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Gel to glass transformation in base catalysed silica

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ABSTRACT

The effects of heat-treatments on silica xerogels prepared from base catalyzed hydrolysis and condensation of TMOS are studied by low-frequency Raman scattering, scanning electron microscopy, small angle X-ray scattering and BET measurements.

Raman scattering in the range 3-700 cm^{-1} reveals a low-frequency band that arises from the discrete particulate character of base-catalysed gels at very small scale. A continuous evolution of the structure inside particles is observed during the thermal treatment and the Raman spectra is similar to the fused silica one after treatment at 1050°C.

Electron microscopy observations of the nanostructure of the xerogels correlate with the particle Raman band maximum.

Complementary SAXS and BET measurements allows us to propose a model for the gel-to-glass transformation.

INTRODUCTION

Recent low frequency Raman scattering measurements of base-catalyzed silica aerogels showed the presence of a maximum at very low frequencies (1). This maximum arises from scattering from surfaces modes of structural units or spherical particles. For silica xerogels prepared in acid conditions and dried in atmosphere, no low frequency maximum was observed as in the base catalyzed aerogels (2).

On the other hand, Raman scattering from heat-treated base catalyzed silica aerogels showed three stages in the transformation to glass (3): 1) modification of the particle surface 2) coalescence of the particles and 3) change of the internal structure and glass relaxation.

From these results, it appears interesting to follow the transformation of a base catalyzed xerogel with temperature by Raman scattering, but also by SAXS, scanning electron microscopy and BET measurements in order to understand the densification process.

EXPERIMENTAL

A) Technique

Gels were prepared by the hydrolysis and condensation of a solution of TMOS, methanol and water, in the presence of NH_4OH and

dimethylformamide (4). After drying at 160°C during 24 h, the xerogel obtained had a specific surface of about 617 m²/g, a pore volume of 1.46 cm³/g and a mesopore radius of about 43 Å, as determined by BET measurements. The apparent density was about 0.56 g/cm³.

The Raman measurements were obtained with a DILOR monochromator using the 5145 Å line of an argon ion laser as an excitation source and a cooled photomultiplier. The range investigated varied from 3 to 700 cm⁻¹. Fracture surfaces of Au20%Pt coated gels were observed with an HITACHI type S-800 scanning electron microscope.

The SAXS measurements were performed on a RIGAKU high power rotating anode generator (12 KW) with a position sensitive detector. A multichannel analyser connected to a microcomputer allows fast measurements. The X-rays beam of wavelength 1.54 Å (CuKα) is focused on the detector plane by a curved monochromator. The X-ray beam is held under vacuum in order to reduce air scattering. Point-like slit conditions with an irradiated cross section of about 1 mm² are used.

BET measurements were realized by the adsorption-desorption of nitrogen by the sample at very low temperature (-196°C).

B) Experimental results and discussion

Figure 1 shows the small angle X-ray scattered intensity in function of the scattering vector Q for xerogels annealed in air between 160°C and 1050°C. On the one hand, the presence of a maximum located at 0,019 Å⁻¹ for the sample dried at 160°C (a) is observed. This peak is attributed to a correlation distance (about 332 Å) between particles or clusters in the material. On the other hand, the SEM picture of this sample (figure 2) shows a microstructure consisting of spherical clusters with a mean diameter of about 300 Å constituted of particles with a diameter of about 60 Å. This allows to confirm that the maximum observed in figure 1 corresponds to the average distance between these clusters.

Secondly, Figure 1 shows also a shift of the maximum toward higher values of Q with the increase of the temperature of heat-treatment. At 700°C (b) the correlation distance is about 314 Å, at 980°C (c) about 300 Å and at 1030°C (d) about 290 Å. This shift reveals a collapse of the texture which is reorganized in the xerogel and that diminish the distance between the clusters. This phenomenon is confirmed by the increase of the width of the peak and by the decrease of the pore volume between 160°C (1.46 cm³/g) and 1030°C (0.3 cm³/g). At 1050°C (e) the spectrum shows no scattering, attesting the transformation of the xerogel to glass.

Figure 1. Sxas intensity (counts) in function of the scattering vector Q from base-catalyzed xerogels: (a) dried at 160°C (b) annealed for 30 mn at 700°C (c) annealed for 30 mn at 980°C (d) annealed for 30 mn at 1030°C (e) annealed for 30 mn at 1050°C. The time of the sxs experiment is 1000 s.

Figure 2: Scanning electron microscopy image of the xerogel dried at 160°C.

Now we can have informations about the structure of the material at shorter distance.

Figure 3 shows the reduced Raman spectra $I(\omega)/(n(\omega)+1)$ (where $I(\omega)$ is the Raman intensity, ω the frequency and $n(\omega)$ the Bose factor) up to 200 cm^{-1} for xerogels annealed in air between 160°C and 1050°C . At first, we can see the presence of a very low frequency band located at 17 cm^{-1} for the sample dried at 160°C (a). This kind of peak has already been observed with base catalysed aerogels (1) and can be attributed to surface-vibrational modes of particles which are aggregated to form the gel. The frequency ω_0 of the maximum is a function (5) of the sound velocity v in the particle and of the diameter $2a$: $\omega_0 = 0.8(v/2a)$. Choosing a velocity $v = 4000\text{ m/s}$, value slightly smaller than in silica, it is found $2a = 60\text{ \AA}$, value which correlate with SEM observations (figure 2). The spectrum of this sample shows a line about 32 cm^{-1} probably due to the presence of DMF and organic compounds in the xerogel.

The spectrum of the sample annealed at 700°C for 30 mn (b) shows no modification of the position of the low frequency band but reveals a narrowing of it. The spectrum of the sample annealed at 980°C (c) shows again a narrowing and a small shift of the band to 14 cm^{-1} . After the annealing at this temperature, the calculated diameter of the particle is $76\text{ \AA}$. This evolution of the very low frequency Raman scattering shows the growth of the largest particles at the expense of smaller ones due to the diminishing surface energy (6). At last, the spectrum of the sample annealed at 1050°C (d) is similar to the fused silica one (e), attesting the transformation of the xerogel to glass at this temperature.

Figure 3. Low-frequency Raman reduced intensity from base-catalyzed xerogels: (a) dried at 160°C (b) annealed for 30 mn at 700°C (c) annealed for 30 mn at 980°C (d) annealed for 30 mn at 1050°C . The spectrum of fused silica (e) is also represented.

Now it is interesting to consider Raman scattering at higher frequencies, due to the vibrational modes inside the particles. In figure 4 the direct spectra $I(\omega)$ up to 700 cm^{-1} for the different previous heat-treatment are presented. We can see that the broad band (characteristic of the disorder at short distance) is located at 400 cm^{-1} for (a) and about 440 cm^{-1} for (b). It reveals that there is a modification of the internal structure in the particles between 160°C (apparent density $= 0.56\text{ g/cm}^3$) and 700°C (apparent density $= 1\text{ g/cm}^3$) which changes the disorder at short distance. On the other hand, the apparition of the line at 608 cm^{-1} (which corresponds to a 3-fold planar ring formed from three tetraedra(8)) for the sample heat-treated at 700°C reflects the modification of the surface of the

particles. The surface which was rough becomes smooth (7). The line observed at 640 cm^{-1} for (a) is probably due to the presence of DMF and organic compounds in the dried gel at 160°C . The comparison of these two spectra also shows that the line at 478 cm^{-1} observed in (a) shifts to about 490 cm^{-1} in (b). These lines at 478 and about 490 cm^{-1} can be assigned to the 4-fold planar ring, respectively at the surface and

inside the particles (9). This shift reflects again the modification of the surface of the silica particles from rough to smooth. The comparison between (b), (c) and (d) reveals that the line due to the 4-fold planar ring (located about 490 cm^{-1}) increases compared to the line at 608 cm^{-1} due to the 3-fold planar ring. It shows the progressive evolution of the structure of the xerogel to the glass with the increasing of temperature, also reflected by the increasing of the intensity of the broad band compared to the line about 490 cm^{-1} . At 1050°C (apparent density = 2.19 g/cm^3), the spectrum (d) is similar to the fused silica one (e).

CONCLUSION

Our study allows the process of densification of base-catalyzed xerogels to be described. Two principal phenomena can be distinguished. The first is revealed by SAXS, BET and SEM and shows that the texture of the material consisting of clusters with a diameter of about 300 Å (constituted by beads of diameter about 60 Å) collapse with the increase of temperature. The second is showed by Raman scattering and reveals a modification of the structure at shorter distance with three stages: smoothing of the particles (beads), small growth of their size, modification of the structure inside the beads.

Figure 4. Raman intensity from base-catalyzed xerogels: (a-e) same samples as in figure 3

REFERENCES:

- (1): A. Boukenter, B. Champagnon, E. Duval, J.L. Rousset, J. Dumas and J. Serughetti, J. Phys. C: solid state phys. 21 (1988) L 1097-1102
- (2): A. Boukenter, B. Champagnon, E. Duval, J. Dumas, J.F. Quinson and J. Serughetti, Phys. Rev. Letter 57 (1986) 2391.
- (3): J.L. Rousset, E. Duval, A. Boukenter, B. Champagnon, A. Monteil, J. Dumas, and J. Serughetti, Journal of non-crystalline solids 107 (1988) 27-34
- (4): T. Adachi, S. Sakka, Journal of materials science 22 (1987) 4407-4410
- (5): E. Duval, A. Boukenter and B. Champagnon, Phys. Rev. Letter 56 (1986) 2052
- (6): C.A.M. Mulder, J.G. Van Lierop and G. Frens, Journal of non-crystalline solids 82 (1986) 92-96
- (7): F.L. Galeener, Sol. St. Commun. 44 (1982) 1037
- (8): R. Vacher, T. Woignier, J. Pelous and E. Courtens, Phys. Rev. B 37 (1988) 6500
- (9): G.E. Walfaren, M.S. Hokmamedi and N.C. Holmes, J. Chem. Phys. 85 (1986) 771