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SILICA AEROGELS PREPARED BY HYPERCRITICAL ACETONE EVACUATION

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Résumé — Le tétraméthoxysilane est le précurseur utilisé. La réaction d'hydrolyse, effectuée en milieu acétone, conduit à des gels monolithiques dans un grand domaine de compositions. Le séchage hypercritique est directement réalisé sur les gels tels qu'ils ont été obtenus. Les conditions permettant d'élaborer des aérogels monolithiques sont précisées. L'analyse structurale des aérogels montre qu'ils sont similaires à ceux obtenus dans des conditions d'évacuation hypercritique de solvants alcooliques. Cependant, la distribution des groupements hydroxyles est fortement affectée par la nature du solvant employé. L'évolution de la structure des aérogels en fonction de la température est étudiée. Le frittage s'effectue à des températures supérieures à 1000°C et l'aérogel se-transforme en verre.

Abstract — Tetramethoxysilane is used as the silica source. The hydrolysis reaction, carried out in acetone, leads to gels which are monolithic in a large domain of compositions. The hypercritical drying is directly performed on the gels as obtained. Conditions to prepare monolithic aerogels are reported. The structural analysis of the aerogels shows that they are similar to those obtained from hypercritical drying in alcoholic medium. However, the hydroxyl group distribution is strongly affected by the nature of the solvent. The evolution of the structure of the aerogels as a function of temperature is investigated. Sintering occurs above 1000°C and the aerogel transforms into glass.

1 - INTRODUCTION

Synthesis of gels from organometallic compounds is a very flexible method allowing gels to be obtained under different experimental conditions. Particularly, various organic solvents are suitable to dilute metalalkoxide compounds /1/. Among solvents, alcohols are widely used. Meanwhile, acetone presents many advantages with regard to alcohols. It is known as a dehydrating solvent for materials containing aqueous solutions. It is totally miscible with water and alcohols. Its critical temperature and pressure are \( T_c = 235°C \) and \( P_c = 4.7 \) MPa respectively. These values are close to those of alcohols. On another hand, the solubility of silica into water-acetone mixture is very low even for temperatures higher than 200°C /2/. That last feature leads to the belief that textural modifications resulting from hypercritical drying will be decreased. Interest in that solvent also comes from its high ability to be diluted into liquid \( \text{CO}_2 \). When one wants to perform a silica aerogel by hypercritical \( \text{CO}_2 \) evacuation, the exchange treatments will be shortened if the initial solvent is acetone.

2 - PREPARATION CONDITIONS

The gels result from hydrolysis and condensation reactions of tetramethoxysilane (TMOS). Acetone plays the role of a mutual solvent for both TMOS and \( \text{H}_2\text{O} \). In the adopted nomenclature, \( V \) is the volume ratio \( \text{(TMOS}\times10^2)/(\text{TMOS+solvent}) \) and \( n \), related to the hydrolysis conditions, is the molar ratio \( \text{H}_2\text{O}/\text{TMOS} \).

The samples will be labelled \( X V-n \) where \( X \) refers to the nature of the solvent. The miscibility region of the ternary system \( \text{CH}_3\text{COCH}_3/\text{H}_2\text{O}/\text{TMOS} \) is shown on figure 1a. In this figure, the miscibility domain of \( \text{CH}_3\text{OH}/\text{H}_2\text{O}/\text{TMOS} \) is also plotted. As observed, the miscibility region is lower when acetone is the solvent. A similar remark can be made for a higher molecular weight alkoxide compound : the tetraethoxysilane (TEOS) [Fig. 1b].
Figure 1: Behaviour of ROH or CH₃COCH₃/H₂O/Si(OR)₄ solution at 25°C
- (a) R = CH₃ - (b) R = C₂H₅.

The gelation rate of the solutions CH₃COCH₃/H₂O/TMOS is quite slow. The solution is systematically raised to 37°C in a thermostated bath to accelerate the gelation.

The gelation time (tg) for solutions hydrolysed with n = 4 depends on the dilution [Table 1].

Table 1: Gelling times of solutions CH₃COCH₃/H₂O/TMOS vs V.

<table>
<thead>
<tr>
<th>V(%)</th>
<th>tg (day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>21</td>
</tr>
<tr>
<td>20</td>
<td>4 - 5</td>
</tr>
<tr>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
</tr>
</tbody>
</table>

For dilutions lower than 40% the mixture is no longer homogeneous and the results are not reported here.

The number of water molecules plays a very important role on the gelation time irrespective of the dilution [Fig. 2].

Figure 2: Gelling times of solutions CH₃COCH₃/H₂O/TMOS vs n.

All the wet gels are monolithic. However, gels for which V lies between 30 and 40 when n is less or equal to two appear cracked after the autoclave treatment. The curves presented in figure 2 are limited by the quantity of water molecules which induce
immiscibility when it is too high. This feature occurs for $n$ values above five in systems where $V = 40$. For $V = 30$ the studies are done for $n$ up to nine.

It clearly appears that monolithicity is always obtained when the hydrolysis is carried out under stoechiometric conditions ($n = 4$). Thus we have chosen to synthetize aerogels under those last conditions of hydrolysis. This was done so that a simple comparison may be made with aerogels previously elaborated under hypercritical evacuation of methanol /3/.

The hypercritical drying is performed in an autoclave of 1 litre capacity. The total amount of acetone used is 250 cc which corresponds to 200 cc of additional solvent. The autoclave is heated at a rate of 1.5°C/min. The pressure at 300°C is 10 MPa. At this temperature the evacuation is performed at a rate of 5 MPa/hour.

3 - CHARACTERIZATION OF THE AEROGELS

The aerogels produced from gels hydrolysed with four molecules of water per mole of alkoxide are all monolithic. They are macroscopically homogeneous. The influence of the dilution on the density and on the shrinkage during the autoclave process is reported on table 2. Moreover, the densest gels are the most transparent.

Table 2: Apparent density and linear shrinkage of aerogels vs their dilution.

<table>
<thead>
<tr>
<th>$V$ (%)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>Linear shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.16</td>
<td>16</td>
</tr>
<tr>
<td>30</td>
<td>0.19</td>
<td>17</td>
</tr>
<tr>
<td>40</td>
<td>0.28</td>
<td>20</td>
</tr>
</tbody>
</table>

The structural evolution of an aerogel coming from a gel produced in acetone (A) of 0.28 g/cm$^3$ density is studied as a function of temperature using IR transmission spectroscopy. The sample thickness ($e$) is 0.89 mm [Fig. 3]. Its thermal evolution may be compared to that of a classical aerogel produced by hypercritical drying in methanol (M) ($e = 0.82$ mm; $\rho = 0.29$ g/cm$^3$) [Fig. 4]. The thermal treatment is performed at the desired temperature for thirty minutes.

At room temperature, the two aerogels A and M exhibit some little differences in their structures. This is shown by the presence of some additional or differently distributed bands in the spectrum of aerogel A [Fig. 3] with regard to the spectrum of aerogel M [Fig. 4].

First, the intensity of the band due to free silanol groups (3740 cm$^{-1}$) is higher than that ascribed to hydrogen bonded silanols (3680 cm$^{-1}$) in the spectrum of aerogel A. Such a distribution of hydroxyl groups is unusual for classical methanolic aerogels.

Both spectra of aerogels A and M show several absorption bands located around 3000 cm$^{-1}$. They are situated at the same frequencies and are assigned to the stretching vibrations of C-H bonds. However, the ratio of the intensity of those bands to the intensity of bands relative to silanol groups is less in aerogel A than in aerogel M. Meanwhile, the existence of such bands in the spectrum of aerogel A clearly demonstrates that it undergoes a methoxylated reaction as does aerogel M. As a consequence, aerogels elaborated in acetone are also hydrophobic.

Several explanations may be proposed to account for this reaction of esterification in acetone medium. It may result from the methanol released during the hydrolysis reaction. On another hand, it is known that acetone, submitted to high temperature and pressure, can undergo decomposition and condensation reactions /4/. The by-products may react with the gel. This last assumption is supported by the fact that the spectrum of aerogel A shows two unusual absorption bands. Those bands are located at 1710 cm$^{-1}$ and 1650 cm$^{-1}$.

A gas chromatography study of the condensed liquid, removed from autoclave during the hypercritical drying step, shows that it contains, in addition to acetone, several other heavier compounds.

Experiments are in progress to better understand the origin of the esterification reaction occurring into the autoclave.

The structural evolution of aerogels A and M with temperature are very similar. The appearance, in a small temperature range (around 300°C), of an absorption band located at 1730 cm$^{-1}$ is due to by-products of oxidation, as previously demonstrated /5,6/.
Measurements of the weight losses of the aerogels as a function of temperature are performed with an heating rate of 3°C/min. Between 200°C and 400°C the weight losses of aerogels A are lower than those of aerogels M of the same composition. They evolve in a similar manner for temperatures above 400°C [Fig. 5]. However, as the density of aerogels A increases, TGA curve exhibits pronounced weight losses situated at 260°C-300°C and 450°C respectively. This feature is probably related to the desorption of chemical species produced by the oxidation reaction. The total weight losses between 270°C and 600°C for gels A are identical irrespective of the dilution. However, the losses decrease as the amount of water used to carry out the hydrolysis increases.

Figure 3: IR Spectra of aerogel A 40-4 as a function of temperature.

Figure 4: IR spectra of aerogel M 50-4 as a function of temperature.

Figure 5: Weight losses of different aerogels as a function of temperature.
The densification of the aerogel A 30-4 begins at 850°C and becomes very fast at 950°C as observed using dilatometric measurements carried out at a heating rate of 5°C/min. This sample was previously annealed at 500°C for ten hours in order to fully oxidize the organic residues. The total linear shrinkage of this sample, heated up to 1100°C, is about 45% [Fig. 6].

![Figure 6: Linear shrinkage of aerogel A 30-4 as a function of temperature.](image)

The evolution of the density of aerogel A 40-4 under an isothermal treatment performed at 1040°C is shown on figure 7. To avoid fracture, the sample, annealed at 500°C for ten hours, is then heated at a rate of 10°C/min to the above-mentioned temperature. At this temperature the density of the aerogel increases first linearly with time. The density evolves slowly after six hours of treatment. More than ten hours of treatment are necessary to achieve the aerogel-glass conversion. The obtained silica glass has a refractive index similar to that of usual silica.

![Figure 7: Density variation of aerogel A 40-4 as a function of time. The isothermal treatment is carried out at 1040°C.](image)

The final water content is determined by IR spectroscopy on a massive sample using the intensity of the band situated at 2.73 μm. With an extinction coefficient equal to 77.5 l/mole/cm the measured water content of the glass is near 3500 ppm in weight.
4 - CONCLUSION

Silica gels may be elaborated from organosilicon compounds by an hydrolysis reaction performed with acetone as solvent. The monolithicity of the gels is easily obtained and they can be transformed into aerogels by hypercritical evacuation of the solvent. Monolithicity is preserved during this process and permits us to transform aerogels into glass by a simple thermal treatment. The densification occurs above 1000°C which indicates that the sintering is due to a viscous flow phenomenon. The thermal evolution of these aerogels is analogous to that of aerogels elaborated in alcoholic medium. This behaviour can be related to their structures which were demonstrated to be similar by IR spectroscopy.

REFERENCES