Thermal and FT-IR study of the hybrid ethylene-glycol–silica matrix

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Abstract Hybrid organic-inorganic materials, silica—ethylene glycol (EG), were prepared by the sol-gel process from mixtures of tetraetoxysilane (TEOS) and EG under acidic catalysis. The resulting hybrid material was studied through thermal analysis and FT-IR spectroscopy. This techniques evidenced the presence of EG in the silica matrix in three forms: free in the hybrid matrix pores, hydrogen bonded with the silanol groups and chemically bonded (through condensation) in the silica network. Through the thermal treatment of the hybrid matrix, we obtained a silica matrix, with specific surface of 360 m^2/g.

Keywords Sol-gel · Ethylene glycol · Hybrid materials · Thermal analysis · FT-IR

1 Introduction

The sol-gel method is a practical and promising method for obtaining porous materials through a relatively simple process. The relationship between working conditions and the resulting micro- and mesoporous structures is of great interest in practice and has been studied extensively [1]. In order to control the porous structure of the resulting materials, the sol-gel method was used to synthesize hybrid gels of silica with organic compounds, which can be later eliminated by combustion, resulting in silica matrixes with a controlled porous structure [1–3].

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The design of hybrid (organic-inorganic) nanocomposites is of great interest for science and technology. Many applications of these are in view for the future, in fields such as optical materials, mechanics, iono-electronics, biosensors, membranes [4, 5]. Practically, inorganic precursors (alkoxides of silica) and organic polymers (most frequently polyethylene glycol and polyvinyl alcohol) are mixed to obtain a "hybrid" solid matrix using hydrolysis-condensation under various catalytic conditions. These hybrid materials were studied through various techniques (thermal analysis, FT-IR spectrometry, H- and Si-NMR, texture analysis, SEM, SAXS, etc.) to determine their morphology and porous structure [6, 7].

In the current literature, the effect of organic additives (ethylene glycol [8, 9], glycerol [10], formaldehyde [11], polyethylene glycol [6]) on the gelling process (hydrolysis and condensation) is explained mostly by the formation of hydrogen bonds both with water and the ≡Si–OH groups.

In our previous papers [12, 13], we have synthesized Ni–Zn ferrite in a silica matrix starting from the respective metallic nitrates and different polyols (as precursors of ferrite) and TEOS (as precursor of the inorganic matrix), respectively. The main role of the polyol in this case was to undergo a redox reaction with NO_3^- ions and form carboxylic compounds. These carboxylic compounds, in turn, would form complex combinations together with the metallic ions that are present in the system and the complex combinations would serve as precursors of the ferrite nanoparticles. If polyols are available in large quantities during the gelling phase, this will affect the morphology and porous structure of the silica matrix and, implicitly, the dimensions of the ferrite nanoparticles. This has made it necessary to carry out investigations to observe the interaction of various polyols (ethylene glycol – EG, 1,2 propanediol – 1,2PG, 1,3 propanediol – 1,3 PG, glycerin – GL) with TEOS in the gelling phase.

Another aspect that needed to be analyzed was the effect of this interaction on the morphology and porous structure of the inorganic matrix obtained after thermal treatment.

In this paper we present a study on the thermal analysis and FT-IR spectrometry of a hybrid matrix obtained from TEOS as a silica precursor and EG, for different molar ratios of EG/TEOS. The purpose was to establish the nature of the interaction between EG and the hydrolysis products of TEOS in the gelling phase.

2 Experimental section

2.1 Synthesis

The materials used for the synthesis of gels were of analytical grade purity (Merck): ethylene glycol, absolute ethanol, tetraethylorthosilicate, and concentrated HNO_3.

The synthesis of the hybrid matrix was performed at room temperature, under continuous magnetic stirring of the TEOS ethanol solution which was added to the hydroalcoholic solution of EG, previously acidulated with HNO_3 (c_{ac} = 0.001 mol/L). After 30 min of stirring, the resulting clear solution was left to gel at room temperature.

After that, the obtained gels were crushed in a mortar and dried at a temperature of 65°C for 10 h. The synthesized samples had different molar ratios for EG/TEOS, but the H_2O/TEOS ratio was constant (= 4). We have also synthesized a gel without EG and without additional water (the only water came from HNO_3 used for acidulation). The composition of the synthesized samples and their characteristics are shown in Table 1.

Part of the dried gels was then thermally treated at various temperatures (130°C, 220°C, 300°C).

The resulting samples were studied by means of FT-IR spectrometry and thermal analysis (TG, DTA). Specific surfaces were measured for samples synthesized with and without EG, subjected to thermal treatment at 280°C.

2.2 Experimental techniques

The synthesized samples were studied by means of:

– differential thermal analysis (DTA), thermogravimetry (TG) with 1500 D MOM Budapest Derivatograph, 20–

500°C, 5°C/min, α-Al_2O_3 as inert material, Pt crucibles in the form of plates, m = 0.100 g; air or N_2 atmosphere;
– FT-IR spectroscopy with a JASCO 430 FT-IR spectrometer, in a KBr pellet, in the range 400–4000 nm;
– measurement of the specific surface with MICROMERITICS ASAP 2000.

3 Results and discussions

The process for obtaining silica-gel involves the hydrolysis of TEOS – reaction (1) and the condensation of hydrolysis products with elimination of water – reaction (2) or alcohol reaction (3), depending on the H_2O/TEOS ratio.

$$\equiv Si–OR + H_2O \Leftrightarrow \equiv Si–OH + ROH \quad (1)$$

$$\equiv Si–OH + HO–Si \equiv \Leftrightarrow \equiv Si–O–Si \equiv + H_2O \quad (2)$$

$$\equiv Si–OR + HO–Si \equiv \Leftrightarrow \equiv Si–O–Si \equiv + ROH \quad (3)$$

These reactions (1–3) lead to the formation of various linear intermediates in the system, either branched or cyclic. In the end, a three-dimensional network is formed and the solvent is embedded in its pores. The solvents can be eliminated from the pores by drying. If drying is performed at temperatures close to room temperature and atmospheric pressure, a xerogel is obtained [14]. During the drying process, the elimination of the solvent from the pores results in some cracks that hinder the formation of monoliths. One way to avoid a collapse of pores during the drying process is to add organic DCCA (drying control chemical additives).

Adding organic additives to the TEOS–H_2O system in the initial phase (sol) influences both the hydrolysis and the condensation process, trough the formation of hydrogen bonds both with water and the silanol groups, according to the literature [6, 8–11].

In our case, EG is present in the system, since we have used it as a precursor in the synthesis of Ni–Zn ferrite embedded in the SiO_2 matrix. A distinctive feature of the investigated systems is the high value of the EG:TEOS ratio, compared to the ones in the specialist literature [2, 10, 15]. This is because

Table 1 The amounts of the reactants and some characteristics of the gels

Sample	Quantity (mole)				Molar ratio (TEOS: EG: H_2O)	t_{gel} (h)
	TEOS	EG	EtOH	H_2O		
G0	0.045	–	0.130	0.180	1: 0: 4	34
G1	0.045	0.012	0.130	0.180	1: 0.25: 4	54
G2	0.045	0.045	0.130	0.180	1: 1: 4	118
G3	0.045	0.180	0.130	0.180	1: 4: 4	222
G	0.045	–	0.130	–	1: 0: 0.03	144

its role is not that of an additive, but of a raw material used for obtaining ferrite.

In our attempt to determine how ethylene glycol interacts with the hydrolysis products of TEOS during the gelling process, we have synthesized a series of gels with different compositions (see Table 1). These were then investigated by means of thermal analysis and FT-IR spectrometry.

3.1 Thermal analysis

Figure 1 shows the TG and DTA curves of the gels without EG: G0 (H_2O/TEOS $= 4$) – curves (1) and G (H_2O/TEOS ≈ 0.03) – curves (2).

The evolution of curve TG(1) for gel G0 shows that up to $\sim 100°C$, there is a rapid weight loss of $\sim 15\%$ due to the elimination of water and ethanol (products of the polycondensation reaction). This process appears on the DTA curve (1) as a weak endothermic effect. A slow weight loss can be observed up to $500°C$, which is attributed to the progress of the condensation reaction with the elimination of the silanol groups. No other effects can be observed on the DTA curve (1) for this temperature range.

According to the current literature [16, 17], for a ratio of H_2O/TEOS ≤ 4, hydrolysis occurs quickly until the initial water is consumed entirely, since the speed of the hydrolysis reaction (1) is much higher than the sum of speeds of the condensation reactions both with elimination of water (2) and elimination of alcohol (3). Complete hydrolysis only occurs for values of the ratio H_2O/TEOS >7, because of steric hindrance caused by the $Si–OC_2H_5$ groups. For values of the ratio <6, when the amount of water is not sufficient, there is a polymerization of species that undergo incomplete

hydrolysis and these form linear intermediates with residual organic groups. The result is that the particles and pores are smaller.

If a large number of residual ethoxy groups ($–OC_2H_5$) remains in the matrix, the DTA curve will display an exothermic effect around $300°C$ [12] when these are eliminated by combustion, a behavior that is not present for gel G0 that we have synthesized.

The shape of the two thermal curves TG (1) and DTA (1) suggests that the matrix synthesized at a ratio H_2O/TEOS $= 4$ is predominantly of silanol type in nature.

The thermal analysis of gel G synthesized without adding water resulted in the thermal curves TG (2) and DTA (2) in Fig. 1. Curve TG(2) shows a small weight loss ($\sim 5\%$) up to a temperature of $250°C$, a fact that demonstrates the hydrophobic nature of the synthesized matrix, caused by the high concentration of residual ethoxy groups.

There is a weight loss of $\sim 10\%$ in the range $250–400°C$, also accompanied by a wide exothermic effect (curve DTA (2)), with a peak at $\sim 320°C$. In this case, the peak can only be attributed to the pyrolysis of the residual ethoxy groups ($–OC_2H_5$) [8].

The matrix synthesized at a ratio H_2O/TEOS ≈ 0.03 has a large number of residual ethoxy groups.

After being dried at $130°C$, the gels with varying contents of ethylene glycol (varying ratio of $e =$ EG:TEOS): G1 ($e = 0.25$), G2 ($e = 1$) and G3 ($e = 4$) were subjected to thermal analysis in air.

Figure 2 shows the thermal curves TG and DTA of gels G1 – curves (1), G2 – curves (2) and G3 – curves (3). One can see that the corresponding curves are clearly different than those for the gels without ethylene glycol.
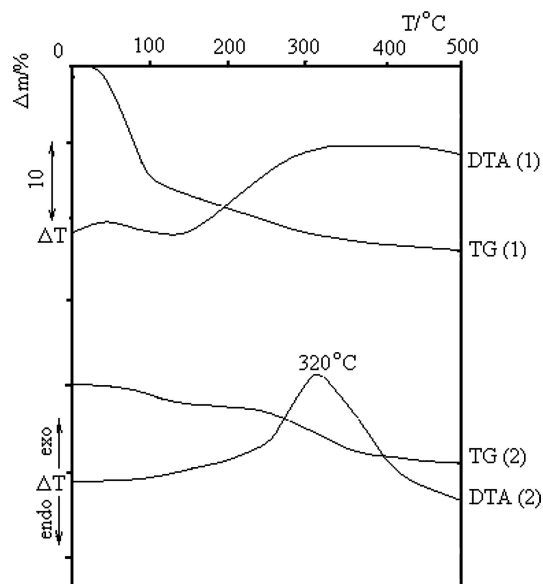

Fig. 1 Thermal curves TG and DTA for gels without ethylene glycol dried at $130°C$: (1) G0 (H_2O/TEOS $= 4$); (2) – G (H_2O/TEOS $= 0.03$)
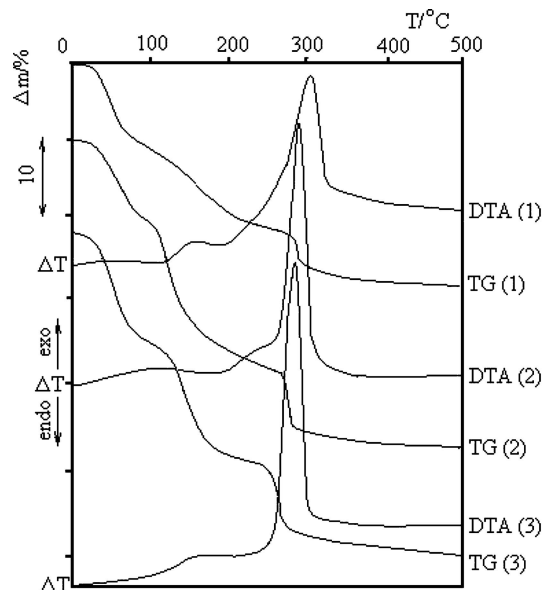

Fig. 2 Thermal curves TG (**a**) and DTA (**b**) for the synthesized gels dried at $130°C$: (1) G1; (2) G2; (3) G3

Five stages can be observed in the evolution of curves TG (1), (2), (3)—Fig. 2 for samples G1, G2, G3 with the ratios EG/TEOS = 0,25; 1; 4 and the ratio H_2O/TEOS = 4:

1. up to ∼100°C, volatile products of the condensation reaction are eliminated;
2. in the range 100–200°C, the weight loss can be attributed to the evaporation of EG that is free in the pores or hydrogen bonded with the silanol groups of the matrix;
3. in the range 200–270°C, there is a slow weight loss due to the progress of the polycondensation reaction between the Si–OH groups and between Si–OH and OH–C_2H_4–OH, followed by
4. a quick weight loss in a narrow temperature range (270–290°C), which we attribute to the elimination of organic groups generated by the chemical interaction of EG with the Si–OH groups of the matrix;
5. up to 500°C, there is a slow weight loss when the polycondensation process of the Si–OH groups completes.

If we have a look at the DTA curves (1), (2), and (3), we can observe the intense exothermic effect at ∼290°C, corresponding to phase (iv) in the weight loss, and this is probably due to the elimination through oxidation of the organic groups intertwined in the network.

An analysis of the TG and DTA curves shows that EG is present in the matrix in three states: free in the matrix pores, hydrogen bonded with the silanol groups and chemically bonded in the matrix network.

Figure 3 shows the thermal curves TG and DTA for gel G3 (with a ratio EG/TEOS = 4), dried at 65°C – curves (1), at 130°C – curves (2), and 220°C – curves (3).

Curve TG (1) of gel G3 dried at 65°C shows that there is a weight loss of ∼75% up to a temperature of 130°C, which is due mainly to the evaporation of a large quantity of free EG from the matrix pores, but also of H-bonded EG. We can also observe a weight loss in the range 280–300°C, accompanied by the exothermic effect with a peak at ∼310°C (curve DTA (1)).

By heating gel G3 to 130°C, the free EG volatilizes and the shape of curves TG (2) and DTA (2) is similar to curves TG (3) and DTA (3) in Fig. 2. Here we can clearly see phase (ii), attributed to the elimination of H-bonded EG.

For sample G3 treated thermally at 220°C, we can observe in curve TG (3)—Fig. 3 – that phase (ii) disappears as a result of the volatilization of H-bonded EG. Curve TG records the weight loss up to 100°C that is due to the adsorbed water, and the quick weight loss at ∼280°C that corresponds to phase (iv), the combustion of organic groups intertwined in the network. This loss is accompanied by a strong exothermic effect, with a peak at 290°C.

Given all of the above, the presence of EG in the matrix in the three states (free, H-bonded and intertwined in the matrix network) is confirmed.
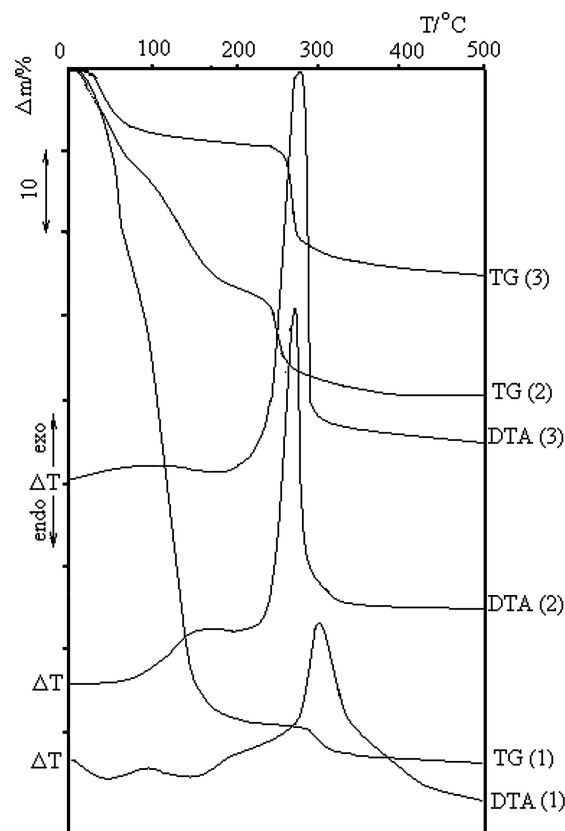
Fig. 3 Thermal curves TG and DTA for gel G3 treated thermally at various temperatures: 65°C – curves (1); 130°C – curves (2), and 220°C – curves (3)

We think that part of the ethylene glycol present in the system in the initial phase (sol) interacts with the silanol groups (resulting after the hydrolysis of TEOS) through hydrogen bonds. Later, as the polycondensation process advances, ethylene glycol condenses at one (≡Si–O–CH_2–CH_2–OH) or both ends (≡Si–O–CH_2–CH_2–O–Si≡) and forms a hybrid matrix. Under these circumstances, the weight loss in phase (iv) can be attributed to the combustion of fractions (–CH_2–CH_2–) or (–CH_2–CH_2–OH) in the network of the hybrid matrix.

To confirm the chemical interaction of EG with the silanol groups of the matrix we have performed the following experiments:

(a) We have made a mechanical mixture (dried at 85°C) between gel G0 (silanol type) and ethylene glycol; this was then subjected to thermal analysis and we have recorded thermal curves TG (1) and DTA (1) shown in Fig. 4.

From the TG and DTA curves evolution, which is similar to that of the curves presented in Fig. 2, we can consider that EG interacts with the Si–OH groups of the matrix both through H bonds (the 10% weight loss in the range 100–200°C) and chemically, through condensation with
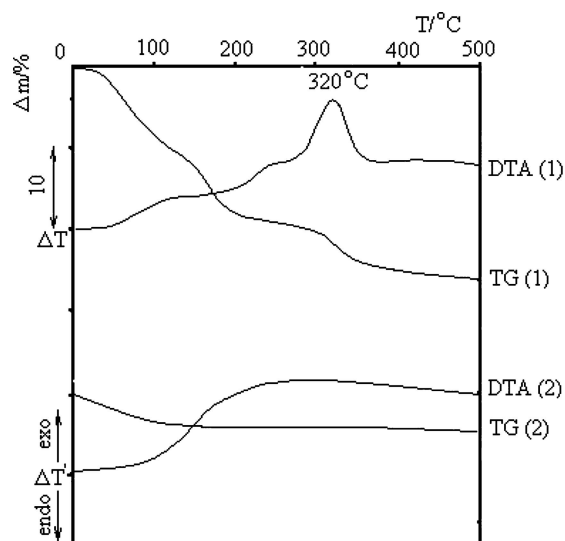
Fig. 4 Thermal curves TG and DTA for mechanical mixtures dried at 85°C: (G0 + EG) – curves (1); (quartz + EG) – curves (2)

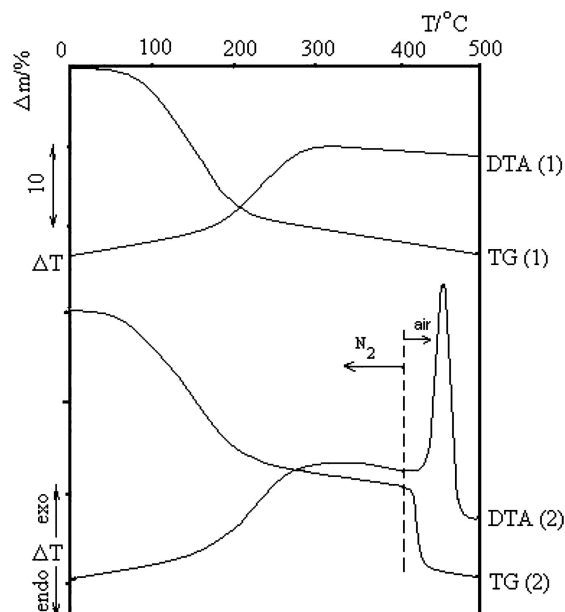**Fig. 5** Thermal curves TG and DTA for gel G3 ($e = 4$) dried at 130°C in nitrogen – curves (1), and nitrogen and air – curves (2)

the Si–OH groups, which generates a 5% weight loss due to its combustion at 300–350°C with exothermic effect at ∼ 320°C.

(b) In the thermal analysis of a mechanical mixture (dried at 85°C) consisting of quartz – EG, thermal curves TG (2) and DTA (2) (Fig. 4) display no modification up to 500°C, since EG volatilizes during the drying process and it does not interact with the matrix (it does not contain –OH groups).

(c) The thermal analysis of a mechanical mixture (dried at 85°C) between gel G (ethoxy type) and ethylene glycol did not indicate any changes compared to the thermal curves of gel G (Fig. 1 – curves (2)). As a result, the interaction of ethylene glycol with the matrix is insignificant due to the large number of residual ethoxy groups in the matrix structure.

(d) Figure 5 shows the TG and DTA curves for gel G3 ($e =$ 4) dried at 130°C, in inert N_2 atmosphere – curves (1) and N_2 atmosphere followed by insertion of air at 400°C – curves (2).

The shape of curve TG (1) shows that the weight loss up to 200°C is identical with the one recorded in air – curve TG (3) (Fig. 2) and it is attributed to the same processes whereby volatile substances, free EG and H-bonded EG, are eliminated.

Since the exothermic effect recorded in air at ∼ 290°C disappears on the DTA curve, it confirms that the effect is a result of oxidation combustion of organic groups in the hybrid matrix (–CH$_2$–CH$_2$– and –CH$_2$–CH$_2$–OH, respectively).

It should be noted that there is no weight variation on curve TG (1) in the temperature range 280–300°C, which corresponds to an elimination of organic groups bonded in the network. Since the carbon that results after the decomposition of organic groups remains in the matrix and the sample's weight is approximately constant up to 500°C, we can conclude that the decomposing groups are of type (–CH$_2$–CH$_2$–). As a result, EG bonds in the network at both ends.

Curves TG (2) and DTA (2) are identical with curves (1) up to 400°C, when air was introduced into the oven atmosphere. In the range 400–500°C, a weight loss is recorded that is accompanied by a strong exothermic effect because of the combustion of residual carbon in the matrix.

We can draw the following conclusions after the thermal analysis studies:

(i) for the ratio H$_2$O/TEOS = 4 used in the process, a silica matrix is obtained, which is predominantly silanolic;

(ii) the ethylene glycol introduced in the synthesis distributes in the matrix in three states: free in the pores, H-bonded with the silanol groups and chemically bonded (by condensation with the silanol groups during the thermal treatment) in the matrix network;

(iii) depending on the ratio $e =$ EG/TEOS, the mass losses due to the H-bonded EG (100–200°C) and to the chemically bonded EG (250–320°C) are:

  – for $e = 0.25$ the mass losses are: 9% (100–200°C) and 4% (250–320°C);
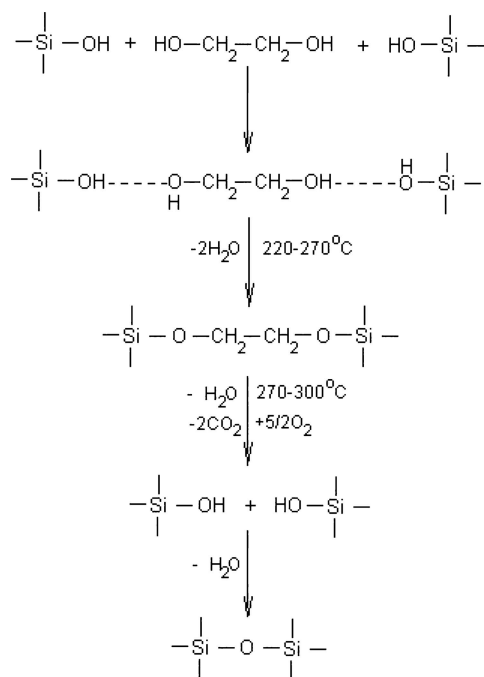
Scheme 1

– for $e = 1.0$ the mass losses are 15% (100–200°C) and 8% (250–320°C);
– for $e = 4.0$ the mass losses are 14% (100–200°C) and 10% (250–320°C).

It results that the amount of EG chemically bonded and H-bonded in the matrix depends not only on the EG/TEOS ratio, but also on the number of Si–OH formed groups.

(iv) if there are Si–OH groups in the matrix, EG is bonded, even when the two are mechanically mixed;

(v) thermal analysis in nitrogen confirmed that the condensation of EG occurs at both ends and the organic groups in the network are eliminated by a break of the O–C bonds.

A possible mechanism for the interaction of EG with silica matrix during the thermal treatment is presented in Scheme 1.

3.2 FT-IR analysis

To sustain the conclusions obtained by thermal analysis, some of the synthesized samples were also studied by means of FT-IR spectrometry.

Figure 6 presents the FT-IR spectra in the range 400–4000 cm^{-1} for gels without EG dried at 130°C: G0 (ratio H$_2$O/TEOS = 4) – spectrum (1) and G (no water added) – spectrum (2).

Spectrum (1) in Fig. 6 for gel G0 presents the absorption bands characteristic to the silica matrix: at 480 cm^{-1} attributed to the vibrations of the Si–O bond, a shoulder at 580 cm^{-1} attributed by some authors [18] to cyclic Si–O–Si
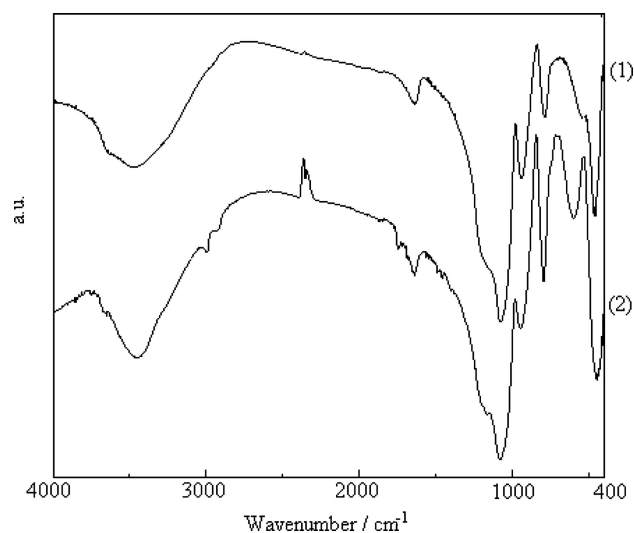

Fig. 6 FT-IR spectra of gels without ethylene glycol: G0 (ratio H$_2$O/TEOS = 4) – spectrum (1) and G (no water added) – spectrum (2)

structures, at 798 cm^{-1} attributed to the SiO$_4$ tetrahedron, at 945 cm^{-1} attributed to the Si–OH groups and at 1080 cm^{-1} with a shoulder at 1200 cm^{-1} attributed to the bond stretching vibrations of Si–O–Si. The band at 1650 cm^{-1} is attributed to the deformation vibrations of the H–O–H bond, which indicates the presence of water incorporated in the silica matrix. The wide band with a minimum in the range 3400–3500 cm^{-1} is attributed to the –OH groups in water and in the matrix [19].

Spectrum (2) of sample G, with no water added, also contains bands other than the ones mentioned for spectrum (1). There are bands at 2850 cm^{-1}, 2993 cm^{-1} that are characteristic to the bond stretching vibrations of C–H and in the range 1400–1500 cm^{-1} [20] attributed to the deformation vibrations of the C–H bond, due to a large content of residual ethoxy groups. We can also observe the pronounced band at 580 cm^{-1} caused by the cyclic Si–O–Si structures; a gelling of gels with a very low content of water mainly occurs through some linear and cyclic intermediates [16]. The low intensity band at 1165 cm^{-1} can be attributed to the vibrations of the SiO–C [21, 22] bond, which proves the presence of ethoxy groups in the gel structure. The band at 1730 cm^{-1} was attributed by some authors [23] to some C=O bonds possible to be formed by the thermal treatment.

The bands characteristic to the vibrations in the ranges 2800–3000 cm^{-1} and 1400–1500 cm^{-1}, [20] are missing in spectrum (1) for gel G0. These are typical for the C–H bond and they confirm the predominantly Si–OH character of the matrix, in agreement with the results of the thermal analysis.

Figure 7 shows the FT-IR spectra of gels with varying contents of EG (varying ratio of e = EG/TEOS) G0 (e = 0) – spectrum (1), G1 (e = 0.25) – spectrum (2), G2 (e =
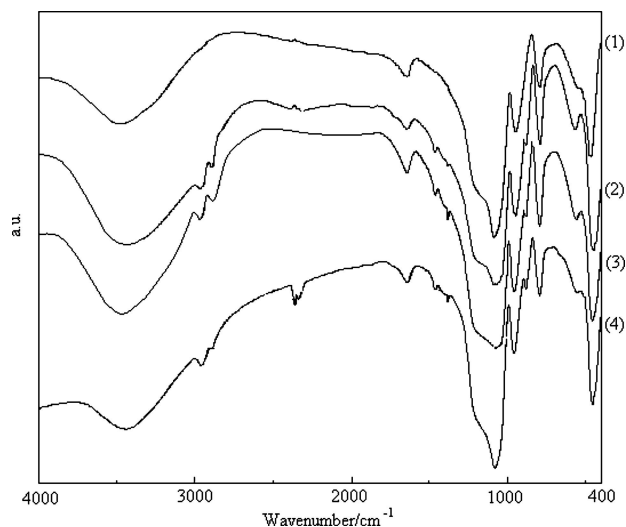
Fig. 7 FT-IR spectra of gels dried at 130°C, with different ratios of e = EG/TEOS:(1) e = 0; (2) e = 0.25; (3) e = 1.0; (4) e = 4.0

1) – spectrum (3) and G3 (e = 4) – spectrum (4), dried at 130°C.

Spectra (2), (3), and (4) corresponding to the samples with ethylene glycol not only display the bands characteristic to the silica matrix (G0 – spectrum (1)), but a series of bands that are caused by the presence of EG. This way, bands characteristic to the C–H bond appear in the ranges 2800–3000 cm^{-1} and 1400–1500 cm^{-1}, which are attributed to the $-CH_2-$ groups in free ethylene glycol or bonded in the matrix. There is also the band at 880 cm^{-1} that is characteristic to the deformation vibrations of the C–C bond in EG [24].

In order to track EG in the gel, depending on the temperature applied for thermal treatment, we have recorded the FT-IR spectra of gel G3 (e = 4) treated thermally at different temperatures chosen according to results of the thermal analysis: 130°C (drying temperature), 220°C (temperature where
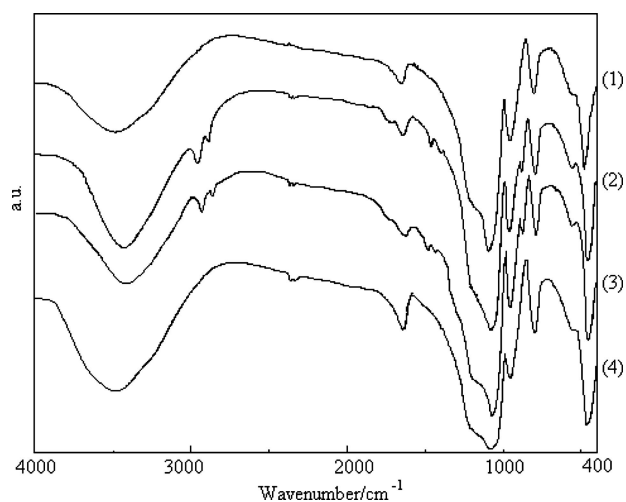

Fig. 8 FT-IR spectra of samples: (1) G0 treated at 130°C; (2) G3 treated at 130°C; (3) G3 treated at 220°C; (4) G3 treated at 300°C

free EG or H-bonded EG evaporated) and 300°C (temperature at which the combustion of organic groups in the matrix network was complete).

It can be observed that spectra (2) and (3) of gel G3 treated thermally at 130°C and 220°C, respectively, presents the absorption bands in the range 2800–3000 cm^{-1}, 1300–1400 cm^{-1} and 880 cm^{-1}, characteristic to EG present in the matrix, H-bonded or intertwined in the matrix network.

Spectrum (4) obtained for sample G3 treated thermally at 300°C (after elimination of the organic groups bonded in the matrix) differs significantly from spectra (2) and (3). It can be observed that the bands at 880 cm^{-1}, 1300–1400 cm^{-1} and 2800–3000 cm^{-1} are missing. The spectrum of this sample is identical with spectrum (1) of sample G0 (130°C) and only displays the bands characteristic to the silica matrix.

According to the above, the presence of ethylene glycol in the matrix is obvious even at temperatures higher than its evaporation temperature (196°C), which confirms the chemical interaction of EG with the silanol groups of the matrix.

In order to observe the effect of EG on the morphology of the silica matrix, we have determined the specific surface of samples G0 (without EG) and G2 (e = 1) treated thermally at 280°C for 3 h. For G0, a specific surface of 27 m^2/g was obtained and for G2, the specific surface was 360 m^2/g. This demonstrates a significant influence of ethylene glycol on the porous structure of the silica matrix. This aspect is important for us, for obtaining fine ferrite nanoparticles, embedded in silica matrix and will be the object of a future study.

4 Conclusions

This paper focused on the interaction of EG with the hydrolysis products of TEOS in the gelling phase with the obtaining of hybrid EG- silica gels. Thermal analysis of the hybrid gels turned out to be an adequate technique for such a study. After the thermal analysis of the synthesized gels, EG was identified in the matrix in three states: free in the pores, H-bonded with the Si–OH groups of the matrix and chemically bonded at both ends, by condensation with the Si–OH groups. We have established the way in which chemical bonding of EG occurs in the matrix network, as well as the way in which the organic groups break away from the network. FT-IR spectrometry has confirmed the hypotheses of our thermal analysis, thus being an additional argument to sustain our findings.

In the given conditions for synthesis (high molar ratio of EG/TEOS), it can be stated that a hybrid matrix is obtained. After thermal treatment, a SiO$_2$ matrix is obtained, with large specific surface area and potential applications in various fields.

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