

TEXTURAL CHARACTERISTICS OF SILICA AEROGELS FROM SAXS EXPERIMENTS

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Small angle X-ray scattering measurements on silica aerogels give systematically low values for the solid phase density. In order to explain these results, a hierarchical structure is proposed. Textural parameters such as specific surface area, size and density of clusters, and pore size are a function of the number of levels in the structure. Experimental values are consistent with values calculated for a hierarchy of two to four levels, depending on the initial sol concentration. The model can explain the fractal features for lower density aerogels.

1. Introduction

Silica aerogels are porous media, the apparent density and specific surface area of which are a function of the initial concentration of organometallic precursor. The solid phase density determined from He-pycnometry [1] as well as from wide angle X-ray scattering (WAXS) experiments [2] is close to that of fused silica. However, values obtained from small angle X-ray scattering (SAXS) are much lower [3,4].

In this paper, a simple geometric model is proposed to describe the textural of silica aerogels. It will be shown that He-pycnometry and SAXS give results which are representative of the structure on different length scales.

2. Structural parameters from SAXS experiments

The preparation of aerogels from TMOS alcoholic solutions has been described in detail elsewhere [5]. The general code for the samples will be AXC. A means aerogel, X represents the volumic concentration of TMOS in methanol and C indicates the type of catalyst (A B and N for

acid, basic and neutral catalyst respectively). The apparent density and BET surface area of the different samples are reported in table 1.

Thin slices of material of approximately 0.1 mm thickness were used for SAXS measurements. The experiments were carried out at LURE (Orsay), using synchrotron radiation facilities ($\lambda = 1.54 \text{ \AA}$). The typical scattering curves are shown in fig. 1. For $q > q_a$ the scattered intensity obeys Porod's law, while for $q < q_a$ a departure from Porod's law is observed. The parameter $a = 1/q_a$ which corresponds to the maximum radius of hard particles giving rise to Porod scattering is listed in table 1. The size of the network-forming particles is influenced by the catalyst used. The following sequence is observed $a_{\text{Basic}} > a_{\text{Acid}} > a_{\text{Neutral}}$. For the neutral series, a is also correlated to the sol concentration: the higher the concentration, the bigger the particles.

For length scales greater than a , it is not clear from the SAXS curves if aerogels are fractals. Nevertheless, a small q region where the intensity follows a power law is observed for the neutral and the basic series, as well as for A30A. The corresponding fractal dimensions are listed in table 1. The denser samples of the acidic series show

Table 1
Experimental microstructural parameters for silica aerogels

sample	Apparent density (g/cm ³)	Specific surface area (m ² /g)	Fractal dimension	a (Å)	R_g (Å)	ρ (g/cm ³)	ρ'
A30A	0.21	380	2.13	12	70	2.1	0.23
A30A	0.39	465	*	12	61	3.6	0.46
A70A	0.52	170	*	12	52	3.25	0.62
A30B	0.14	480	2.67	12	114	2.35	0.15
A40B	0.17	425	2.42	14	96	2.45	0.18
A50B	0.20	465	2.39	14	90	2.5	0.22
A20N	0.10	670	2.7	6	195	2.5	0.10
A30N	0.15	695	2.45	8	180	2.5	0.16
A40N	0.23	735	2.25	8	137	2.3	0.25
A50N	0.28	850	2.3	8	118	2.15	0.32
A60N	0.32	740	2.25	9	96	2.15	0.38

* Values not determined.

a positive departure from Porod's law. This is attributed to a fluctuation in electronic density [6]. If a two phase-model (solid matrix and pores) is assumed, the density of the aerogel skeleton can be calculated [3]. According to Babinet's principle, two values ρ and ρ' are found (table 1). ρ (respectively ρ') is calculated on the basis of a scattering by the solid phase (respectively the pores).

In the low q region, the gyration radius R_g can be calculated (table 1) and is related to the mean size of the scattering particles (pores or solid) for a dense system R_g should be interpreted as a correlation length.

3. Structural Model

Let us assume that the structure of a silica aerogel can be modelled by a fractal multiple cluster (fig. 2) as previously proposed by Zarzycki [7]. Each level is built up with 13 spheres in contact and the size ratio between two successive levels is 3. The fractal dimension of such a set is $D = 2.3347$.

If the microstructural details of the i -th level do not appear at the i th (i.e. the porosity is too small to be detected), the textural parameters (specific surface area, cluster size and density,

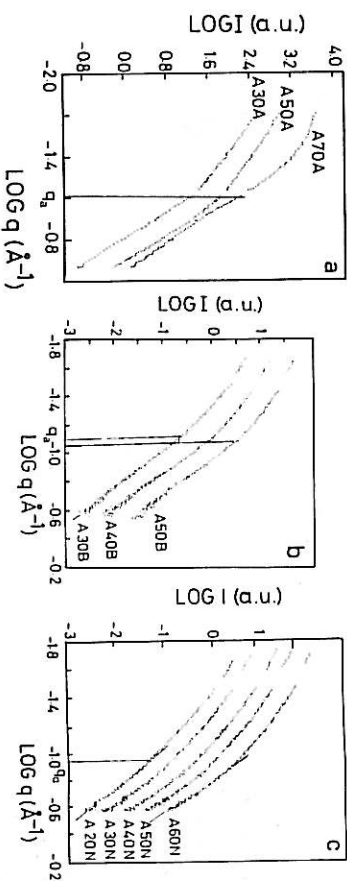


Fig. 1. Scattering curves of (a) acid-catalysed aerogels, (b) basic-catalysed aerogels and (c) neutral-catalysed aerogels.

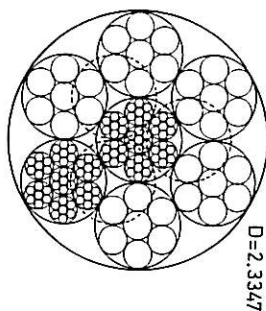


Fig. 2. Fractal multiple cluster (after ref. [7]).

pore size) are a function of the level considered. If R_0 , ρ_0 and S_0 are respectively the radius, the density and the specific surface area of the smallest spheres (level 0), the same parameters can easily be calculated for an n -level cluster by the following relations:

$$\text{cluster radius } R_n = 3^n R_0, \quad (1)$$

$$\text{cluster density } \rho_n = (N_1 \dots N_n) \rho_0 / 27^n, \quad (2)$$

$$\text{cluster area } S_n = 9^n S_0 / N_1 \dots N_n. \quad (3)$$

N_i is the number of spheres composing the i th level. As the coordination of silica spheres forming the aerogel network is still unknown, $N_i - 1$ is assumed to be close to the mean coordination of a disordered compact of hard spheres [8]. An n -level pore can be assimilated to the volume of the space between 4 spheres of the same level (tetrahedric insertion site). Its radius r_n is then given by the expression

$$r_n / R_n = 0.225. \quad (4)$$

For silica aerogels, ρ_0 can be taken as 2.2 g/cm³ in agreement with refs. [1] and [2]. R_0 is estimated from SAXS and is set equal to a . Table 2 lists R_n , S_n and ρ_n for the different values of a , assuming a constant value $N_i = 13$.

The main problem in SAXS experiments on silica aerogels is the assignment of the type of scattering phase and therefore the determination of the solid phase density. The proposed model may help us to understand the low experimental values both for the specific surface area and the matrix density, if they are compared with the calculated values.

3.1. Acid-catalysed aerogels

If the high density hypothesis is to be taken the values of ρ are to be compared to ρ_0 . The measured specific surface area is much lower than the total surface area of the smallest spheres (see tables 1 and 2). Further, the pores of the first level are really too small to be penetrated by nitrogen molecules.

On the other hand, for A50A and A70A samples the values of ρ' are consistent with the same order as ρ_0 to the density of a 2-level cluster. For A30A, ρ' is close to the density of a 3-level cluster. The BET specific surface area is of the same order as S_3 for A50A and A70A and is close to S_2 for A30A. If the scattering is due to the pores, the gyration radius is the mean size of the porosity. R_g can be compared

with r_3 for all the samples of the acid-catalysed series.

3.2. Base-catalysed aerogels

The textural parameters are consistent with a hierarchical structure: the matrix densities lie between ρ_2 and ρ_3 , while the specific surface area is close to the total surface area of a 2-level cluster for all the samples. The gyration radius is of the same order as r_2 .

3.3. Neutral-catalysed aerogels

ρ' is close to ρ_4 for A20N, ρ_3 for A40N. It is situated between ρ_3 and ρ_4 for A30N, while it lies between ρ_2 and ρ_3 for A60A and A50N samples. The specific surface area of a porous solid is related to the size of its particles: the smaller the particles the higher the surface area. The high specific surface areas of these samples are thus explained by low a values. They are consistent with a 3-level cluster for A20N and with a 2-level cluster for the other samples. The high gyration radius can be compared with r_4 .

4. Discussion

From the above comparison between experimental and calculated textural parameters, the combination of BET together with SAXS experiments seems to be a medium range characterisation of the aerogel network, while He-pycnometry provides a determination of the inner level of the structure.

The proposed structural model, despite its simplicity, allows the high density hypothesis (scattering by the pores) to be chosen: the aerogel thus appears as an aggregation of light clusters, the characteristic radius of which (or correlation length) is about 100 Å. In a BET experiment, the nitrogen molecules are adsorbed on their rough surface and penetrate inner shells of the structure only partially. The idealised hierarchical structure permits the calculation of the density and specific surface area of the clusters. It would be necessary to know the real coordination and the change of

coordination from one level to the following, to better fit the experimental values. The gyration radius is a measure of the size of the biggest pores detected by SAXS. The discrepancy between the experimental and calculated values is explained by the fact that no pore size distribution is taken into account in the model, while it is expected in the samples. The narrower porosity (encountered inside the characteristic clusters) is responsible for the decay of the matrix density as the distance is increased. This can be seen from the SAXS intensity for $q < q_a$.

The samples having a low apparent density (neutral series and A30A) are well represented by a 3-level structure. The fractal region is thus observed on more than one order of magnitude. The self-similarity domain is sufficiently extended to appear on the scattering curves. The measured fractal dimension is not so far from the theoretical value. The basic samples exhibit a fractal feature but their structure is described by only two levels. For denser samples, even though the aggregation concept is used to build up their structure, it is not relevant to consider them as self-similar media because their correlation length is too small (the number of hierarchical levels is too low). No fractal behaviour is observed on the scattering curves. The positive departure from Porod's law is explained by the presence of electronic density fluctuations [6] which are related to the porosity embedded in the light clusters [9].

5. Conclusion

It is worth noticing that both low matrix density and low specific surface area of silica aerogels are well explained by the hierarchical structure. The experimental parameters are consistent with a structure exhibiting two or four levels. It appears that the SAXS method corresponds to a characterisation of the porous body on a 10 to 100 Å scale which is complementary to He-pycnometry and WAXS methods. The proposed model could be refined, taking into account some physical-chemical factors to differentiate the samples: pore size distribution, sphere coordination, ... The

R_0 (Å)	n	R_n (Å)	S_n (m ² /g)	ρ_n (g/cm ³)	r_n (Å)
6	0	6	2250	2.2	1.35
	1	18	1557.7	1.06	4.05
	2	54	1078.4	0.51	12.15
	3	162	746	0.245	36.45
8	4	486	516.9	0.118	109.35
	0	8	1687.5	2.2	1.8
	1	24	1168	1.06	5.4
	2	72	808	0.51	16.2
9	3	216	560	0.245	48.6
	4	648	387	0.118	145.8
	0	9	1500	2.2	2.025
	1	27	1038	1.06	6.075
12	2	81	719	0.51	18.22
	3	243	498	0.245	54.67
	4	729	345	0.118	164.03
	0	12	1125	2.2	2.7
14	1	36	779	1.06	8.1
	2	108	539	0.51	24.3
	3	324	373	0.245	72.9
	4	972	258	0.118	218.7
14	0	14	964	2.2	3.15
	1	42	667	1.06	9.45
	2	126	462	0.51	28.35
	3	378	319	0.245	85.05
4	1134	221	0.118	255.15	

textural parameters could be calculated more precisely.

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