

New route for producing crack-free xerogels: Obtaining uniform pore size

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Abstract

We propose an innovative strategy to obtain crack-free gels by using a surfactant as a template for the silica pores. We use a neutral surfactant – *n*-octylamine – which weakly interacts by hydrogen bonding with the silica precursor. This allows it to be removed by simple drying in ambient air. We investigate the effect of the surfactant in simple inorganic silica obtained from tetraethoxysilane (TEOS) and an organic–inorganic hybrid xerogel, containing TEOS and polydimethylsiloxane (PDMS), as precursors. Although both the syntheses promote the formation of a crack-free uniform mesoporous silica gel, the hybrid gel network exhibits a larger pore size than the gel containing exclusively the silica from TEOS.

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1. Introduction

The sol–gel process is a popular method for manufacturing materials that need precise microstructural control. The selection of suitable conditions for synthesis makes it possible to control the properties of final products. It is well-known that one serious limitation of the method is the occurrence of cracking during the drying phase. This limitation has prevented the more widespread use of the sol–gel route for producing monoliths and films. As Scherer reported [1], the gel cracking occurs as a result of stresses caused by the existence of a meniscus at the liquid–vapor interface, which generates a differential capillary pressure within the gel. This makes the network shrink until it becomes stiff enough to resist the stress imposed by the capillary pressure. At this point, the maximum capillary tension is reached inside the network. Its value is given by

the Young–Laplace equation, which (assuming cylindrical pores) is

$$P_{\max} = \frac{2\gamma_{LV} \cos \theta}{r_p}, \quad (1)$$

where γ is the liquid–vapor tension, θ is the contact angle of liquid to pore wall and r_p is the pore radius.

The cracking network actually results from the capillary tension gradient across the gel network and not from its absolute value. Hence, if the capillary pressure were uniform, the network would be uniformly compressed, and there would be no cracking. Since the pressure gradient is reduced as the evaporation rate is also decreased, the most direct solution for avoiding cracking would be to let the liquid evaporate at a very low rate. Therefore, limiting drying rate by means of pinholes apertures is a common procedure for synthesizing monolithic gels.

In recent years, numerous attempts have been made to develop monolithic gels by reducing capillary pressure. Hench and Ulrich [2] reduced the surface tension of the

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liquid inside the gel pores by adding drying control chemical additives (DCCA). The most popular example of DCCA is formamide. This popular strategy has been applied in recent papers [3–5]. Another approach is suppressing the liquid–vapor interface by gel drying at supercritical conditions [6]. Other successful trials were to increase the gel pore size by including silica colloid particles in the starting sol [7–10].

The object of this work is to investigate an innovative strategy for obtaining crack-free silica gels. Since the gel cracking actually results from the capillary pressure gradient across the network, our target is to maintain a uniform capillary pressure inside the gel network by making its pore size as uniform as possible. We recently used this strategy for synthesizing consolidants for monumental stonework [11]. Commonly, the consolidants are applied as sol and they then polymerize in the pores of the decaying stone through a classical sol–gel process. We prevented the typical cracking of the gel inside the stone by using a surfactant as the template for the network of pores. So as to make a surfactant removal procedure unnecessary, our approach is based on self-assembly by hydrogen bonding between a neutral primary amine and the silica precursor. We are able to demonstrate that the surfactant can then be removed by simple air drying.

In the present work, we used two alternative pathways in order to prepare crack-free xerogels. First, we synthesized mesoporous silica from a typical TEOS sol by using *n*-octylamine as template. Secondly, we prepared a hybrid organic–inorganic mesoporous framework by co-condensation of TEOS and an organosiloxane, PDMS, in the presence of the same surfactant. In previous works [12–14], hybrid organic–inorganic molecular sieves were prepared by adding a neutral amine at critical micellar concentration (CMC) to the initial sol. After removing the surfactant by calcination or ethanol extraction, uniform mesopore silica with a high degree of crystallographic ordering is obtained. Our approach is slightly different because we used a relatively low concentration of surfactant template, below CMC. We rely on the ability of the surfactant molecules to act as directing agents for gel self-assembly even though critical micellar concentration is not reached.

2. Experimental section

2.1. Synthesis of xerogel from TEOS

Monolithic mesoporous xerogels have been prepared from a typical starting sol containing tetraethoxysilane (TEOS), in the presence of an amine primary surfactant (*n*-octylamine). The silica sol in turn was prepared by refluxing TEOS, ethanol, water and 0.07 N hydrochloric acid at 60 °C for 90 min. Next, *n*-octylamine was added to the mix under vigorous stirring. The mole ratios of the mixture were 1TEOS/5H₂O/11EtOH/0.004HCl/0.0028 *n*-octylamine. The sol was stirred at ambient temperature for 10 min.

In order to characterize the role played by the surfactant in the final properties of the material, another xerogel was synthesized according to the typical process described above, but without adding surfactant.

2.2. Synthesis of hybrid xerogel from TEOS and PDMS

Crack-free xerogel has also been prepared from TEOS and hydroxyl-terminated PDMS oligomers, in the presence of *n*-octylamine. The PDMS used presents a degree of polymerization of 12 and a percentage of OH ranging between 4 and 6% w/w. The sol was prepared by mixing TEOS, ethanol and water. In order to promote the hybrid network formation, PDMS was added, drop by drop, under high-power ultrasonic agitation (60 W cm⁻³). Finally, *n*-octylamine was added to the mix under vigorous stirring. The mole ratios of the mixture were 1TEOS/4H₂O/4EtOH/0.04PDMS/0.0028 *n*-octylamine.

After completing the synthesis, sols were cast in plastic cylinders of 1.38 cm diameter and 4.8 cm in length (the mold is shown in Fig. 1). Dried xerogels were obtained by simple exposure of the sols to laboratory conditions (relative humidity of 60% and temperature of 20 °C) until a constant weight was reached. The xerogels are denoted: S-TEOS and S-TEOS–PDMS for the surfactant-templated silicas. The gel synthesized without surfactant is denoted N-S-TEOS.

2.3. Characterization procedures

Powder X-ray diffraction (XRD) was measured on a Bruker D8 advance diffractometer equipped with Cu tube X-ray and using Cu α radiation.

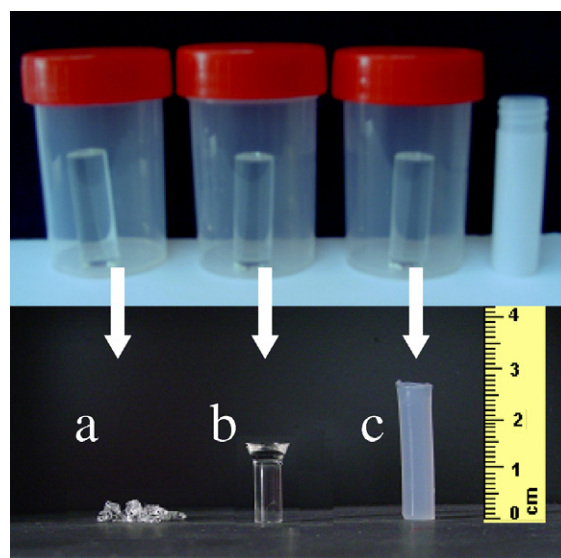


Fig. 1. Upper image: wet gels obtained immediately after the gelation. The mold used for the gels can be seen on the right. Lower image: xerogels obtained after drying in laboratory conditions (a) from TEOS without surfactant; (b) from TEOS in presence of surfactant and (c) from TEOS/PDMS in presence of surfactant.

Table 1
Textural properties of the xerogels under study

Sample	S_{BET} (m ² /g)	V_{pore} (cm ³ /g)	Pore size (nm)
N-S-TEOS	424 ± 3.3	0.23 ± 0.02	–
S-TEOS	968 ± 4.0	0.78 ± 0.04	3.5 ± 0.2
S-TEOS-PDMS	527 ± 1.5	1.20 ± 0.05	5.5 ± 0.3

Standard deviations are also included.

Powdered xerogel samples were visualized by scanning electron microscope (SEM) using a JEOL JSMT-300 microscope.

The nitrogen adsorption–desorption isotherms were determined on a Sorptomatic 1990 from Fisons Instrument. The BET surface area was calculated from the linear part of the BET plot [15]. Pore size distribution was calculated from desorption branch data according to the BJH method [16].

The degree of surfactant residue in the dried gels was based on the nitrogen content, determined through elemental analysis on a Leco CHNS-932 elemental analyzer. The amine residue was also evaluated by means of Fourier transform infrared spectrophotometry (FTIR). The spectra were recorded in KBr pellets using a Vertex 70 Spectrophotometer from Bruker (4 cm⁻¹ resolution) in the region from 4000 to 400 cm⁻¹.

For all the tests carried out, the arithmetic mean and standard deviation for three samples are shown in Table 1. Error bars are not included in figures for better readability. The uncertainty in respect of all the plots can be assumed as negligible (<5%).

3. Results

The gel time of the sols synthesized in the presence of *n*-octylamine was 12 and 13 h for the TEOS sol and TEOS–PDMS sol, respectively. In the case of the TEOS sol prepared without surfactant, the gel time was significantly longer, around 20 days. This suggests that the surfactant promotes silica condensation. Fig. 1 (upper) shows the wet gels immediately after the gelation. As the same mold was used, the three gels present the same size. After drying under laboratory conditions, we obtained crack-free xerogels from the two sols synthesized in presence of surfactant, whereas the gel prepared without octylamine showed significant cracking (see Fig. 1 (lower)). As can be appreciated in the figure, the shrinkage of the gels during their drying was slightly greater for the material prepared without surfactant (around 92% of the wet gel volume). In the case of the materials synthesized in presence of surfactant, shrinkage was 90% for gel obtained from TEOS and 84% for the gel containing PDMS. Another variation between the two surfactant-templated materials is that the hybrid xerogel exhibits a coloring of notable whiteness, whereas xerogel from TEOS is transparent.

The X-ray pattern of the powder gels under study is given in Fig. 2. The X-ray patterns of the three materials

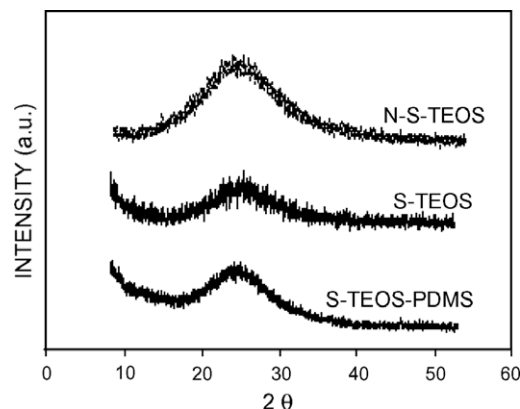


Fig. 2. XRD patterns for the materials under study.

were characteristics of typical amorphous silica without any detectable ordered structure. As would be expected, the pattern of the silica material without surfactant was also amorphous.

Textural properties of the silicas under study were determined from the nitrogen adsorption–desorption isotherms (Fig. 3) and are given in Table 1. As would be expected from a typical gel from TEOS, the xerogel synthesized without adding surfactant exhibits adsorption at low relative pressures (below 0.1), which then levels off; this is indicative of adsorption in micropores (type I isotherm). When the surfactant was used in the synthesis, we observed some significant differences in the curves obtained. In the case of the isotherm of the gel prepared from TEOS sol, we observed an intermediate profile between type I and type IV isotherms, with linear to step-shaped uptakes at partial pressure between 0.1 and 0.6. As Kruk and Jaroniec reported [17], this adsorption at low relative pressures (below typical values, which are above $p/p_0 > 0.4$) is typical of materials consisting of a mesoporous uniform network with pore size close to the micropore range. In addition, this material exhibits a parallel and almost horizontal hysteresis loop at high pressures (type H4), which appears in many uniform materials presenting a primary porosity created by the surfactant and a low percentage of larger pores.

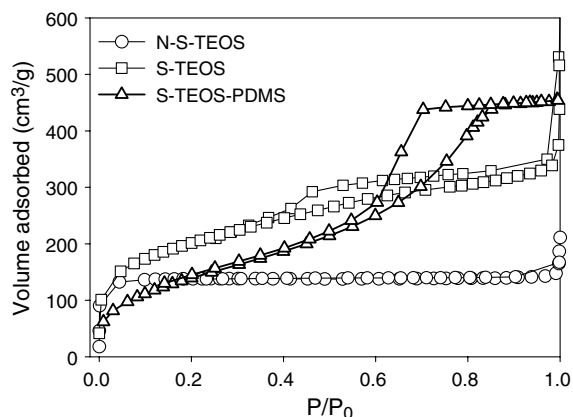


Fig. 3. Nitrogen adsorption isotherms for the silica xerogels under study.

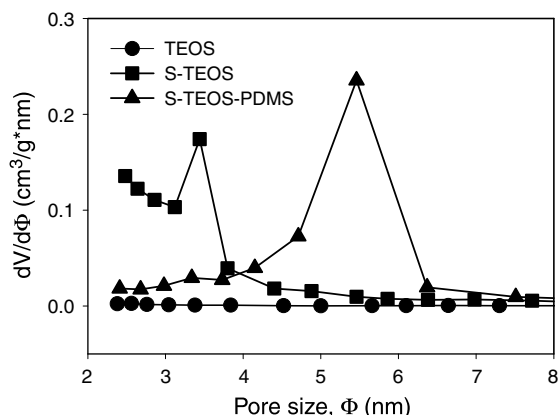


Fig. 4. BJH pore size distribution for the silica xerogels under study.

The hybrid organic–inorganic silica isotherm shows a type IV profile, which is typical for surfactant-templated materials with accessible mesopores showing a higher size than those from previously reported silica. The hysteresis loop has the triangular shape, typical of H2 loops. As reported [17], this profile may correspond to a material with uniform cage-like pores.

The BJH pore size distribution for the materials under study is shown in Fig. 4. The two surfactant-templated silica exhibited a narrow pore size distribution which is a clear indication of a uniform pore size network. However, the silica synthesized without the surfactant does not show pores in the mesoporous range. Therefore, we can conclude that these uniform mesopores are created by the surfactant molecules acting as template agents. Furthermore, the materials synthesized in the presence of surfactant exhibit a high surface area and pore volume, which are typical of surfactant-templated materials.

Concerning the effects on textural properties, in the silica produced using the hybrid organic–inorganic pathway, a significant increase in the pore size is observed (see Fig. 4 and Table 1). Furthermore, pore volume is also greater.

Results obtained from SEM studies provide supporting evidence. As illustrated in Fig. 5(a), the silica synthesized without surfactant is a typical dense material, in which pores are not observed. Silicas prepared in the presence of *n*-octylamine show a typical mesostructure. The SEM image of the hybrid silica reveals a more uniform morphol-

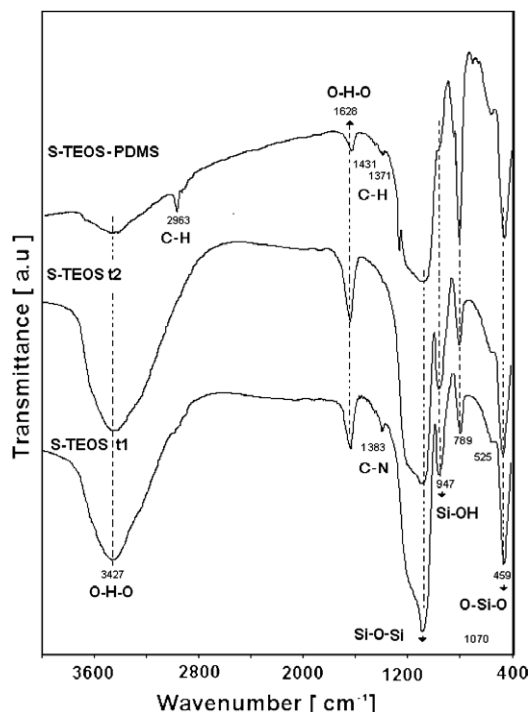


Fig. 6. FTIR spectra for inorganic and hybrid organic–inorganic silica xerogels. The time elapsed after the synthesis was 6 months for t1, and 8 months for t2. In the case of the hybrid, the time was 2 months.

ogy, consisting of a park of uniform spheres with a size around 70 nm (Fig. 5(c)) than its inorganic counterpart (Fig. 5(b)).

The presence of residual surfactant in the silicas under study was investigated by FTIR at several time intervals. Fig. 6 shows the spectra of inorganic silica material at 6 and 8 months. In the case of the hybrid organic–inorganic silica, no differences are observed in the spectra at different times. Therefore, we show the spectra obtained at 2 months. As would be expected, all spectra show the typical peaks from silica materials. Specifically, the band ranging 1060–1070 cm^{-1} is attributed to asymmetric Si–O–Si stretching motion, while the band at 790–800 cm^{-1} is attributed to the symmetric counterpart; the peak centered at 450 cm^{-1} corresponds to the bending O–Si–O mode. In addition, the band at 940–990 cm^{-1} is attributed to SiOH

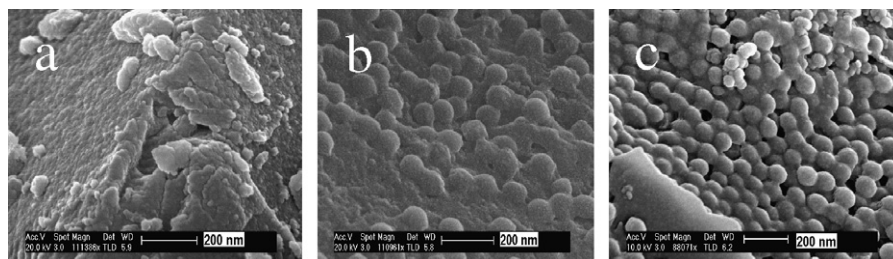


Fig. 5. SEM micrographs of the xerogels under study: (a) xerogel from TEOS without surfactant; (b) xerogel from TEOS, prepared in the presence of octylamine and (c) hybrid xerogel from TEOS and PDMS, prepared in the presence of octylamine.

stretching, and the broad band at 3750–3250 cm^{-1} is attributed to the hydrogen-bonded silanols groups with absorbed molecular water. Finally, the peak at 1640 cm^{-1} is attributed to molecular water vibrations.

In the inorganic silica spectrum recorded at 6 months, we can confirm the residual amine presence [18] since a weak peak at 1412 cm^{-1} , attributed to amine C–N stretching, is observed. After the longest elapsed time, 8 months, this peak has disappeared, confirming that the surfactant has been removed.

For the hybrid organic–inorganic silica, the surfactant was removed at 2 months (the band attributed to C–N stretching is not detected). In addition, typical bands from the organic group, which are not detected in inorganic silica, are observed. In particular, the weak bands between 1370 and 1430, and the sharp peak at 2963 cm^{-1} , are attributed to the bending and stretching, respectively, of the C–H of the organic groups [19]. Finally, the typical band attributed to CH_3 symmetric bending appears at 1240 cm^{-1} .

The results from the elemental analysis show that the air drying of the hybrid inorganic–organic silica fully eliminates the surfactant at 2 months (no traces of nitrogen were detected). However, traces of nitrogen (0.08% w/w) were detected for the inorganic silica after 8 months.

4. Discussion

The main point to elucidate is the validity of the method employed for avoiding gel cracking during the drying phase. As clearly observed in Fig. 1, the two surfactant-templated syntheses proposed are an effective procedure for preventing cracks during drying.

The second point is to establish the underlying mechanism for avoiding gel cracking. It is obvious that the pore structure of the gels synthesized in the presence of *n*-octylamine was close to that corresponding to gels containing formamide or some other DCCA agent. As reported [2,20,21], formamide leads to the formation of small oligomers that condense together in a cross-linked structure, resulting in a network composed of polymeric balls. This condensation promotes the coarsening of the gel network, increasing the size and uniformity of the network pores. The structures visualized by SEM for the surfactant-templated gels prepared in our laboratory (Fig. 6) were also composed of silica balls. In addition, like formamide, the surfactant increases the pore size and the uniformity of the size distribution (Table 1, Fig. 4). However, despite these similarities, we consider that the mechanisms implied in the two routes are different. As reported in the literature, formamide addition, under acid-catalyzed conditions, should allow an efficient hydrolysis followed by a rapid condensation. It promotes the formation of the coarse gel composed of the silica balls. This structure tends to produce a more uniform pore size than typical silica gels with a relatively narrow range (usually around 10–20 nm) of pore sizes. In the surfactant-templated materials prepared in our laboratory, all the pores fall within a size range of

2 nm for the hybrid material, and 1 nm for the gel without PDMS. This implies that the pore sizes obtained are practically equal because they are created by the surfactant acting as template. The nitrogen adsorption test clearly demonstrates the role played by the surfactant molecules as template agents of the pore structure of the gel, generating a uniform mesoporous distribution.

Moreover, the surfactant-templated syntheses, proposed in this paper, do not promote an ordered pore structure as is clearly evidenced by XRD, which is typical of most materials synthesized via a surfactant-templated. We assume that the low surfactant concentration used, below CMC, prevents the formation of micelles, which are responsible for the ordered pore structure.

By comparing the two surfactant-templated procedures tested in this paper: surfactant-templated synthesis and its hybrid organic–inorganic counterpart, we can establish that the color (degree of whiteness) of the xerogel synthesized by the hybrid organic–inorganic pathway is related to the large size of their particles, clearly observed by SEM. Moreover, their lower shrinkage during drying would be associated with their larger pore size, shown in the pore size distribution obtained from nitrogen adsorption test (Fig. 4). As the capillary pressure supported by the gel network during drying is inversely proportional to the gel pore size, these syntheses clearly promote a lower capillary pressure during drying.

The increase in the pore volume and the pore size of the gel network containing the organic component (see Fig. 4 and Table 1) has been fully explained by the literature. As widely reported [22], the organics form chemical bonds with the oxide gel matrix, producing an enlargement of the pores as well as an increase of the pore volume of the gel network. This group of materials was denominated ‘ormosils’ – organically modified silicates – by Schmidt [23]. The rubbery elasticity of this family of materials was well explained by Mackenzie et al. [24] according to an idealized microstructure, in which the units of silica are spheres joined to other adjacent spheres via PDMS chains. The modulus of the elasticity is expected to be very low because the primary reaction to the stress is the coiling of the PDMS chains; these findings are completely corroborated for the hybrid organic–inorganic gel synthesized in our laboratory. The typical microstructure, proposed by Mackenzie, composed of adjacent silica spheres is clearly observed in the SEM micrograph of our hybrid gel (Fig. 5(c)). The only difference is that our spheres present the same size – due to the role played by octylamine – whereas the classical microstructure of ormosils presents spheres of different sizes.

Regarding the removal of the residual surfactant, we obtain two important conclusions. Firstly, the removal of surfactant by air drying is effective for the surfactant-templated materials synthesized, but requires a longer time for the inorganic silica. We assume that the very large pore size of the hybrid material promotes the faster removal of surfactant. Secondly, the presence of organic groups shown in the FTIR spectra of the hybrid xerogel confirms that the

organosilane molecules are integrated into the TEOS matrix. Finally, the elemental analysis corroborates the notion that removal of the template is easier for the silica with a larger pore network.

5. Conclusions

A novel route for preparing crack-free silica xerogels has been developed. We conclude that, by means of the interaction of a non-ionic surfactant with siloxane and organosiloxane precursors, a mesoporous silica with a tailored uniform pore size structure can be obtained. It is clear that a uniform pore size material exhibits a uniform capillary pressure in which cracking is prevented.

Furthermore, the hybrid silica route has the advantage of promoting a larger pore size in the gel network, which also facilitates surfactant removal by simple air drying.

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