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Structural development of silica gels aged in TEOS

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Abstract

It has been shown that wet gels can be strengthened and stiffened by providing new monomers to the alcogel after gelation by aging in a tetraethoxysilane (TEOS) solution. Xerogels with properties similar to aerogels can be obtained by drying at ambient pressure. Structural changes of gels during the aging in TEOS were studied by small angle neutron scattering (SANS). The SANS measurements show only a slight increase in the volume fractal dimension of the porous gel network with increasing aging time indicating no significant change in the geometry and connectivity of the network. However, there is an increase in both primary particle size and cluster size when silica is precipitated from the aging solution. While the primary particle size stay–s relatively constant after only 6 h aging cluster size shows a steady increase. In addition, to obtain further information about the structural development, skeletal density of corresponding aerogels has been measured both as a function of aging time and heat treatment time. The skeletal density is higher if the wet gel is aged; however, it is independent of the aging time. A skeletal density close to the theoretical value is reached at about 350°C for both aged and unaged samples.

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1. Introduction

To enhance the commercial viability of aerogels one of the important preconditions for large-scale application is to avoid supercritical drying. A cheaper, simpler, and safer process results from drying at ambient pressure; however, xerogels normally crack and shrink during drying. Possibilities to reduce shrinkage and cracking during drying have been discussed and the main issues are to obtain a springback effect at the end of drying [1,2] or to improve the strength and stiffness of the wet gel [3–7].

Previous work concentrated on increasing strength and stiffness of the wet gel without reducing the pore size significantly by aging in a silane solution [3–7]. New monomers were added to the already formed network and hydrolysis, condensation, and specific reaction of these monomers favorably increase the strength and stiffness of the alcogel. Aging by adding additional monomers before or after the gel point is also known from the sodium silicate/silica systems [8,9]. Present work focused on structural development of the gels as a function of aging time in TEOS. Since small angle neutron scattering (SANS) is an excellent

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method to study nanoscale structure we used SANS to study low density xerogels prepared by aging in TEOS. Scattering data were fitted to a model where both the structure of the primary particles and the clusters are taken into account [10,11]. Skeletal density measurements on the corresponding aerogels have also been performed as well as a study of the development in skeletal density as the aerogels were heated in air to 350°C. Papers describing properties of corresponding gels and the prediction of gel shrinkage during drying have been published [7,12].

2. Experimental procedure

Alcogels were prepared from TEOS, H_2O, ethanol, HCl, and NH_4OH in the total molar ratio $1:3.5:3.9:7.8 \times 10^{-4}:5.7 \times 10^{-3}$ by a procedure similar to that described by Brinker et al. [13]. The TEOS was hydrolyzed in a solution with molar ratios TEOS:H_2O:Ethanol:HCL equal to $1:1:3.9:7.8 \times 10^{-4}$ under reflux for 1.5 h at 60°C. This solution was mixed with the remaining water and NH_4OH, cast into Teflon® tubes with an inner diameter of 8.6 mm, and kept at 40°C for 1 h for gelation. The rod shape of the gels was needed for the measurements of mechanical properties of the gels [3]. To study the effect of aging time in TEOS/ethanol the gel rods were first soaked in a *washing solution* (20 vol.% H_2O/ethanol) for 24 h at 60°C and second in an *aging solution* 70 vol.% TEOS/ethanol) for times from 6–72 h at 70°C. During aging, the wet gels gain weight and hence the *wet density*, which is the density of the dried gel if there were no shrinkage during drying, increases. In addition, reference samples were prepared by washing only in ethanol or 20 vol.% H_2O/ethanol for 24 h at 60°C. Generally the volume ratio gel : washing or aging solution was 1:3.1.

After aging in TEOS, the gels were washed in ethanol and dry *n*-heptane (max 0.01 wt% water) four times within 24 h at 50°C before drying at ambient pressure in steps of 24 h duration at 70, 90, 120 and 180°C. The evaporation rate was limited during the drying by keeping the gels in a container with only a pinhole. The gels were dried from *n*-heptane since this is a liquid with low surface tension (γLV, *n*-heptane (90°C) = 13.4 dyne/cm) [14] giving less shrinkage during drying [7,12]. To be able to follow the development in skeletal density with heating temperature, corresponding aerogels dried from CO_2 at 40°C were prepared since ambient pressure drying demands temperatures up to 180°C. The aerogels were prepared by a procedure previously reported by Scherer et al. [12].

The SANS measurements were performed at the SANS facility at Risø National Laboratory, Denmark. The instrumental settings were ranging from 1 to 6 m for the sample to detector distance and 3 to 9 Å for the wavelength, which allowed a *q*-range of 0.002 to 0.5 Å^{-1}. The instrument was equipped with a Helium-3 filled area detector with a diameter of 58 cm. The samples were measured in vacuum at 25°C. The scattering intensity, *I*, was measured as a function of the scattering wave vector $q = (4\ \pi/\lambda)\ \sin(\theta/2)$, where λ is the incident neutron wave length and θ the scattering angle. The scattering curves were corrected for the instrumental background and normalized with respect to H_2O. The xerogels were heat treated in air at 300°C to remove organic residue before SANS.

Skeletal density was measured by helium pycnometry (Micromeritics, AccuPyc 1330, 1 cm^3 sample chamber) using a sample size near 1 cm^3. To obtain stable results, we found it necessary to heat the samples in vacuum at 50°C for about 12 h to remove adsorbed water prior to measurement. To follow the development in skeletal density with temperature the aerogels were heated to 120°C, 150°C, 200°C, 250°C, 300°C and 350°C in air for 2 h. After heat treatment to 350°C a shrinkage of 0.6% was observed.

Xerogel bulk densities were calculated from sample weight and volume after drying to 180°C and heat treatment in air at 300°C. The hydraulic radius, r_h, was calculated from $r_h = 2V_p/\mathrm{SA} = 2(1 - \rho_{xero}/\rho_s)/(\rho_{xero}\mathrm{SA})$, where SA is the surface area measured by N_2 adsorption (Micromeritics ASAP 2000) and V_p is the specific pore volume of the xerogel given by the xerogel bulk density, ρ_{xero}, and the skeletal density, ρ_s.

3. Results

Table 1 summarizes the wet density, hydraulic radius of wet gels, density of xerogels/aerogels, hydraulic radius of the xerogels, and surface area of the different gels.

A log–log plot of the SANS measurements of the samples with increasing aging times are shown in Fig. 1. Each scattering curve is characterized by an almost flat section at small q-values, a small peak and fractal like slopes at higher q-values. The small peak, which is due to structural correlations, motivates the introduction of a structure factor.

The scattering curves were fitted to a model of fractal network [10]

$$I(q) = P(q)S(q)\Phi(q), \tag{1}$$

where $P(q)$ is the intra structure factor. For a sphere, $P(q)$ can be approximated to

$$P(q) = 1/(1 + 0.22(qR)^{6-D_S}), \tag{2}$$

where R is the radius, D_S is the surface fractal dimension of the sphere and the factor 0.22 is experimentally determined [10]. $S(q)$ is the inter-particle structure factor which is dependent upon the interactions between the particles in a cluster. For a fractal structure, Texeira [11] has developed Eq. (3) describing the structure factor:

$$\begin{aligned} S(q) = {} & 1 + ((D_v)/(qR)^{D_v})(\Gamma(D_v - 1)) \\ & /(1 + (1/(q\xi)^2)^{(D_v-1)/2} \sin[(D_v - 1) \\ & \tan^{-1}(q\xi)]), \end{aligned} \tag{3}$$

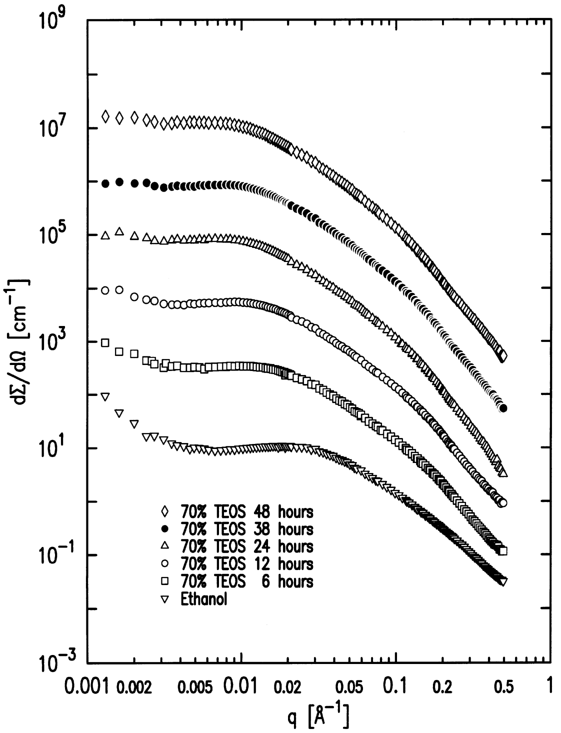

Fig. 1. SANS scattering curves for samples aged at different time intervals in a TEOS solution. The sample marked ethanol is only washed in ethanol prior to drying from n-heptane. The curves are separated by multiple powers of 10.

where D_v is the volume fractal dimension and ξ is the correlation length of the cluster. $\Phi(q)$ is dependent on the concentration of clusters and can in the case of hard spheres be approximated to

$$\Phi(q) = 1/(1 + pj_1(qD)), \tag{4}$$

Table 1

Wet density, hydraulic radius of wet gels, xerogel and aerogel density after heat treatment to 300°C, hydraulic radius of xerogel and surface area of gels aged at different time intervals in a TEOS solution and samples only washed in ethanol or 20 vol% water/ethanol solution prior to drying from n-heptane

Aging treatment	ρ_{wet} (g/cm^3)	$r_{h,wet}$ (Å)	ρ_{xero} (g/cm^3)	ρ_{aero} (g/cm^3)	$r_{h,xero}$ (Å)	SA (m^2/g)
Ethanol	0.100 ± 0.005	–	0.692 ± 0.005	–	–	–
20% water/ethanol	0.117 ± 0.003	155.3 ± 9.1	0.355 ± 0.006	0.123 ± 0.005	45.5 ± 1.9	1029 ± 10
70% TEOS 6 h	0.133 ± 0.003	147.3 ± 7.1	0.299 ± 0.005	–	60.1 ± 2.5	958 ± 9.7
70% TEOS 12 h	0.158 ± 0.004	136.5 ± 7.6	0.267 ± 0.006	0.189 ± 0.005	70.0 ± 5.1	846 ± 9.5
70% TEOS 24 h	0.192 ± 0.004	119.5 ± 6.2	0.232 ± 0.005	0.227 ± 0.005	97.2 ± 5.2	779 ± 10.3
70% TEOS 38 h	0.205 ± 0.009	125.0 ± 11	0.220 ± 0.004	–	115.6 ± 5.5	706 ± 9.6
70% TEOS 48 h	0.225 ± 0.006	117.0 ± 7.4	0.229 ± 0.004	0.287 ± 0.005	115.5 ± 7.0	665 ± 9.5
70% TEOS 72 h	0.261 ± 0.001	–	–	0.291 ± 0.005	–	–

Table 2
Particle radius, correlation length of the clusters, size of the largest clusters, volume fractal dimensions, and surface fractal dimension of xerogels prepared at different aging times in a TEOS solution

Aging treatment	Particle radius $R \pm 0.3$ (Å)	Cluster correlation length $\xi \pm 1$ (Å)	Largest cluster diameter D (Å)	D_s ±0.04	D_v ±0.04
Ethanol	6	26	185 ± 3	–	2.19
70% TEOS 6 h	9	52	273 ± 6	2.75	2.14
70% TEOS 12 h	9	55	342 ± 9	2.38	2.27
70% TEOS 24 h	9	61	423 ± 11	2.00	2.36
70% TEOS 38 h	9	56	436 ± 11	2.00	2.38
70% TEOS 48 h	10	65	516 ± 18	2.00	2.38

where p is the packing fraction chosen to be 0.5, D is the size of the largest cluster and $j_1(qD)$ is the first order spherical Bessel function [10].

In our analysis we used Eq. (1) with a fixed value of the surface fractal dimension, D_s. The fixed value was determined from simple model fitting to $q^{-(6-D_s)}$, where the exponent corresponds to the Porod slope. The results are given in Table 2. D_s decreases and reaches 2.0 after 24 h of aging, which corresponds to a smooth surface of the primary particles. The fit to the model in Eq. (1) for the scattering data from the gel aged for 12 h is shown in Fig. 2 and Table 2 includes the results from the fit of all the SANS data to this model. The volume fractal dimension of the clusters, D_v, increases only slightly from the non-aged gel, and remains about 2.3 after 12 h aging time. The primary particle radius increases from 6 to 9 Å after 6 h of aging followed by only a small change. The primary cluster size shows a steady increase from 26 to 65 Å after 48 h of aging. In the same manner the parameter D increases from about 185 to 520 Å in the same aging period.

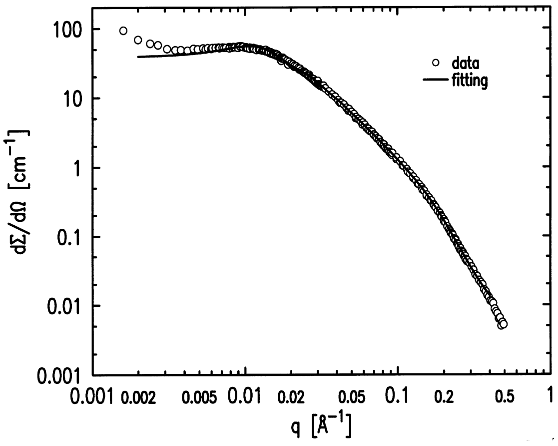

Fig. 2. An example of fitting the scattering curve for the sample aged for 12 h in a TEOS solution.

Table 3 gives the skeletal density of the aerogels as a function of aging time and as a function of heat treatment temperature. All the gels washed in 20% H_2O/ethanol or washed in 20% H_2O followed by aging in TEOS showed the same skeletal density of about 1.91 g/cm^3 after supercritical drying from CO_2 and heat treatment at 50°C. This skeletal density is significantly higher than for corresponding gels washed only in ethanol. The difference in skeletal density between aged and unaged samples is maintained to about 250°C.

4. Discussion

During washing in 20% water/ethanol prior to aging in TEOS strength and stiffness of the alcogel increase due to dissolution and reprecipitation of silica from the primary particle surfaces to the contact point to minimize negative radius of curvature [15]. Due to this stiffness increase [15] there is a large reduction in density of the xerogel compared to the gel washed only in ethanol (Table 1). However, this increase in stiffness is not sufficient to eliminate shrinkage and a density as high as 0.355 g/cm^3 is obtained. As can also be seen from Table 1 there is a rather high increase in ρ_{wet} during the aging in TEOS showing that silica is added

Table 3
Skeletal density in g/cm^3 of aerogels as a function of aging time in TEOS and heat treatment temperature

Aging treatment	50°C	120°C	150°C	200°C	250°C	300°C	350°C
Ethanol	1.76	1.78	1.73	1.76	2.09	2.15	2.15
20% water/ethanol	1.91	1.90	2.00	1.95	2.10	2.20	2.18
70% TEOS 12 h	1.92						
70% TEOS 24 h	1.90	1.90	1.90	1.93	2.07	2.15	2.23
70% TEOS 48 h	1.90						
70% TEOS 72 h	1.91						

Uncertainty is within ±0.05 g/cm^3.

to the original network. Due to the lower solubility of silica in the smallest pores and at the necks between the particles (concave surfaces) it is believed that silica is first deposited in these places and hence, the surface area of the resulting xerogel decreases with aging. Also a significant decrease in hydraulic radius of the wet gels with increasing aging time is observed. However, the decrease in hydraulic radius is only about 25% for an increase in ρ_{wet} of almost 100%. Hence, a large pore size is maintained during the aging in TEOS. The density of the aerogels follows the increase in ρ_{wet} while for the xerogels there is a minimum in density after 38 h of aging. At this aging time the stiffness is sufficiently high that the linear shrinkage is almost eliminated [12,16]. On further increase in ρ_{wet}, an increase in xerogel density is observed because there is no shrinkage during drying. Due to the reduced shrinkage during drying giving a decrease in xerogel density, the pore size represented by hydraulic radius in Table 1 increases to about 38 h of aging in TEOS.

The structural development during aging was further studied by SANS measurements. The structure of the gels can be elucidated from the scattering data in Fig. 1 using the model described in Eq. (1). The radius R of the primary particles, see Table 2, is nearly doubled and the volume is increased more than three-fold during the first 6 h of the aging process. Thereafter, primary particle size increases only slightly.

Like the primary particle radius, cluster size also increases with aging. The cluster size shows a continuous growth; however, the increase is much slower after 24 h of aging, see Table 2. After 24 h of aging, the cluster size is more than doubled and this increase is larger than that which an increased primary particle radius can account for. Mass added to clusters must come from addition of new primary particles and filling the necks between particles. Assuming that the growth of the clusters is solely due to particle number growth and a packing fraction of 0.5, the number of primary particles in the clusters increases from 5 before aging to 17 after 24 h of aging.

The larger dimension D derived from the model in Eq. (1), can be associated with cluster–cluster distances, and thus represents largest cluster size. D increases from about 185 to 520 Å after 48 h of aging as can be seen in Table 2. The hydraulic radius of the xerogels given in Table 1 is about twice the size of the cluster correlation length. Compared to the parameter D, the cluster–cluster distance, the hydraulic diameter is about 40–50% of D.

In Fig. 1, a straight section is observed in the scattering curves, which indicates that the gel structure is fractal or has some fractal components. Eq. (1) gives both the surface fractal dimension of the primary particles, assumed to be a fixed value, and the volume fractal dimension, D_{v}, of the gel. The volume fractal dimension, which describes porosity of the structure that makes up the gel network [15], can never exceed 3 which represents a solid body. As can be seen from Table 2, D_{v} increases only slightly with increasing aging time. It reaches a value of approximately 2.3, which is slightly below the value found by Vacher et al. [17] using the same model on a tetramethoxysilane (TMOS)-based gel. The constant D_{v} value shows that the network structure geometry does not change during aging. However, as seen above, structural size associated with gel increases with aging. The primary particles as well as the clusters grow, but there is no significant change in the structure, hence, the connectivity remains unchanged.

The skeletal density reported in Table 3 shows an increase to about 250°C and the theoretical density of amorphous silica of 2.19 g/cm^3 is reached at 350°C. The samples washed only in ethanol after gelation show a much lower skeletal density to about 200°C; however, the same behavior is observed above 250°C. The increase in skeletal density from about 250°C is most probably due to ethoxy group oxidation which takes place between 200°C and 300°C [18–20]. During oxidation large ethoxy groups on the gel surface are exchanged by smaller hydroxy groups which gives higher skeletal density. In addition, condensation reactions might occur between the hydroxyl groups giving a small shrinkage as was observed. Ayral et al. [20] observed a similar increase in skeletal density with oxidation heat treatment to 400°C for TMOS based gels.

There is a significant difference between the gels washed only in ethanol and those washed in 20% water or washed in 20% water followed by aging in a TEOS solution. Gels washed only in ethanol exhibit a lower skeletal density to about 250°C. This difference in skeletal density is attributed to the presence of water during the washing in the water solution and the aging in TEOS solution. The presence of water causes solution/reprecipitation to occur giving a smoother network. In addition, and probably more important, continued hydrolysis and condensation reactions occur giving denser particles. From Table 1 it is observed that ρ_{wet} increases from 0.100 to 0.117 g/cm^3 during washing in 20% water solution compared to the ethanol washing. This increase must be due to a reduction in volume of about 15% since no silica was added and is most possibly caused by increased condensation reactions. A water content of 0.51 wt% was measured after the four washings in ethanol confirming a low water content during that washing. We have previously shown that gel esterification does not occur during washing in ethanol solutions [21] and increased esterification during the ethanol washing cannot explain the difference in observed skeletal density.

It should also be pointed out that the skeletal density of the aerogels is independent of aging time in TEOS even if the weight increase during the aging is 160%. This constant skeletal density shows that the silica precipitated from the aging solution has the same skeletal density as the original silica network. This is consistent with the almost constant volume fractal dimension obtained from the SANS measurements for all the aging times.

5. Conclusions

SANS measurements of xerogels prepared from TEOS-based alkogels aged in TEOS solution show an increase in both primary particle size and cluster size. However, while the primary particle size stays relatively constant after only 6 h of aging, the cluster size continues to increase. The volume fractal dimension shows only a small increase during aging in TEOS and reaches 2.0 after 24 h aging. Skeletal density of corresponding aerogels is higher if the wet gel is aged either in a water or a TEOS solution; however, it is independent of aging time. Skeletal density close to the theoretical value is reached at about 350°C for both aged and unaged samples.

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