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Scientific Journal SLP

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Infrared spectroscopy analysis as a tool to follow structural evolution in silica xerogels

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ARTICLE INFO

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ABSTRACT

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Infrared spectroscopy has been used to analyse structural changes in samples prepared by the sol-gel method. Silica xerogels powders were prepared from tetraethylorthosilicate (TEOS), distilled water, and ethanol with different H2O/TEOS molar ratios. A low water to TEOS molar ratio gives a incomplete hydrolysis of the TEOS molecules and yielding to oligomeric structures, whereas a high water to TEOS molar ratio yield to a full hydrolyzation facilitating the cross-linking of polymeric chains and producing a three-dimensional interconnection of siloxanes.

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Introduction

The infrared spectroscopy has been reported as a good technique to study and characterise materials, although interpretation beyond the direct spectral structure calculation due to large structural parameters numbers. However the technique is a good direct structural proof of non crystalline solids. In general the use of complementary techniques as Raman spectroscopy, NMR, X-ray diffraction are required.

The infrared absorption has been a powerful technique when the structural interpretation of spectra is facilitates using procedures that increase the observable numbers.

In particular this spectroscopic technique allow us to know the structural conformation of SiO2. In this work we introduce a interpretation criterion about the absorption bands of silica xerogel that can be used as reference for the study of local atomic structure of silicates and silicate glass and can be included as laboratory practice in courses of materials science.

The silica xerogel studied in this work was prepared via the sol-gel method using different molar H2O/TEOS ratios to produce structural differences. The absorption infrared spectrum allow us knowledge the structural conformation of the SiO2 and to obtain information about the chemical bonds entail in the SiO2 structure and the stequiometric of the compound.
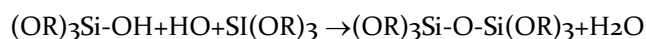
In the last fifteen years, the sol-gel method to prepare complex glasses has received important attention. A great variety of researches have been realized; however a detailed analysis about the conformation of the structure whereas the chemical reaction is been carried out it is not clear; several species have been proposed as the

hydrolysis products of the alkoxides [1-3]. Some of the major variables in the alkoxysilane polymerisation process (the hydrolysis and condensation sequence) are i) the type of alkoxysilane and its functionality, ii) the catalyst type (OH- or H+) and iii) the water/alkoxide ratio (R). These variables will control the polymerisation through the growth and aggregation of the sol/silicate species throughout the transition from the sol to the gel state [4].
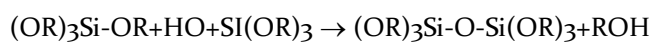
The hydrolysis reactions of alkoxysilanes occurs by the nucleophilic attack of the water oxygen upon the silicon atom [4]. The mechanisms used to explain both the hydrolysis and condensation chemistry are nucleophilic substitution (SN) and nucleophilic addition (AN). In the hydrolysis reaction a hydroxyl ion becomes attached to the metal atom, as in the following reaction

$$Si(OR)_4 + H_2O \ \rightarrow \ HO\text{-}Si(OR)_3 + ROH.$$

Two partially hydrolyzed molecules can link together in a condensation reaction, such as

$$(OR)_3Si\text{-}OH + HO\text{+}SI(OR)_3 \rightarrow (OR)_3Si\text{-}O\text{-}Si(OR)_3 + H_2O$$

or

$$(OR)_3Si\text{-}OR + HO\text{+}SI(OR)_3 \rightarrow (OR)_3Si\text{-}O\text{-}Si(OR)_3 + ROH$$

By definition, condensation liberates a small molecule, such as water or alcohol. As long as this type of reaction continues the silica tends to form linear molecules that are occasionally cross-linked, these molecular chains entangle and form additional branches resulting in a three-dimensional network (polymerisation). Hydrolysis and condensation are carried out in a mutual solvent such as ethanol.

It has been well demonstrated that the use of infrared absorbance spectroscopic provides information on the structural and compositional properties of SiO_2 [5-11]. This technique is convenient to approach the sol to gel reaction and gel to glass conversion, because it gives information on the backbone structure of siloxane network as well as the organic side groups. Although several authors have analysed the silica gel evolution in its early stages by IR spectroscopy [8 and references therein], Raman and NMR [3,12]; the complexity of the chemical and physical processes of silica glass by the sol-gel route and structural details of the evolution of TEOS to silica gel, and glass are not fully understood yet.

Using the above exposed hydrolysis and condensation reactions and taken into account the chemical species expected, we can correlate the changes on the IR absorption bands with the absence/presence and evolution of these chemical species. Table I describe the IR absorption frequency ranges and their assignation, according to the literature, for the participating chemical species. The hydrolysis and condensation reactions as well as the structural evolution can be analyzed in terms of the indicated bands.

The main aim of this work is try to determine the evolution of the different species (siloxane network as well as the organic side groups) during the gel to glass transition, analysing the IR absorption spectra changes of xerogels. In order to do that, the hydrolysis and condensation of TEOS, water and ethanol systems has been followed by FTIR spectroscopy. The hydrolysis ratio is in relationship with the water content, in low quantities of water the hydrolysis is incomplete, whereas for greater water content the hydrolysis ratio is increased. This ratio is in relationship with structural aspects that have been followed by infrared spectroscopy [5,6]. In a previous work we have analysed the structural evolution of silica gel concluding that exist different populations of structures including linear chain and n-membered rings depending of the conditions of preparation of the initial solutions [7,8]. In this evolution, the early stages of the gelation process are determinant for the final structural conformation. In those gelation stages, the process the hydrolysis and condensation reactions are the principal cast.

Experimental

To follow appropriately the hydrolysis and condensation process an under stoichiometric molar ratio water to TEOS was used. Samples of SiO_2 were prepared by mixing tetraethyl orthosilicate (TEOS), water, and ethanol. We used a constant ethanol:TEOS molar ratio of 4:1 and three different molar ratio of water to TEOS (R) under stoichiometric of $R=1$, $R=3$ and $R=11$. The solutions were prepared mixing the TEOS and the ethanol separately; a homogenous solution of all the components was obtained mixing them together with water, for about 15 minutes using a magnetic stirrer. In order to reduce the gelation time, the solution was catalyzed with HF; the molar ratio of HF to TEOS was 0.015. The HF was mixed with water and the process of gelation was carried out at room temperature; when the viscosity that accompanies the gelation reached a specific point such that the solid phase starts to appear, small pieces of the sample were dried at room conditions. Several samples were prepared under the same conditions at different times of gelation. The time in which the samples and IR spectra were obtained corresponds to the order of hours between one to other; the gelation times for the sample with $R=1$ are shown in table II.

The infrared (IR) spectra were carried out in a Nicolet IR spectrometer model Avatar 360 FT-IR using the diffuse reflectance technique (DR), for which 0.05 gr. of powder sample were mixed with 0.3 gr. of KBr.

Results and Discussion

Figure 1 show a set of IR measurement in the range of 400 to 4000 cm^{-1} for the sample with $R=1$ at different gelation times. The bands 1, 3, and 5 are ascribed to the presence of the siloxane (Si-O-Si) network, as we can see, these bands suffer significant changes in their shapes and relative intensities as long as the gelation is occurring; specifically the band 5, assigned to the stretching

of the Si-O-Si bond, evidences a noticeable evolution, evolving from three well-defined sharp peaks to the well-known broad band at 1080 cm^{-1}. Since this band is strongly correlated to the conformation of the oxide network we will give a detailed explanation of its evolution in a posterior paragraph. The IR absorption bands 6 and 8 correspond to the presence of C-H groups [3,13]; several sharp peaks compose indeed these bands. We can see how these bands or peaks are hardly appreciable for T_1, starting to be prominent at T_3, diminishing after T_4, and finally disappearing for T_8. It is well known that the evaporation rate of the ethanol is very high at atmospheric conditions, hence the presence of the molecular ethanol can be neglected, and the bands 6 and 8 are indicators of the presence of non-hydrolysed and partially hydrolysed TEOS molecules; the relative intensities of these bands depend on the population of these species. The band 7, assigned to molecular water, shows a monotonic increment in its intensity according to the gelation time. As we have mentioned before, ethanol and water are produced as consequence of the hydrolysis and condensation reactions, however whereas most of the ethanol molecules are evaporated the molecular water remains trapped in the pores of the oxide network even for large times of gelation.
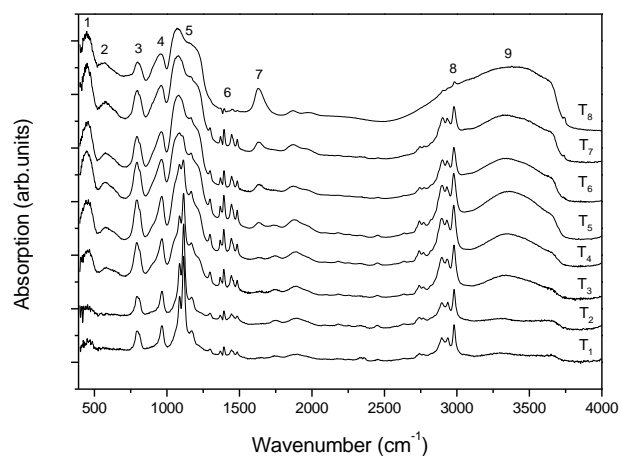

Figure 1. IR absorption spectra for samples with composition of R=1 at gelation times of T_1 to T_8

The bands 4 and 9 have a similar behaviour than band 7; both bands show an increment according to the gelation time. These bands are directly related to the OH groups, band 4 is assigned to Si-(OH) vibrations and band 9 corresponds to O-H vibrations. It has been reported by many authors that silica active gel is covered by OH groups [3,4,6,7]. Bands 4,7 and 9 might be used to evaluate the grade of polymerisation, the porosity, the surface area and the density of the gels. For example, from the figure we can see that for the early stages when the hydrolysis reaction is still incomplete just a few molecules of water are trapped in the gel. On the other hand, has been reported that for heat-treated samples, the intensities of the bands 4 and 9 diminish considerably and band 7 disappear completely indicating a densification of the gel. The band located at about 560 cm-1, indicated by the number 2, is attributed to the skeletal deformation of the 4-fold siloxane rings. Because, cyclic tetrasiloxanes are stable toward hydrolysis [4], they can constitute a large fraction of the oligomeric species in TEOS-derived systems. Observing this band, we see that the 4-fold ring structure produced in the early stages of hydrolysis and condensation reaction is increased according to the gelation time and retained in the resultant SiO_2 gels.

As we have mentioned before, the band at 1000 to 1350 cm^{-1} (see table I) deserves special attention; fig. 2 shows the IR spectra at this range. This band is composed, in its first stages, for three well-defined sharp bands, all of them assigned to TEOS, at 1087 cm^{-1} (C-O asymmetric stretching), 1116 cm^{-1} (C-O symmetric stretching), and 1168 cm^{-1} (CH3 rocking). Form the figure we can observe that according to the gelation time is increased the intensities of these bands diminish and finally they disappear, at the same time some new bands start to appear at 1047 cm^{-1} (C-O symmetric in Et-OH), 1079 cm^{-1} (Si-O-Si asymmetric stretch), and 1222 cm^{-1}. The 1047 cm^{-1} band indicates the ethanol formation; the appearing of this band coincides with the decrease of the TEOS bands. The peaks

at 1079 cm^{-1} and at 1222 cm^{-1} indicate the formation of Si-O-Si species, and give information about the condensation and polymerisation processes. The 1079 cm^{-1} peak is associated to the principal band in the SiO_2 structure, and correspond to the O-Si-O asymmetrical stretch motion in which adjacent O atoms move in phase with each other. The peak at about 1222 cm^{-1} has been described as another vibrational state of the main TO mode. It is important to mention that TEOS, ethanol, and SiO_2 have additional IR bands at wavenumbers lower than 1000 cm^{-1} [3].

Table I. Assignment of infrared vibrations for the bands obtained in a sample of silica xerogels

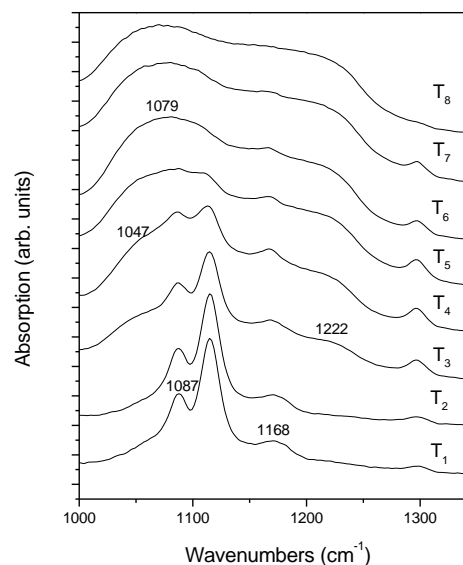| Band	Frequency	Group	Ref
1	~450	Si-O-Si (R)	[14]
2	570		[1]
3	~850	Si-O-Si (B)	[14]
4	900-980	Si-(OH)	[6]
5	1000-1250	Si-O-Si (S)	[17]
6	1250-1500	C-H	[3,13]
7	~1650	H_2O	[18]
8	2830-3000	C-H	[3,13]
9	3000-3750	O-H	[18]

Figure 2. IR absorption spectra in the reduced scale from 1000 to 1350 cm-1 for the same samples of figure 1.

In figure 3 we show the IR spectra for the sample with $R=1$ at the range of 400 to 1000 cm^{-1} in which is observed the first four mentioned bands, even when some of these bands have been commented in former paragraph, their evolution also deserve a more detailed observation. The intensities of the bands 1 and 2 are increased according to the gelation time, indicating that the population Si-O bonds is being increased; obviously, it is mean an increment of the siloxanes species population. The presence of 4-fold rings implies that kind of structures are produced in the early stages of hydrolysis and condensation reaction of alkoxysilanes and can be retained in the resultant SiO_2 gels. The band number 3 have contributions of TEOS from the peaks at 785-790 cm^{-1} due to SiO_4 asymmetric stretching and at 810 cm^{-1} due to Si-O-C rocking; this peak tends to decrease and the 880 cm^{-1} peak for ethanol increased. The ethanol formation was simultaneous to the frequency shift in the 964 cm^{-1} peak from to 954 cm^{-1} indicating the formation of silanol (Si-OH).
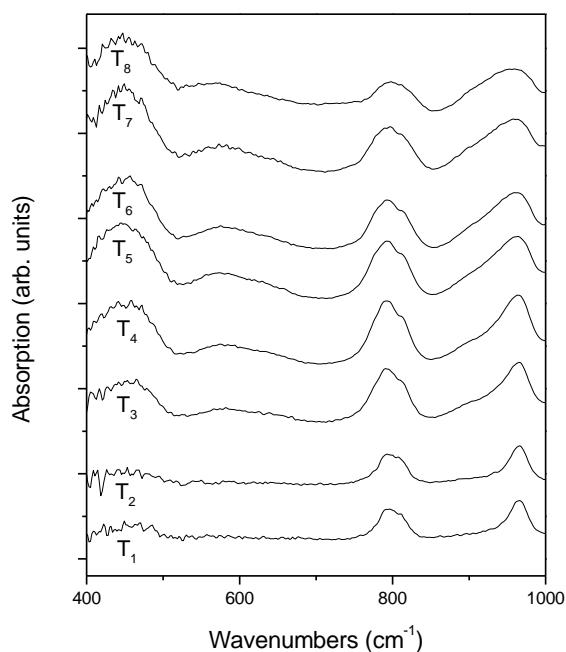
The decrease of the band 720-853 cm^{-1} was accompanied with a relative increment of the peak at 799 cm^{-1} indicating the formation of Si-O bonding; this peak is assigned to the Si-O-Si bond bending (symmetric stretching). The region between 950-970 cm^{-1}, in which both the silanol (Si-OH) and TEOS (CH_3 rocking) bands occur, is of particular interest. The peak in this region, as have been described early, appears to shift to lower wavenumber during the hydrolysis but there are actually two peaks in this region; the TEOS peak due to CH_3 rocking at 964 cm^{-1} decrease with a subsequent growth of the Si-O stretch at approximately 954 cm^{-1}. This fact is in accordance with the comportment of the main band discussed before, and indicate how is the hydrolysis process.
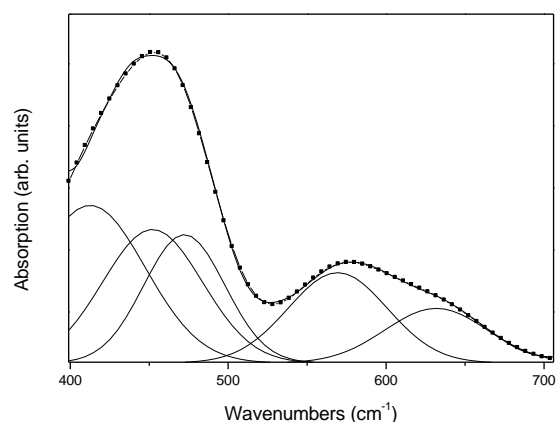

Figure 4. Deconvolution on the IR spectra in the range 400 to 700 cm^{-1} for sample T_4.

The band centred at 450 cm^{-1} and at 600 cm^{-1} have three and two components as can be seen in figure 4 where we show a deconvolution on the IR spectra in the range 400 to 700 cm^{-1} for sample T_4. The spectra was descomposed in five absorption bands, which gave the best fitting to the experimental data. The continuous curve corresponds to the measured absorption and the doted square one are the sum of the five absorption bands (solids one) obtained from the descomposition. The components are located at 412, 452 and 475 cm^{-1} for the band centred at 450

Figure 3. IR absorption spectra in the reduced scale from 400 to 1000 cm^{-1} for the same samples of figure 1.

cm^{-1} and 577 and 631 cm^{-1} for the band centred at 600 cm^{-1}. These components are assigned to ethanol (412 cm^{-1}), TEOS (O-C-C deformation) (475 cm^{-1}), formation of Si-O-Si (450 cm^{-1}), 4-fold siloxane ring structure (575 cm^{-1}) and a skeletal deformation of 3-fold siloxane rings (630 cm^{-1}) [10], by referring to various cyclic siloxane compounds and silicate minerals [1].

Figure 5 show the IR absorption spectra for the set of samples with R=1, R=3 and R=11 without heat treatment. The bands assigned to SiO2 are present in all spectra; however, in some frequency intervals we can observed notable differences. These ranges are indicated in the figure with the numbers 1,2,3 and 4; figure 5a.

As we have discussed, the band 1 and 2 are assigned to the presence of C-H groups and indicate the presence mainly of TEOS molecules. Those bands tends to disappears when the R value is increased, indicating that the increase of water concentration favour de hydrolysation process and the formation of gel diminish the number of species of C-H groups. This is in relationship with the presence of the peak at 1168 cm^{-1} located at the band 3, assigned to the rocking mode of CH3. The bands 1, 2 and the peak at 1168 cm^{-1} disappears when the molar ratio R=11, and the process of hydrolysis is full. In this case molecules are cross-linked, these molecular chains entangle and form additional branches resulting in a three-dimensional network.

The position of the principal band, indicated by number 3, varies with the R values. When R=1 their position is at 1072 cm^{-1}, whereas for R=3 and 11 the position band shift to 1083 cm^{-1}, figure 5b. This situation is agree with the central force model [14,15] in which the stretching mode frequency is given by $\nu=\nu_o \sin(\theta)$, where 2θ is the mean angle of Si-O-Si bond and ν_o=1117 cm^{-1} [11] (ν_o is obtained when is used the condition that ν=1078 cm^{-1} when the intertetrahedral angle 2θ=150°, that are characteristics values of thermic oxides). The variation at the position of the band is associated to variation of the stretching mode

frequency and then a increase in the intertetrahedral angle occur. This change in the intertetrahedral angle indicate us that the 5-member rings and up are favoured.
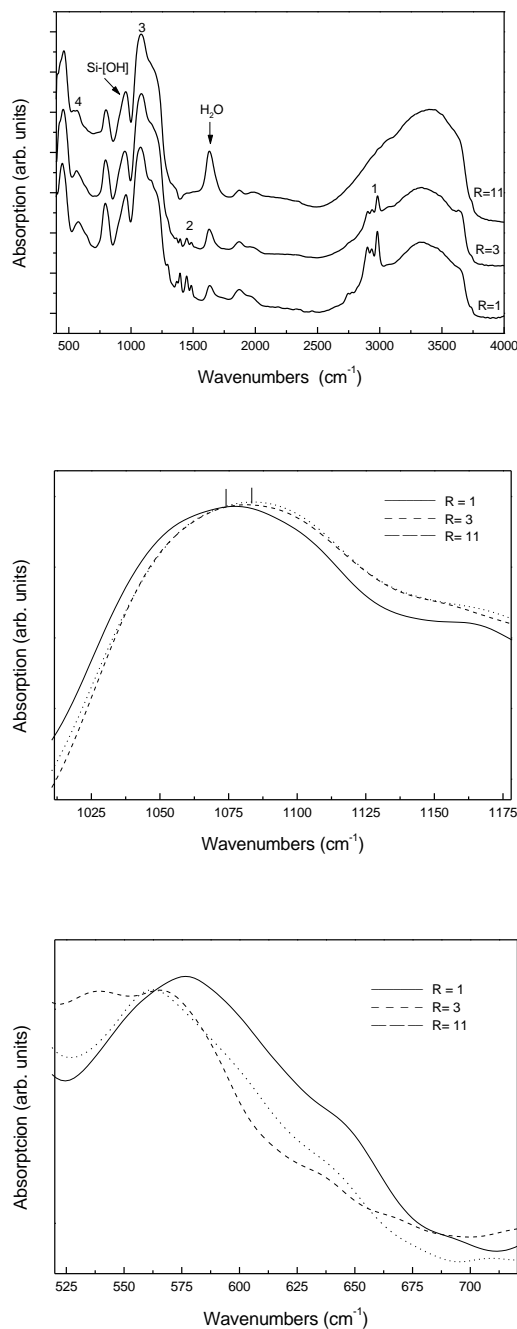

Figure 5. IR absorption spectra for samples with composition R=1, 3 and 11 without heat treatment in the range of a) 400 to 4000 cm^{-1}, b) in the reduced range from 1000 to 1180 cm^{-1} and c) in the reduced range from 500 to 720 cm^{-1}.

The band 4, figure 5a, is assigned to the deformation of tetraciclosiloxanes [1]. This band has components at 577 and 631 cm^{-1} as we have discussed previously and has been assigned to oligisilsesquioxanes compound of 4-members and 3-members rings, respectively [16]. In the figure 5c we show the IR spectra at scale reduced for the band 4; in this figure we can observe that the position of the peak of larger intensity shift to lower wavenumbers when is increased the water concentration. The position peak for $R=1$ is at 580 cm^{-1} and shift to 560 cm^{-1} when $R=3$ and shift to 547 cm^{-1} when $R=11$, indicating that for low water concentration, when the hidrolysis in non-fully, the formation of ciclotrisiloxanes species are carried out and conform the water concentration is increased this species tends to disappears and the ciclotetrasiloxanes are favoured. This situation agree with the comportment of the principal band, indicated by the number 3, in which the intertetrahedral angle growth when the water concentration increase favoured the formation of m-membered ring higher than 3.

Conclusions

Using different H2O/TEOS molar ratio under-stoichiometric of $R=1$, $R=3$ and $R=11$ we analyze the hydrolysis and condensation reactions using IR spectroscopy. Small values of R do lead to the retention of alkoxy groups in the xerogel, as indicated for example, by the C-H scissors and deformation modes at 1453 cm^{-1} that correlate with the intense C-H stretching bands in the 2800-3000 cm^{-1} region of the spectrum. For small values of R the absorption peaks assignable to C-H vibration in –OEt groups are observed at around 3000 and 1300-1500 cm^{-1}. These bands indicate that the –OEt groups are retained in the gel at because of incomplete hydrolysis of TEOS. The removal of organic substituent is evident in the IR spectrum. Notice the diminishment of relative intensities of the sharp bands near 2900 and 1400 cm^{-1} (assigned to C-H and C-O stretching

vibrations, respectively) and the shoulder at 1160 cm^{-1} assigned to various M-OR stretching vibrations. The results show a rapid disappearance of TEOS, although hydrolysis may be far from to be complete at these stages. In fact, condensation will start while hydrolysis is still in progress. A variety of species such as siloxane networks as well as the organic side groups are formed in this process. In which we can remark the following: We found that as long as TEOS and ethanol are present the formation of Si-O-Si bonds such as that is indicated in the discussion of the comportment of the band at around 450 cm^{-1}. At the same time in which appears the Si-O-Si a band centred at about 600 cm^{-1} appears simultaneously; this band is assigned to several oligosilsesquioxanes, which are composed of 4-fold siloxane rings and cyclic trisiloxanes. Our results also show evidences that the species produced at the early stages of the gelation process, remain during the conformation of the final structure. At relative high water content a full-hydrolyzation is favoured and the molecular chains entangle and form additional branches resulting in a three-dimensional network.

We conclude that the infrared spectroscopy is a powerful tool to analyze structural feature of materials, in particular we apply the technique to the silica xerogels.

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