Flexible silica based xerogels and aerogels for spatial applications

Luísa Durães[1*], Sofia Nogueira[1], Ana Santos[1], Carlos Preciso[1]
Jessica Hernandez[2], António Portugal[1]
[1] CIEPQPF–CEM group, Department of Chemical Engineering, University of Coimbra,
Pólo II, Rua Sílvio Lima, 3030–790 Coimbra, Portugal
[2] Active Space Technologies, Rua Pedro Nunes, 3030–199 Coimbra, Portugal

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Abstract

Flexible silica based xerogels and aerogels were synthesized via sol-gel technology with methyltrimethoxysilane (MTMS) precursor. A two-step acid-base catalyzed sol-gel process was used, followed by Ambient Pressure Drying or Supercritical Fluid Drying to produce the xerogels or the aerogels, respectively. The obtained materials have shown promising properties for aerospace applications, namely low density (40-100 kg/m^3), high surface area (~ 400 m^2/g), small pore size (~ 30 Å), high hidrofobicity (> 130º) and moderate flexibility.

1 Introduction

In the last few years, new synthesis technologies for advanced materials were developed. Commercial demand and environmental and energy restrictions have been the driving force for research on this area. The sol-gel technology is a good example of this trend, offering competitive advantages over traditional techniques: high homogeneity and purity of the product, low temperature required, preparation of new crystalline and noncrystalline solids and special products such as films and aerogels. By sol-gel technology, materials with improved and tailored properties may be prepared, as the product microstructure can be controlled during the synthesis and drying stages. Mainly, it is a wet technology, which starts from a homogeneous solution, that gives rise to a colloidal solution – sol, and evolves gradually to an integrated solid network – gel. In the end, a xerogel or an aerogel is obtained, if the gel is dried at ambient pressure or in supercritical conditions, respectively.

Silica aerogels synthesized with $Si(OR)_4$ precursors exhibit a nanostructured three-dimensional solid network with low density (~ 40 Kg/m^3), high surface area (~ 1000 m^2/g), low thermal conductivity (0.02 W/mK) and high transparency (~ 90 %). These unique properties allow their use in several applications, namely as thermal or acoustic insulators, dielectric or optical materials, filters and catalysts (Pierre and Pajonk, 2002, Rao *et al.*, 2006). However, they are brittle, absorb moisture and deteriorate with time. Flexible and hydrophobic aerogels would allow improved performance of these materials in particular applications, namely aerospace applications. An aerogel for applications in space should meet the targets/properties indicated in Table 1. The key property to tailorable aerogels for space is porosity: a high porous structure gives aerogels very low thermal conductivity and density, making them competitive with current space insulation materials. Also, if the application involves insulation from water, especially for electric components insulation, it is fundamental to have a material with high hydrophobicity. Aerogels in space have a wide range of applications, such as: thermal and structural insulators for re-entry and Mars vehicles, spacecraft components and cryogenic tanks; protection coatings for solar panels and thermal blankets; semi-flexible coatings for cables, ribbon Printed Circuit Boards (PCB's) and Multi Layer Insulation Blankets (MLI's) in space suits and spacecrafts; collection of

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[*] Corresponding author. Tel + 351-239-798737. E-mail: luisa@eq.uc.pt

Table 1 Indicative values for the properties of a suitable aerogel for aerospace applications.

1. Low thermal conductivity	⇨ Thermal properties:	Thermal conductivity (air)	0.017 W/(m K)
		Thermal conductivity (vacuum)	0.004 W/(m K)
		Thermal tolerance	500 ºC
		Melting point	1200 ºC
		Coefficient of thermal expansion	2-4 x 10^{-6} K^{-1}
2. Low weight **3.** Flexibility **4.** High acoustic insulation	⇨ Physical and acoustic properties:	Density	2-350 kg/m^3
		Surface area, BET	400-1000 m^2/g
		Percent solids	0.13-0.15%
		Mean pore diameter	4-30 nm
		Primary particle diameter	2-5 nm
		Sound velocity through the medium	100 m/s
5. Robustness and strength	⇨ Mechanical properties:	Poisson's ratio	0.2
		Young's modulus	106-107 N/m^2
		Tensile strength	16 kPa
		Fracture toughness	0.8 kPa/m
		Compressive modulus	0.3 MPa
6. Tailorable electrical conductivity	⇨ Magnetic and electric properties:	Dielectric constant	0.14(18-40 GHz)
		Electrical resistivity	1015 Ω cm
		Electrical resistivity (carbon doped)	0.1-1 Ω cm
7. Tailorable optical properties	⇨ Optical properties:	Refractive index	1-1.05
		Colour	Translucent

space debris; reinforced composites for re-entry or low pressure atmospheres devices; acoustic insulators for spacecrafts and for the International Space Station (ISS); radiation shielding; windows and optical instruments (if translucent); *etc.*

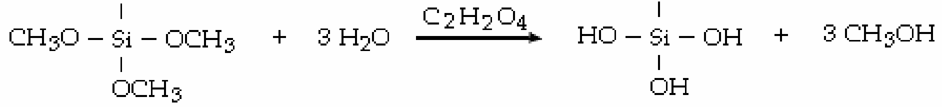
Using methyltrimethoxysilane (MTMS) as precursor in sol-gel chemistry, as proposed by Rao *et al.* (2006), the obtained silica based aerogels can fulfil the major part of the targets listed above. In MTMS, one OR group of $Si(OR)_4$ is replaced by R, being $R=CH_3$. This group does not suffer hydrolysis during the synthesis and remains in the aerogel structure, providing the hydrophobicity and flexibility required (Rao *et al.*, 2006, Baghat *et al.*, 2007). The density, the surface area and porosity are also controlled by the drying technique, being the xerogels denser and less porous than aerogels. However, both have very low density, very high surface area and porosity, and consequently very low thermal and electric conductivities.

In this work, flexible silica based xerogels and aerogels were obtained via sol-gel technology with MTMS precursor. The materials were chemically and physically characterized, for assessment of their suitability to aerospace applications.

2 Materials and Methods

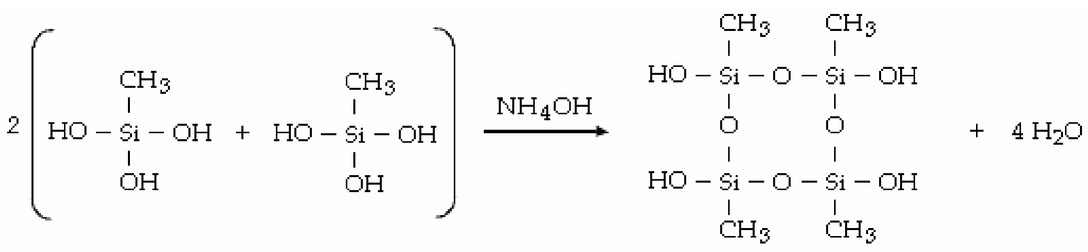
The applied sol-gel technology to synthesize the silica based xerogels and aerogels includes the sol-gel synthesis, which consists of a two-step acid-base catalyzed sol-gel process, pursued by ageing and drying stages. The overall experimental procedure followed the description of Rao, Baghat *et al.* (2006, 2007).

MTMS ($CH_3Si(OCH_3)_3$, 98 %, Aldrich), methanol (CH_3OH, 99.8 %, Riedel-de Haën), oxalic acid ($C_2O_2(OH)_2$, 99 %, Fluka) and ammonium hydroxide (NH_4OH, 25 % in water, Fluka) were used as precursor, solvent, acid and basic catalysts, respectively. At first, MTMS was diluted in methanol and then water was added, in the form of an oxalic acid solution (0.1 M), to promote the hydrolysis of MTMS (reaction 1) in acidic conditions (pH ≈ 2) – acid step.



$$CH_3O-\underset{OCH_3}{\overset{CH_3}{Si}}-OCH_3 + 3\,H_2O \xrightarrow{C_2H_2O_4} HO-\underset{OH}{\overset{CH_3}{Si}}-OH + 3\,CH_3OH \qquad (1)$$

After 24 h, an ammonium hydroxide solution (10 M) was added, drop by drop, and the condensation of monomers began (reaction 2), forming a sol – basic step. As the first drops were added, the pH increases sharply and the medium became alkaline. The pH after the total addition of the basic catalyst solution was ~ 12.

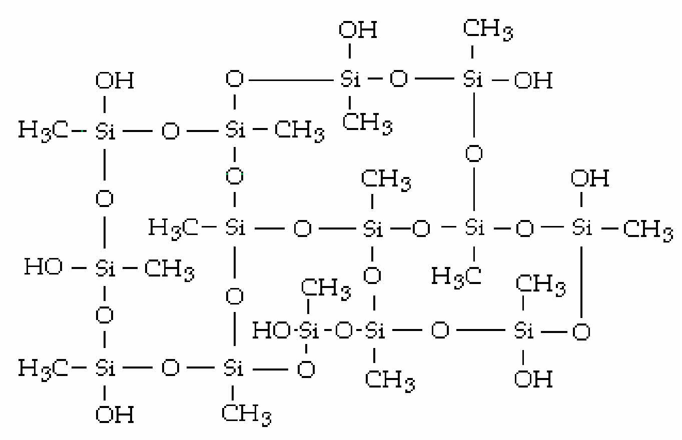


(2)

The acid and basic steps were carrying out at controlled temperature – 25 ºC, by means of a glass jacket with water as cooling agent (Fig. 1). In this work, the molar ratio of MTMS:methanol:acidic water:basic water tested was 1:35:4:[1.8-9.4].

The obtained sol was placed in an oven at 27 ºC and left for gelation. After 4-8 h, a gel was formed. In this stage, the alkaline conditions favours polycondensation reactions, resulting in the building of a tri-dimensional network of Si-O-Si (*cf.* hypothetical structure 3). The water produced in this inorganic polymerization may act as reactant in the hydrolysis and condensation reactions, increasing their completeness.

Figure 1 Experimental set-up for the synthesis stage.



(3)

The resulting gel was aged for two days at 27 ºC. This ageing period promotes the cohesion of the solid network, because the polycondensation of monomers continues as long as neighbouring silanols are close enough to react. Besides this, syneresis and coarsening processes also occur during the ageing (Hench and Orefice, 1992).

To remove the liquid (methanol, water, catalysts), mainly methanol, entrapped in the solid network, the gel was dried in two different ways. Initially, Ambient Pressure Drying (APD) was used to produce xerogels. In this case, the gel was transferred to a ventilated oven, at atmospheric pressure, and submitted to a temperature cycle – 24 h at 60 ºC, followed by three stages, at 100 ºC, 150 ºC and 200 ºC, of one hour each – to evaporate the alcohol (T_b(methanol) = 65 ºC – Goodwin, 1987). This method leads to the shrinkage of the pores due to surface tension effects. Recently, aerogels have been produced using Supercritical Fluid Drying (SFD). To reach the supercritical point of the solvent (T_c(methanol) = 240 ºC and P_c = 80 bar – Goodwin, 1987), the gel was placed in an autoclave (Fig. 2), which was then filled up with methanol. After, the temperature of the autoclave was increased at constant volume, causing an increase in the pressure inside it. When the critical point of the methanol was exceeded, the liquid became a supercritical fluid and, from this condition, the gaseous solvent was released, at constant temperature, and, consequently, the pressure has decreased. Near the atmospheric pressure, the autoclave was flushed with nitrogen to remove the remaining solvent. In this process, the shrinkage is minimized because the liquid-gas saturation line is not crossed (Fig. 3).

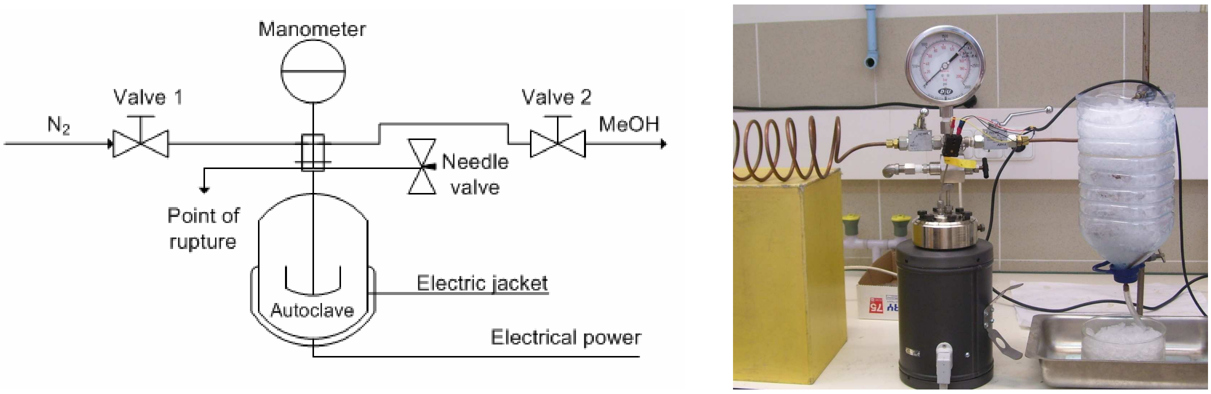


Figure 2 Experimental set-up for the SFD.

The elemental composition (C,H,N,O), chemical structure, surface area, density and contact angle of the xerogels and aerogels were accessed by elemental analysis (*EA 1108 CHNS-O*, *Fisons Instruments*), Fourier transform infrared spectroscopy (*Magna-IR*^{TM} *System 750*, *Nicolet*), nitrogen gas adsorption (*ASAP 2000*, *Micromeritics*), weight-volume measurements and a contact angle technique (*Contact Angle System OCA 20*, *Dataphysics*), respectively.

3 Results and Discussion

During the basic step of the synthesis, a sharp pH increase from ~ 2 to ~ 9 was observed with the addition of the first 2-3 drops of the basic catalyst solution; then, the pH increased slowly towards its final value (pH = 10-11), depending this value on the total amount of the basic catalyst solution added (Fig. 4). The condensation reactions occurred extensively at the very beginning of the basic catalyst addition and the solution became cloudy and milky, proving that the main effect was achieved with a tiny amount of catalyst.

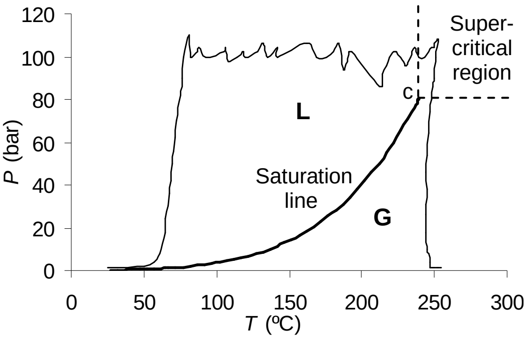


Figure 3 Typical *P*-*T* evolution in the SFD.

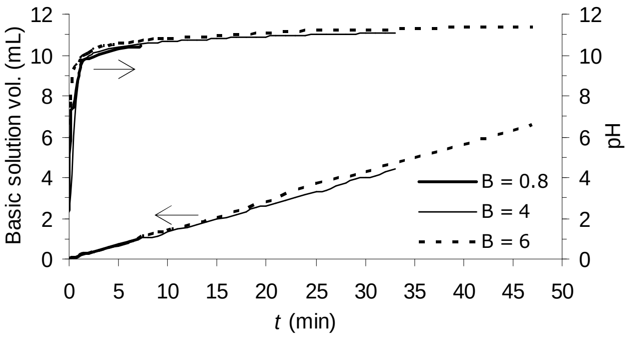


Figure 4 pH evolution during the basic catalysis step.

In a fully condensated material, the repetition units of the inorganic polymer have Si:O:C:H molar ratio of 1:~1.5:1:~3, neglecting the H atoms on the terminal groups (*cf.* structure 3). This corresponds to a theoretical C:O:H mass percent of 18.1:36.3:4.5. Comparing these values with the elemental analysis results – Table 2, it can be concluded that all the samples have only one CH_3 group per Si in its structural formula, since a good agreement for the % C is obtained. Therefore, the hydrolysis was complete. Also, the hypothesis of a fully condensed material is validated by this agreement, especially for samples in which $B \leq 6$. This was expected, since the pH rise is accomplished by a small volume of the basic catalyst solution, as a consequence of its high concentration. The measured values for the % H are higher than 4.5 %, what can be explained by the contribution of H in OH terminal groups. The N content obtained in the experimental results proves the existence of impurity traces in the materials dried by APD or SFD, since only the basic catalyst had N atoms. The theoretical and experimental values for the % O in xerogels are very different, because the temperature used in the elemental analysis (1060 ºC) was not enough to break the Si-O bonds.

Table 2 Elemental compositions, surface areas, pore sizes, and contact angles of the obtained materials.

Molar ratios	Elemental analysis				Surface areas and pore size		Contact angle
B [a]	% C	% H	% O	% N	BET surface area (m^2/g)	BJH pore size [b] (Å)	
XEROGEL							
1.8	19.8	5.8	1.5	0.17	-	-	-
3.0	17.4	5.6	1.6	0.32	315.26 ± 4.53	32.5	152º
4.0	19.1	6.0	1.5	≤ 100 ppm	385.77 ± 6.61	32.3	141º
5.0	-	-	-	-	389,93 ± 8,28	29.8	-
6.0	19.5	5.8	1.5	0.14	388.46 ± 7.08	31.6	-
8.0	16.5	5.6	1.6	0.14	-	-	126º
9.4	15.4	5.4	1.5	≤ 100 ppm	-	-	-
AEROGEL							
1.8	17.1	5.3	-	0.07	-	-	137º
4.0	17.8	5.0	-	0.08	362.87 ± 6.75	29.8	135º

a) $B = (H_2O)_{Basic}/MTMS$; b) Based on desorption isotherms.

The FTIR results for the xerogel and aerogel, for B = 4, are shown in Fig. 5. Materials with different B ratios were also analyzed, but the obtained spectra were almost the same. This is also the case displayed in Fig. 5, being the little displacement between curves due to the intrinsic variability of the laser beam. The intense bands appearing around 760 cm^{-1} and between 1000 and 1100 cm^{-1} are due to symmetric and asymmetric stretching vibrations of Si-O-Si bonds, respectively (Hedge and Rao, 2007, Castro *et al.*, 2005). The band just after 500 cm^{-1} may possibly correspond to bending vibrations of the same bonds (Hedge and Rao, 2007). The bands at ~ 850 cm^{-1} and ~ 1270 cm^{-1} can be assigned to Si-C bonds (Hedge and Rao, 2007, Castro *et al.*, 2005). The little peaks observed at ~ 1400 cm^{-1} and near 3000 cm^{-1} are due to the bending and stretching of the C-H bonds, respectively (Becker *et al.*, 1997, Hedge and Rao, 2007). There are no significant bands between 1600 and 1700 cm^{-1} or after 3000 cm^{-1}, proving that the Si-OH bonds are not abundant, the solvent was properly removed and the adsorbed water is absent (Becker *et al.*, 1997, Hedge and Rao, 2007). These observations confirm that the condensation reactions were very extensive and the obtained materials have a silica based structure, with highly hydrophobic CH_3 groups inside.

A decrease in the density of the xerogels and aerogels with the increase of B is observed – Fig. 6. In the case of xerogels, this decrease is more pronounced up to the sample corresponding to B = 4. For higher B values, the variation is almost within the experimental uncertainty. As the xerogel became more powdery and weak with the increase of B (for B = 9.4, the xerogel was a powder), 4 was considered the optimum B value for the desired properties. Aerogels show considerably lower densities than xerogels. Furthermore, it seems that the stabilizing B value for density is now 3.

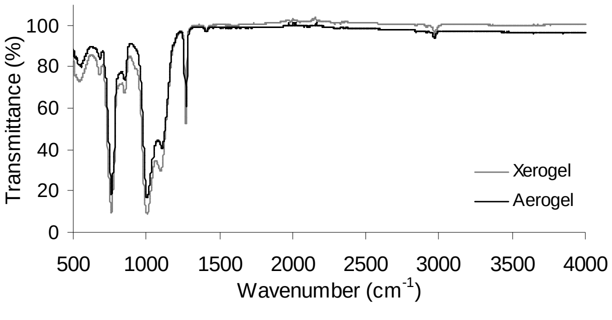


Figure 5 Typical FTIR results for the synthesized xerogels and aerogels.

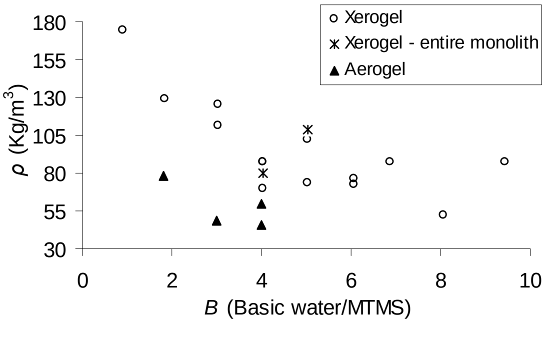


Figure 6 Densities of xerogels and aerogels for several B molar ratios.

Concerning the surface area results – Table 2, in the case of xerogels, the sample for B = 3 has lower surface area than the samples for B = 4-6. This was predictable, because the xerogels for B < 4 are more dense and rigid. The surface areas of the other three samples are comparable. For the aerogels, considering their density, higher BET surface area values were expected. For B = 4, the surface area value is lower then the one of the correspondent xerogel. This means that the results of surface area analysis should be completed and more replicas should be done. The pore sizes obtained for the xerogels and aerogels are consistent with a mesoporous structure, as they are in the interval 20-500 Å.

The contact angle values – Table 2 – confirm the high hydrophobicity of the obtained xerogels and aerogels and allow their classification as non wetting materials. Figures 7 and 8 show the flexibility characteristics of the synthesized xerogels and aerogels monoliths.

Figure 7 Xerogel monolith.

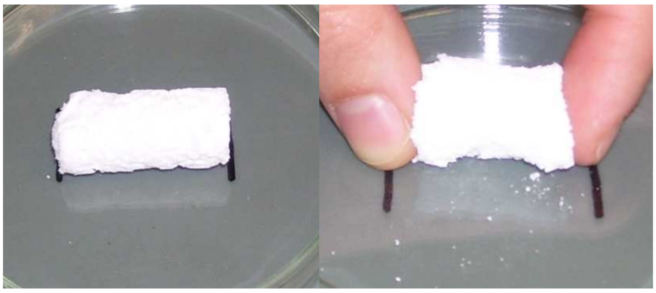


Figure 8 Aerogel monolith.

5 Conclusions

Flexible and hydrophobic silica based xerogels and aerogels were obtained, using MTMS as precursor in a two-step acid-base catalyzed sol-gel process, followed by drying at ambient pressure or at supercritical conditions. The synthesized materials showed suitable properties for aerospace applications, namely very low density (40-100 kg/m3), high surface area (~ 400 m2/g), small pore size (~ 30 Å), high hidrofobicity (> 130º) and moderate flexibility.

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