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ALUMINO-SILICATE AEROGELS

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RESUME - Des aérogels d'alumino-silicates, de densité comprise entre 50 et 250 kg/m3, ont été élaborés à partir du précurseur mixte (BuO)2Al-O-Si(OEt)3.

La diffusion centrale des rayons X montre que les structures des aérogels et des alcogels d'alumino-silicates sont formées d'unités élémentaires dont l'assemblage par un mécanisme d'agréation conduit à des particules fractales en masse. L'auto-similarité est mise en évidence dans les aérogels pour un large domaine de densité.

ABSTRACT - Alumino-silicate aerogels have been prepared from the (BuO)2Al-O-Si(OEt)3 double precursor with different densities (from 50 to 250 kg/m3).

SAXS study indicates that both alumino-silicate alcogel and aerogel structures can be represented by primary units which stick together into mass-fractal clusters (D = 1.8-1.9) by a mechanism of cluster-cluster aggregation. Self similarity is displayed in the alumino-silicate aerogels in a large range of densities.

1 - INTRODUCTION

We have previously shown /1/ that alumino-silicate alcogels can be prepared in the H2O, HOiPr, (BuO)2Al-O-Si(OEt)3 ternary phase diagram within a large range of oxide concentrations. The gelation time is governed by the initial water concentration, showing that the hydrolysis of Si-OR groups is the rate-determining process for the gelation.

The alcogel structure typically contains more than 90% by volume fine pores confining alcohol. To prevent damage to the gel structure caused by interfacial forces, the alcohol removal must be done under supercritical conditions. The resulting low density solid material is called aerogel and is now well known in the pure silica system /2-4/.

In this paper, we report the preparation of alumino-silicate aerogels with different densities and structural results obtained from alcogels and aerogels by small angle X-ray scattering (SAXS).

2 - EXPERIMENTAL

i-Gelation and drying

Alcogels have been prepared in the H2O - HOiPr - (BuO)2Al-O-Si(OEt)3 ternary phase diagram. A mixture of isopropanol and water is slowly poured into a mixture of precursor and isopropanol. The initial composition, noted 1.4.2 corresponds to one volume of water, four of solvent and two of precursor. Other compositions are obtained by dilution with 2-propanol. Samples were kept in sealed glass containers at 25°C and the gel time was defined by observing the stiffness after tilting the container. For all the
samples, no significant change of volume is noted at the gel point.  
Supercritical drying of alumino-silicate alcogels, in an autoclave system (65bars - 245°C) leads to alumino-silicate aerogels which exhibit different densities. The apparent density ($\rho$) measured by Hg volumetry varies from 50 to 250 kg/m$^3$.

ii-SAXS method

Small angle X-ray Scattering (SAXS) data were recorded with a slit type camera (CuK$\alpha$ wavelength). The sample to detector distance was 500mm and the scattered intensity was counted with a linear position sensitive counter. The scattering vector $K=4\pi\sin\theta/\lambda$ where $\theta$ is the Bragg angle, ranges from 6.10$^{-3}$ to 2.10$^{-1}$ A$^{-1}$. Experimental results are corrected for parasite scattering and normalised to equivalent sample thickness, incident intensity and counter efficiency. To study the growth process, a sample cell is used with 0,025 mm "Mylar" windows and 0,5 to 1mm path length. Concerning SAXS measurements from aerogel samples, slices of about 2mm in thickness and 10mm in diameter were used.

Scattering in the Guinier region (low angles) depends on the characteristic dimension $R$ of the scattering entities and from the initial decay of the scattered intensity $I(K)$, one can deduce the electronic radius of gyration $R_g$ using the following formula /5/:

$$I(K) = n_p^2 N \exp\left(-K^2 R_g^2/3\right)$$

$$R_g = (3/5)^{1/2} x R$$

where $K$ is the scattering wave vector, $N$ is the number of scattering particles and $n_p$ the number of electrons in each particle ($n_p=\rho_p V_p$ where $\rho_p$ is the electronic density of particles of volume $V_p$).

Scattering in the Porod region defined as $KR >> 1 >> K_a$, where the monomer size is a, depends on the geometric structure of the scattering entities /5/. The scattered intensity decays as power law $I(K)\sim K^{-x}$ and therefore, in a Log-Log plot of $I(K)$ versus the scattering vector, the slope is sensitive to the geometry of the scatterers. For polymer-like structures /6/ (mass-fractal objects) the classic power-law exponent $x$ observed in the Porod regime is the fractal dimension $D$ which relates the size $R$ of the object to its mass $M\sim R^D$.

3 - RESULTS

i-Growth of alumino-silicate alcogels

Nuclear magnetic resonance /7/, small angle X-ray scattering /8/ and small angle neutron scattering /9/ studies of the gelation from the double precursor $(\text{BuO})_2\text{Al-O-Si(0Et)}_3$ have shown that, in the first steps, a rapid formation of particles takes place by condensation between Al-OH groups. These units formed of Al-O-Al linkages are then agglomerated by a cluster aggregation process chemically limited by the hydrolysis of the Si-OR groups.

Concerning SAXS curves, two regimes are observed on the Porod plots:
- a power law regime with a slope of 1.8 in the $(R_g/2)-10$ Å length range.
- a deviation from this power law (slope of 2.6) in the domain from 4 to 8Å.

This behavior is independent of the precursor concentration and, for a given concentration and a given polymerization state, it does not depend on further dilution. In fact, the slope of 1.8 is observed, at least near the gel point, over a decade of reciprocal space (A very close value of 1.9 has been obtained from S.A.N.S study /9/). Therefore, the exponent, at high length scale (above 10Å), can be reasonably equated to the fractal dimension $D$.

During the gelation, another independent determination of the fractal
dimension can be realized from variations of the extrapolated quantity \( I(K=0) \) by using the Guinier approximation:

\[
I(K=0) \propto n_P Z^N
\]  

(2)

Assuming that \( n_P N \) is constant, i.e., the total mass in solution remains constant, then \( I(K=0) \propto n_P \) and \( I(K=0) \) is proportional to the \( Z \)-averaged number of atoms in the particles. For a mass-fractal object:

\[
I(K=0) \propto R_g^D
\]  

(3)

A plot of \( \log I(K=0) \) versus \( \log R_g \) gives for \( D \) a value very close to 1.8 consistent with a cluster-cluster growth mechanism /10/.

In agreement with other observations of the gelation on silica and alumino-silicate sol-gel systems and in spite of the small range size explored, the SAXS study indicates that inorganic polymers in alcogels consist in primary polymeric particles, whose density depends on the hydrolytic conditions and on the reactivity of the precursor. These units stick together and form mass fractal clusters by a mechanism of cluster-cluster aggregation.

ii-Structure of alumino-silicate aerogels

Figure 1 contains SAXS data for six samples of different densities. For all the samples, two power-law regimes are seen in the Porod range with slopes of -1.85 and -4 (figure 2). The crossover is approximately the same for all the samples and occurs at about \( K=7.5 \times 10^{-2} \) Å\(^{-1}\) corresponding to a length of 13Å.

Using a fractal model to interpret the scattering data, the picture that emerges is a scattering from a smooth surface of homogeneous particles at short length scales (<13Å) and scattering from a mass fractal of dimension 1.85 at larger scales. Therefore, as observed for alcogel samples, the SAXS study indicates that the aerogel structure can be represented by a two level structure: It consists in primary dense particles (density \( \rho_a \) and size \( a \)) attached into mass fractal clusters by a mechanism of cluster-cluster aggregation.

Self similarity previously displayed in the silica system /11/ can be easily shown in the alumino-silicate system:

- Firstly, each sample has the same fractal dimension and the figure 3 clearly indicates that, in the fractal range, the different samples cannot be distinguished. Moreover, for high density samples a third regime exists at small \( K \) consistent with uniform nonfractal long range structure, corresponding to a decrease of the fractal range (\( R(\text{Å}) \) in size) with increasing density.

- Secondly, from the initial decay of the intensity in the Guinier region, we deduce the electronic radius of gyration \( R_g \). From the Log-Log plot of the radius of gyration versus the apparent density \( \rho \) (figure 4), one finds that the function relating the extension of the fractal domain to the density is the same for all the samples: \( R_g=18.7 \times \rho^{-0.84} \).

Using the mass-fractal law: \( \rho_P/\rho_a=(R/a)^D=3 \), taking the same description for primary units and considering as equal the density of the fractal particles and the average density of the sample (\( \rho_P=\rho \)), one finds \( D=1.81 \) from the power-law exponent of figure 4, a value close to the one determined from figure 2 establishing the mutual self-similarity within a large range of densities.

Moreover, it is important to note that, assuming the existence of spherical mass-fractal particles, the prefactor value (18.7) is consistent with the existence of primary units (13Å in size) of density 2.1 g/cm\(^3\), which is relatively close to the one (2.5 g/cm\(^3\)) of the usual alumino-silicate glass with the same composition (Al/Si molar ratio=1.) /12/.

Finally, using equation 3, a plot of \( \log I(K=0) \) versus \( \log R_g \) leads for
Fig. 1 - Scattered intensities for six alumino-silicate aerogel samples. The curves are labelled with $p$ in Kg/m$^3$. Starting from the top, each intensity was divided by two compared to the previous one.

Fig. 2 - Porod plots for alumino-silicate aerogels showing two power-law regimes with slopes of $-1.85$ and $-4$. The crossover approximately occurs at $K=7.5 \times 10^{-2}$ Å$^{-1}$. 
Fig. 3 - Scattered intensities at low K and in the intermediary K range for different alumino-silicate aerogel samples (the curves are labelled with $\rho$ in Kg/m$^3$) showing that each sample has the same fractal dimension and that the different samples cannot be distinguished in the fractal range. Moreover, the fractal range decreases in size with increasing density.

Fig. 4 - Function relating the extension of the fractal domain to the density for alumino-silicate aerogels, revealing that all samples are mutually self-similar.
D to a value of 1.84, which is another verification of the self-similarity in the alumino-silicate aerogels.

CONCLUSION

Alumino-silicate alcogels can be prepared from the \((\text{BuO})_2\text{Al-O-Si(OEt)}_3\) complex precursor in a large range of oxide concentrations. Supercritical drying of alumino-silicate alcogels, in an autoclave system \((65\text{bars} - 245^\circ\text{C})\) leads to alumino-silicate aerogels which exhibit different densities \((from 50 to 250 \text{ kg/m}^3)\).

SAXS study indicates that both alumino-silicate alcogel and aerogel structures can be described by a two level structure: It consists in primary units, polymeric particles for alcogels \((8\text{Å in size})\) and dense particles for aerogels \((density 2.1 \text{ g/cm}^3 and 13\text{Å in size})\), which are attached together into mass fractal clusters by a mechanism of cluster-cluster aggregation. The fractal dimension \((D=1.8-1.9)\) is the same in the two structures.

Self similarity previously displayed in the silica system is also observed in the alumino-silicate aerogels within a large range of densities.

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