

SAXS STUDY OF ISOTHERMAL SINTERING OF SILICA AEROGEL

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Isothermal sintering of SiO_2 aerogels was followed by small angle X-ray scattering using synchrotron radiation. An improved treatment of SAXS data which takes into account the presence of fluctuations explains the discrepancy previously observed with He-pycnometric methods. The matrix density of the gel is shown to increase in several steps, first by a diffusion-controlled mechanism and then by viscous flow.

1. INTRODUCTION

The densification of silica gels has recently been the object of numerous investigations because of the importance of this process in the synthesis of glasses from precursors 1-2.

Dilatometric studies seem to indicate the occurrence of two distinct stages: at lower temperatures (500°-800°C.) the dry gel first undergoes a diffusion-controlled contraction, followed, at higher temperatures (1000-1200°C) by viscous flow sintering 3.

Preliminary studies using small angle X-ray scattering (SAXS) have shown 4-7 that the initial density of the gel matrix is quite small. Values of the order of 0.3-0.4 g/cm³ confirmed the results of independent electron microscopy (TEM) observations 8. These results are, however, in contradiction with skeletal density values obtained by the He-pycnometry which are in the 1.7-2.0 g/cm³ range 9-11.

In the present study an improved treatment of SAXS data is applied to evaluate the results of isothermal sintering studies of SiO_2 aerogels. It will be shown that the previous discrepancy can be explained by the fact that the densities

obtained by different methods are not relative to the same particle scale.

2. SAMPLE PREPARATION

Silica gels were prepared from solutions of tetramethoxysilane (TMOS) dissolved in methanol. The composition was 50 vol% of methanol. To this solution distilled water was added in the molar ratio $\text{H}_2\text{O} : \text{TMOS} = 4$. Sol formation was catalysed by HNO_3 with pH = 2.

After vigorous stirring, gelation occurred in hermetically closed Pyrex tubes kept at 55°C. for one week. The wet aged gels were dried in hypercritical conditions ($P_c = 200$ bar, $T_c = 300^\circ\text{C}$); the resulting aerogels were oxidised at 500°C. for 5 hours under controlled flow of oxygen.

Densification was studied in isothermal conditions at 615°, 780°, 915° and 1060°C. All the samples were taken from the same batch in order to have identical initial characteristics. The nitrogen BET specific area(s) was determined using Micromeritics 2100E equipment, the apparent density (ρ_a) was obtained from Hg-volume

Samples destined for SAXS measurements were cut in the form of thin slices of optimum thickness and polished on both faces.

3. SAXS METHOD

SAXS measurements were obtained at LURE synchrotron radiation facility (Orsay, France) with $\lambda = 1.55 \text{ \AA}$. The point-like cross-section of the beam dispenses from slit-height desmearing procedures. Experimental details have already been described elsewhere ⁴.

The SAXS intensity $I(q)$ vs. modulus of the scattering vector q were obtained on a relative scale. A two-level electronic density model was used to evaluate the SAXS results. The low- q region was interpreted using GUINIER's approximation

$$I(q) = I_0 \exp\left[-\frac{1}{3} \langle R_g \rangle^2 q^2\right]$$

where $\langle R_g \rangle$ is the average gyration radius and I_0 a constant.

In the high- q region positive departures from POROD's law were observed. The $\log I(q)$ vs. $\log q$ plots have systematically a slope greater than 4 and slowly approach 4 for the highest values of q (Fig. 1).

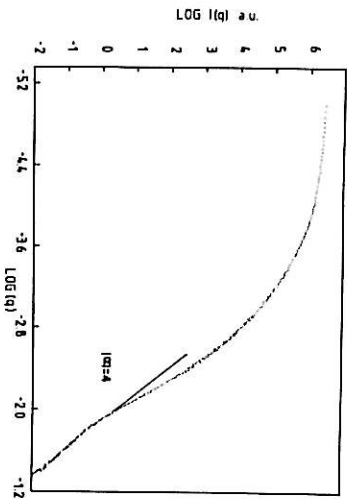


FIGURE 1 Typical $\log I(q)$ vs. $\log q$ plot of SAXS intensity of a silica aerogel.

Therefore RULAND's treatment¹² was adopted here with

$$I(q) = \frac{A}{q^4} + B$$

where B is a measure of density fluctuations. The constants A and B were obtained from $I(q)q^4$ vs. q^4 plot (Fig. 2).

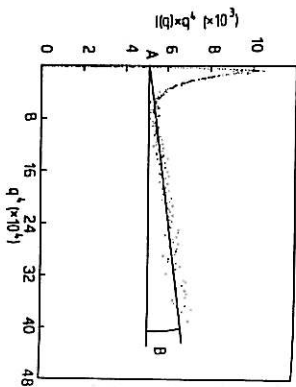


FIGURE 2 $I(q)q^4$ vs. q^4 plot showing the influence of the fluctuation term used to calculate the A and B constants (see text).

The volume fractions ϕ and $1-\phi$ of the two phases were obtained from the expression :

$$\frac{A}{Q_0} = \frac{5\rho_a}{\pi \phi(1-\phi)}$$

where the term Q_0 is the integrated intensity numerically calculated from the experimental curve.

4. RESULTS

The initial characteristics of the oxidised aerogel are : $S = 415 \text{ m}^2/\text{g}$, $\rho_a = 0.42 \text{ g/cm}^3$ and $\langle R_g \rangle = 62.3 \text{ \AA}$.

Table I shows the evolution of S and ρ_a as a function of time for various temperatures of

heat treatment, as well as the calculated value of $\langle R_g \rangle$ and the matrix density $\rho = \rho_a / (1-\phi)$ in the hypothesis of scattering by pores of volume fraction ϕ embedded in a (light) matrix of volume fraction $1-\phi$ ⁴.

For temperatures lower than 915°C, the plots of $\log[\rho(t)-\rho_a]/\rho_a$ vs. $\log t$ where the initial matrix density ρ_a is close to 0.52 g/cm^3 are sensibly linear with a slope close to 0.46 (Fig. 3). This is indicative of a diffusion-controlled mechanism involving fluctuations and nanoporosity which explains the previous deviation from POROD's law. The variations of $\langle R_g \rangle$ are small.

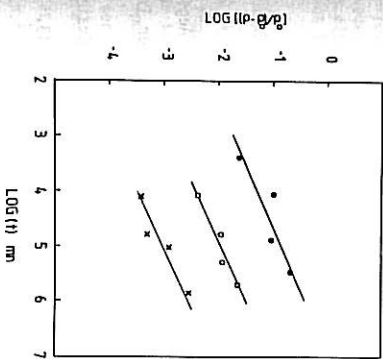


FIGURE 3 Relative increase of matrix density with time during thermal treatments at x 615°C, o 780°C, x 915°C.

At 915°C, the decrease of $\langle R_g \rangle$ and of the pore fraction ϕ to 0.5 as well as an increase of ρ indicate that densification occurs within the matrix (decay of nanoporosity) and that mesoporosity starts to be eliminated. A diffusion-controlled mechanism still seems appropriate for this stage.

For temperatures above 1000°C, the fluctuation term B vanishes which indicates that the

nano-heterogeneities of the matrix are completely eliminated.

Progressive densification of the matrix close to theoretical value is achieved⁵. The variations of $\langle R_g \rangle$ with time show a coalescence-typical behaviour for the pores. The increasing q-domain where POROD's law is obeyed indicates an increase of the length scale where the matrix is homogeneous.

A correlation of the results obtained here with results already published⁵ shows a monotonic variation of ρ vs. ρ_a (Fig. 4).

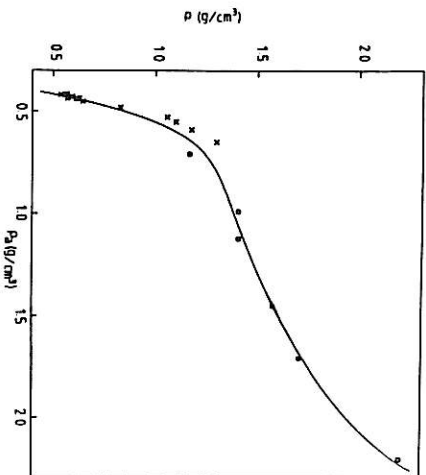


FIGURE 4 Evolution of matrix density ρ versus apparent density ρ_a during sintering x this work, o Ref(5).

The two distinct slopes of the curve clearly indicate two densification regimes : at first, densification of the matrix without much increase of apparent density, then simultaneous increase of ρ and ρ_a which point to the elimination of meso- and macro-porosity.

The apparent discrepancy between various methods of evaluation of ρ is thus readily explained : the light matrix values observed by

TABLE 1 : Evolution of microstructural characteristics for various heat treatments.

Temperature (°C)	time (mn)	S (m ² /g)	ρ_a (g/cm ³)	$\langle R_g \rangle$ (Å)	B x 10 ²	ρ (g/cm ³)
615	60	360	0.42	57.6	1.68	0.558
	120	365	0.42	56.2	2.75	0.560
	150	386	0.44		2.06	0.570
	295	382	0.43	59.3	1.91	0.583
780	60	372	0.43	61	2.19	0.59
	120	376	0.44	61.1	2.24	0.618
	200	374	0.44	62.8	3.29	0.621
	290	370	0.45	62	4.3	0.648
915	30	329	0.48	53	5.19	0.83
	60	325	0.55	54.5	5.51	1.1
	135	331	0.53	51	3.3	1.06
	235	296	0.65	52	4.8	1.3
1060	5	314	0.59	59.4	5.5	1.3
	15	248	0.88	55	1.41	1.1
	25	225	1.00	54	0.42	1.06
	30	212	1.33	55.45	0.42	1.3
	46	90	1.83	66.15		1.3

* the values of $\frac{S \rho_a}{\pi A}$ are greater than 0.25

SAXS correspond to particles 30-100 Å containing (open) nanoporosity. This can be penetrated in He-pycnometry but is seen by SAXS only as fluctuation residues. The ρ -values obtained by SAXS and those by He-pycnometry progressively coincide at later densification stages after elimination of nanoporosity.

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