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SAXS AND BET STUDIES OF AGING AND DENSIFICATION OF SILICA AEROGELS

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Aerogels prepared by hypercritical drying of gels obtained by hydrolysis of TMOS/methanol 50% solution in acid and basic conditions were studied combining SAXS and BET methods. Diffraction results do not seem to reveal a fractal character as the POROD's limit $I(q)\ q^4 \to Cte$ was obtained in all cases without well characterised portions in log I(q) vs log q graphs. Aging produces a small increase in the density of the matrix.
Densification studies indicate that for moderate temperatures 530°-810°C the poresshow a shrinkage due to a diffusion controlled mechanism with an activation energy $\Delta E \sim 9$ Kcal/mole.
For higher temperatures expansion due to bloating was observed. The density of the matrix undergoes only a slight increase.

1. INTRODUCTION

The structure and texture of aerogels are strongly dependent on the preparation and aging conditions and it is well known that these influence their further evolution during thermal densification treatments. The detailed intermediate stages of this gel-into-glass conversion are however, still poorly understood.

The small angle scattering of X-rays (SAXS) together with more conventional BET surface analysis provide a most direct way of characterising the textural features of the intricate gel structures. In particular, more recent developments introducing fractal concepts might prove interesting in this respect. The present study was undertaken in order to explore these possibilities.

2. SAXS METHOD

The texture of the aerogels can be described by a "two density" model in which $\Delta\rho_e$ is the difference between the electronic density of the matrix and that of the pores. The intensity I(q) scattered by a diluted system of N "particles" of volume v (which can be either material particles or voids) is given by the GUINIER's limiting law :

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$$I(q) = N\Delta\rho_e^2 v^2 \exp\left(-\frac{1}{3} R_G^2 q^2\right)$$

where q is the modulus of the scattering vector, $q = 4\pi (\sin\theta)/\lambda$, with 2θ the scattering angle, λ the X-ray wavelength and R_G the (electronic) radius of gyration of the particle. This approximation is valid for $q R_G \ll 1$.

R_G can be obtained from SAXS measurements on a relative scale from log I(q) vs q^2 plots.

For a polydispersed system this procedure leads to an average radius of gyration $\langle R_G \rangle_z$ heavily weighted towards larger particles.

The intensity scattered at higher angles ($q R_G > 1$) can be analysed in terms of a power law using log I(q) vs log q plots :

$$I(q) \sim q^{-\alpha}$$

It has been shown [1,2] that α can be related to *fractal* characteristics of the particles :

* for "mass fractals" of dimension $1 < D < 3$, $\alpha = D$

* for "surface fractals" of dimension $2 < D_S < 3$, $\alpha = 6 - D_S$

For particles having a smooth surface, $D_S = 2$ and $\alpha = 4$ which corresponds to the classic POROD's law :

$$\lim_{q \to \infty} \left| I(q)\, q^4 \right| \to \text{cte} = p$$

In this case, for a system of two phases with volume fractions ϕ and $1-\phi$ the area of the interface per unit volume S/V is given by the relation :

$$\frac{1}{\pi\phi(1-\phi)} \cdot \frac{S}{V} = \frac{p}{Q_0}$$

where Q_0 is the integrated intensity

$$Q_0 = \int_0^\infty I(q)\, q^2\, dq.$$

which serves to normalise the intensities $I(q)$ expressed in arbitrary units.

From BET measurements the value of the interface *per unit mass* $S' = S/Vd_a$ is obtained, where d_a is the apparent density of the sample.

Combining this value S' with SAXS results the parameter $K = \phi(1-\phi)$ can be obtained, thence the two fractions of the coexisting phases.

This model leaves us with two possibilities for interpreting $\Delta\rho_e$:

a) the scattering is due to *solid particles* which form the fraction ϕ of density $\rho = d_a/\phi$, the remaining fraction $1-\phi$ corresponding to air-filled pores of zero density.

b) the scattering "particles" are *pores* which occupy the fraction ϕ , the remaining fraction $1-\phi$ corresponding to the solid matrix of a density $\rho' = d_a/(1-\phi)$

For $K < 0.25$ the concept of the minor and major phase has a meaning and it is usually possible to choose between hypotheses a) and b) from the calculated values of ρ and ρ'[3].

3. PREPARATION OF THE SAMPLES

Silica gels were prepared in a classic way by hydrolysis of solutions of tetramethoxysilane (TMOS), (Fluka) dissolved in methanol (1 :1 in volume). To this solution bidistilled water in proportion of 4 mole H_2O/mole TMOS was added under constant stirring. Two series of samples were prepared using either HNO_3(p_H=2) or NH_4OH(pH=9) as catalyser.

After a few minutes, the solutions were transferred into Pyrex tubes and hermetically closed. After gelation has occurred the tubes were immediately opened and placed in an autoclave for drying by hypercritical solvent evacuation[4]. The critical conditions p_c= 200 bar and t_c= 300°C were reached by the addition of methanol to the autoclave.

The specific surface S' of the dry aerogels obtained in this way was measured by N_2 BET and their apparent density d_a by Hg volumetry.

The samples destined for sintering studies were dried hypercritically *without* previous aging.

No additional oxydation or chlorination treatments were used in this study to remove residual organic groups and water before densification treatments.

The densification was followed isothermally at 530°C, 660°C, 810°C and 912°C.

The samples destined for SAXS studies were cut into thin slices, polished on both faces. Their thickness, adjusted for optimal X-ray transmission, varied with d_a ; it was of the order of 0.5 mm.

4. EXPERIMENTAL

The SAXS experiments were carried out using synchrotron radiation at LURE (Orsay, France). The X-ray source (DC-1 positron storage ring) with an appropriate collimation provides a very intense monochromatic beam with *point-like* cross-section. This type of geometry of collimation avoids the troublesome necessity of mathematical data desmearing for the slit-height effects inevitable in systems using "infinite height" slits and which may affect the precision of results used for testing the possible fractal behaviour.

The white beam of the storage ring is monochromatised by a double crystal monochromator of Si tuned for 8 KeV. The resulting X-ray wavelength was λ =1.55 Å. Two sets of slits define the beam cross-section and reduce the para-

sitic scattering.

A one-dimensional position-sensitive detector was used to record the scattered X-ray intensity from the sample. The parasitic scattering was subtracted in a standard way. All SAXS curves were determined on a relative scale.

5. RESULTS AND DISCUSSION

5-1 Aging

This study was performed on acid- and base- catalysed series.

Table I gives the variations of the specific surface S' and apparent density d_a during aging. It can be seen that while, for acid-catalysed series S' decreases, for base-catalysed series S' actually increases with aging time ; d_a shows a slight increase for both series.

Fig.1 shows the SAXS intensity curves for the *acid series* plotted as log I(q) vs log q. It can be seen that the different curves can be made coïncident for higher values of q and only minor differences for lower q values ($q < 0.04$ Å^{-1}) are apparent as a result of aging. These are shown on a larger scale in the insert of Fig.1. The curves are seen to approach progressively the limiting slope $|\alpha| = 4$ corresponding to POROD's law without any intermediate well-characterised q- interval to which a constant slope with $|\alpha| < 4$ could be ascribed. The approach to the POROD's slope occurs indeed, with values $|\alpha| > 4$ which is an often seen effect . This indicates that the aerogel presents a sharp interface at the ~ 4 Å scale and that no fractal characteristics seem to be present in the samples studied.

For the basic series the same limiting slope $|\alpha| = 4$ is observed, the curves

TABLE I

p_H	Aging time (days)	d_a(gcm^{-3})	S'(m^{2}g^{-1})	$\langle R_G \rangle$(Å)	ρ(gcm^{-3})	ρ'(gcm^{-3})	ϕ
2	0	0.39	465	61	5.0	0.47	0.18
2	7	0.445	440	48	4.5	0.56	0.20
2	14	0.45	413	46.5	5.3	0.55	0.18
2	21	0.47	353	45	5.6	0.57	0.18
9	0	0.17	380	129	3.6	0.18	0.05
9	8	0.18	423	102	2.5	0.19	0.07
9	16	0.19	621	99	2.0	0.21	0.09

show however an intermediate linear portion with values $|\alpha|$ = 2.18, 2.43 and 2.37 respectively for 0, 8 and 16 days of aging. This could correspond to a fractal regime for aggregates of dimensions around 100 Å formed of elementary smooth particles of radius ∿ 15 Å.

The values of $\langle R_G \rangle_z$ obtained from the GUINIER plots are shown in Table 1. It can be seen that $\langle R_G \rangle_z$ systematically decreases which should correspond to the filling-in of the pores during aging.

The calculated values of ϕ, ρ and ρ' are also included in Table 1. The absolute values of ρ being much greater than 2.2, limiting value for solid glass phase, or decreasing for the basic series, hypothesis b) was adopted corresponding to a matrix of density ρ'. This light phase contains closed nanopores which are not detected either by SAXS or by BET. The meso- and macro-pores are the scattering units characterised by $\langle R_G \rangle_z$ and S'. The ρ' values are higher for acid series ; ρ' increases slightly during aging for both series. This could correspond to the increase of the cross-linking while still in the liquid phase or to an isotropic contraction of the matrix due to a syneresis effect.

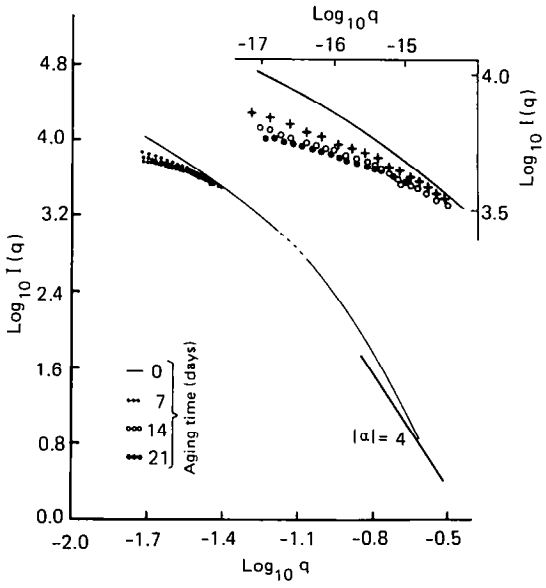

FIGURE 1
Scattered intensity curves for different aging stages ; they are vertically shifted to make the high-q portions coïncide. The insert shows the detail of I(q) variations for lower q values.

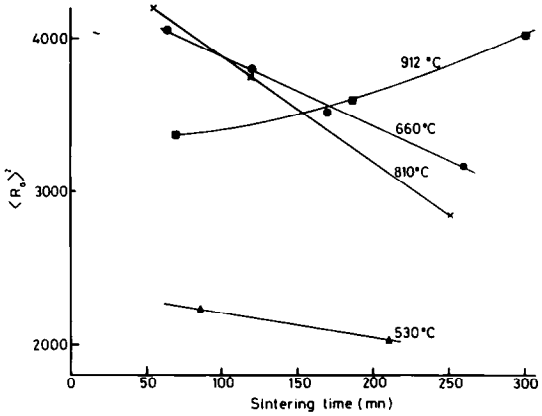

FIGURE 2
Variation of $\langle R_{G_z} \rangle^2$ during isothermal sintering for temperatures indicated

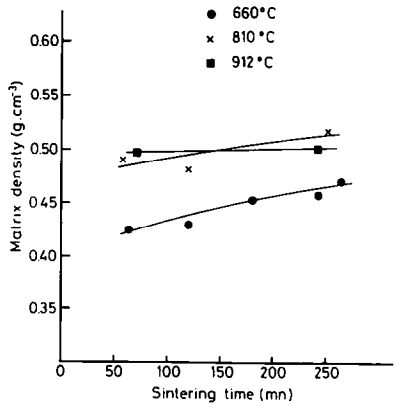

FIGURE 3
Evolution of matrix densities ρ' for various densification temperatures

The pore fraction ϕ shows a transient increase consecutive to the initial contraction of the solid phase and then decreases as the syneresis progresses with time.

5-2 SINTERING

The log I(q) vs. log q plots are similar to those of Fig.1 previously obtainned for aging.

This indicates that POROD's behaviour is obeyed during sintering as would be normal for well defined interfaces which might only undergo further smoothing during this thermal treatment.

No fractal behaviour is observed for intermediate values of q.

Fig.2 shows the values of $\langle R_G \rangle_z^2$ plotted as a function of time for different densification temperatures. The initial values of $\langle R_G \rangle$ may differ as samples issued from several batches were used for technical reasons. It can be seen that for lower temperatures t = 530, 660 and 810°C $\langle R_G \rangle_z^2$ shows a linear decrease while for 912°C an increase with time is observed. This may be interpreted as indicative of a diffusion-controlled shrinkage of the pores - the behaviour at 912°C is due to a bloating process by expansion of gases in closed pores. It is to be noted that for samples previously oxydized no such expansion is noted even at 1080°C and continuous shrinkage of R_G is observed[5].

From the Arrhenian analysis of the velocity constant an average activation energy of about $E \sim 9$ Kcal/mole was obtained. This would confirm an initial sintering mechanism controlled by OH migration[6].

The matrix density shows surprisingly small variations (Fig.3) which might indicate that the densification processes in the temperature range studied here are hindered by previous reesterification of surface layers in the autoclave treatment. Further investigations are in progress.

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