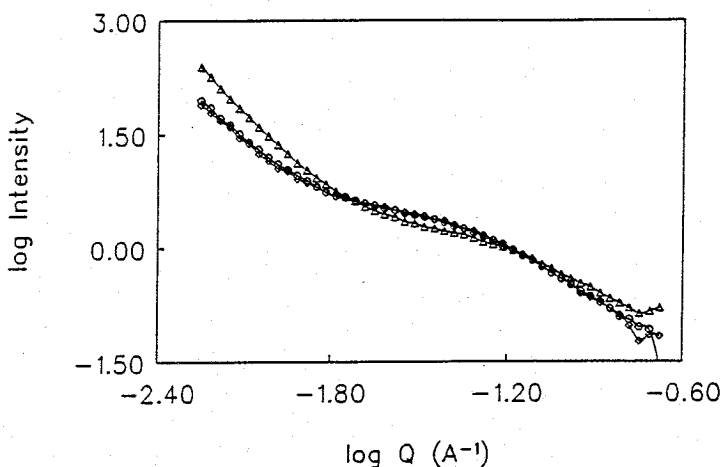


Figure 7: Small angle neutron scattering spectra of dried gel of the fluorine catalysed wet gel at various times (Δ 125 min., \circ 1563 min., \diamond 2943 min.)

A decrease of intensity is also observed at large Q -values during prolonged aging, due to a reorganization of silica. Owing to the transport of silica particles from areas with a positive curvature to areas with a negative curvature smoothing of pores will take place [3]. The steeper decay at high Q -values after prolonged aging might be explained by this reorganisation process.

The size of the porous kernel aged in the wet gel phase under the addition of fluorine, is compared in figure 6 with the results from the gel aged at 80°C . Both gels show an increase of the radius of the porous kernel as a function of time, owing to the reinforcement of the peripheries of the aggregates during aging. The aggregates of the fluorine catalysed gels seem to be growing faster but the ultimate particle size reached is comparable with the particle size reached for the gel aged at 80°C . This might be explained by the formation of elongated particles in the case fluorine was added to reaction solution as was already observed with SAXS [26], resulting in a very fast increase of the radius of gyration. The ultimate particle size reached is depending on the concentration of silica present in the gel, being the same for all gels monitored in this study.

Although the silica bodies are reinforced during the drying process, impregnation with water is still causing distortions (swelling), making comparisons between dry and impregnated systems very difficult. Nevertheless, impregnation with a $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture with the same coherent scattering length as the silica body (63 vol% D_2O), is effectively cancelling the scattering of the fractal pores as shown in figure 8. The straight line in this figure is indicative for a rough fractal surface with

$D_s = 6 - 3.3 = 2.7$ (surface fractal dimension) [23]. After impregnation and partial drying the swollen surface of the porous liquid filled particles has an interface with both liquid and air present.

The particle sizes obtained with these contrast variation experiments are not coinciding with the particles sizes obtained from the scattering spectra from the dried materials. This might be due to the distortion of the structure by the impregnated liquid or to partial emptying of the pores during drying.

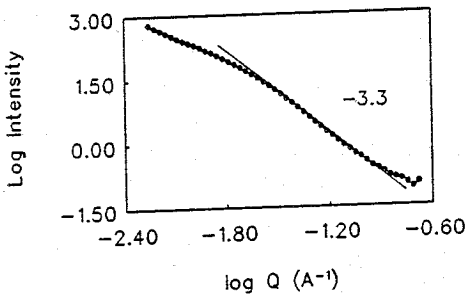


Figure 8: Small angle scattering spectra of the dried gel impregnated with a H_2O/D_2O mixture aged at $80^\circ C$ for 1505 min. in the wet gel state.

The development of structure in the silica as a function of time has also been studied with nitrogen physisorption. Both the radii determined from SANS and physisorption are shown in figure 9 as a function of aging for both investigated gels. The radius of gyration determined from SANS was converted to the radius of the sphere according to $r^2 = 5/3 * R_g^2$, with r the spherical radius and R_g the radius of gyration [27].

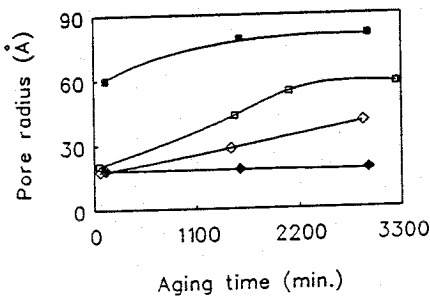


Figure 9: Pore radii determined both with physisorption ($\diamond r_{BET}$) as well as small angle scattering ($\square r_{SANS}$) as a function of aging for both dried gels. Open symbols for gels aged at $80^\circ C$, closed symbols for fluorine catalysed gels.

The gels aged at $80^\circ C$ showed reasonable agreement between the pore sizes obtained from scattering data and pore sizes obtained from physisorption experiment. The deviations may be explained by assuming the presence of non-interconnected pores according to figure 3. Clearly the deviations are much bigger in the fluorine catalysed system. Apart from the presence of isolated pores, this bad conformity between the radii determined can probably be assigned to the presence of slit-like pores in the structure as can be deduced from the adsorption/desorption hysteresis

curve (figure 10) according to the classification of de Boer (type B) [28]. With physisorption the determined radius equals the distance between the walls of the slit. However, with small angle scattering the radius of gyration of the slit is determined, with contributions of both the distance between the walls of the slit and depth of the slit. This radius of gyration should be larger than the radius determined with small angle scattering as shown in figure 9.

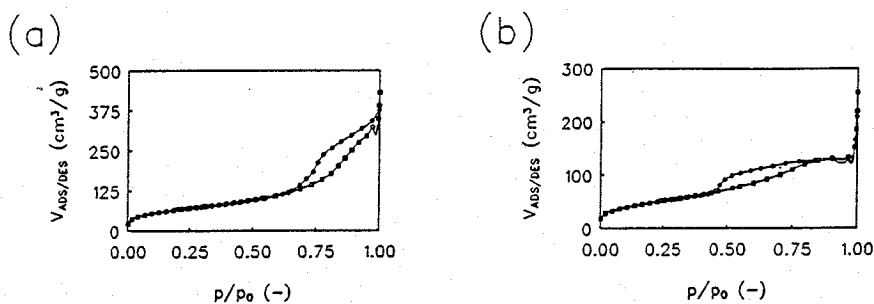


Figure 10: Adsorption/desorption hysteresis curves (a) for the gel aged at 80°C (2888 min.) and (b) the fluorine catalysed gel (2943 min.)

5. CONCLUSION

Small angle neutron scattering results show that in the silica system both the porous kernel and the pores present in the kernel are growing during aging. Aging at 80°C or aging under addition of fluorine results in different pore structures but the same ultimate porous kernel size is reached. Owing to slit like and isolated pores obtained in the fluorine aged sample, the physisorption and SANS results did not coincide while the 80°C aged gels showed reasonable agreement between both techniques. Contrast variation experiments confirmed scattering by the pores, although the structure of the porous silica was distorted by wetting.

6. ACKNOWLEDGEMENT

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REFERENCES

- [1] C.J. Brinker and G.W. Scherer, *Sol-gel Science*, Academic Press inc., Boston, San Diego, New York, London, Sydney, Tokyo, Toronto, 1990, chapter 14.
- [2] L.L. Hench and J.K. West, *Chem. Rev.* 90 (1990) 33-72
- [3] R.K. Iler, *The Chemistry of Silica*, Wiley, New York, 1979, 92
- [4] B.B. Mandelbrot, *The Fractal Geometry of Nature*, Freeman, San Francisco, CA, 1979
- [5] R. Jullien and R. Botet, *Aggregation and Fractal Aggregates*, World Scientific, Singapore, 1987
- [6] M. Kallala, R. Jullien and B. Cabane, *J. Phys. II (Paris)*, 2 (1992) 7
- [7] P. Meakin, *Phys. Rev. Lett.*, 51 (1983) 1123
- [8] M. Kolb, R. Botet and R. Jullien, *Phys. Rev. Lett.* 51 (1983) 1123
- [9] R. Jullien and M. Kolb, *J. Phys. A.*, 17 (1984) L639
- [10] 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
- [11] G.W. Scherer, *J. Non-cryst. Sol.*, 100 (1988) 77-92
- [12] S. Henning and L. Svensson, *Phys. Scripta* 23 (1981) 697
- [13] J. Zarzycki, M. Prassas and J. Phalippou, *J. Mater. Sci.*, 17 (1982) 3371
- [14] G.W. Scherer, *J. Non-cryst. Sol.*, 155 (1993) 1-25
- [15] A. Emmerling and J. Fricke, *J. Non-Cryst. Sol.*, 145 (1992) 113-120
- [16] J.D.F. Ramsay, *Chem. Soc. Rev.*, 15 (1986) 335-371
- [17] D.W. Schaefer, J.E. Martin, P. Wiltzius and D.S. Cannell, *Phys. Rev. Lett.*, 52 (1984) 2371
- [18] J.E. Martin and A.J. Hurd, *J. Appl. Cryst.*, 20 (1987) 61
- [19] J.E. Martin, *J. Appl. Cryst.* 19 (1986) 25
- [20] G. Porod, *Kolloid Z.*, 124 (1951) 83
- [21] J.D.F. Ramsay and M. Scanlon, *Colloids and Surfaces*, 18 (1986) 207-221
- [22] K.D. Keefer and D.W. Schaeffer, *Phys. Rev. Lett.*, 56 (1986) 2376-2379
- [23] P.W. Schmidt, in D. Avnir (Ed.), *The Fractal Approach to Heterogeneous Chemistry*, John Wiley and Sons, Chichester, New York, Brisbane, Toronto, Singapore, 1989, 67-78
- [24] J. Zarzycki, in L.L. Hench and J.K. Wiley, *Chem. Process. Adv. Mater.*, (1992) 77-92
- [25] P.W.J.G. Wijnen, T.P.M. Beelen, K.P.J. Rummens, H.C.P.L. Saeijs, J.W. de Haan, L.J.M. van de Ven and R.A. van Santen, *J. Coll. Interf. Sci.*, 145 (1991) 17-32
- [26] W.H. Dokter, H.F. van Garderen, T.P.M. Beelen, J.W. de Haan, L.J.M. van de Ven and R.A. van Santen, *Colloids and Surfaces A*, 72 (1993) 165-171
- [27] L.A. Feigin and D.I. Svergun, *Structure Analysis by Small-Angle X-ray and Neutron Scattering*, Plenum Press, New York and London, 1987
- [28] J.C.P. Broekhoff and R.H. van Dongen, in B.G. Linsen (Ed.), *Physical and Chemical Aspects of Adsorbents and Catalysts*, Academic Press, London and New York, 1970, 1-59