J Therm Anal Calorim (2009) 97:251–256
DOI 10.1007/s10973-009-0247-5

Study on the influence of teos–diol molar ratio on their chemical interaction during the gelation process

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ICTAC2008 Conference

Abstract Hybrid organic–inorganic materials, silica–diol, were synthesized by the sol–gel process from mixtures of tetraethylorthosilicate (TEOS) and diols: ethylene glycol (HO–CH_2–CH_2–OH) and 1,3 propane diol (HO–CH_2–CH_2–CH_2–OH), in acid catalysis. The gels have been synthesized for a molar ratio H_2O:TEOS = 4:1 and different molar ratios diol/TEOS: 0.25; 0.5; 0.75; 1.0; 1.25 and 1.5. The resulting gels were studied by thermal analysis and FT-IR spectroscopy, in order to evidence the interaction of diols with silica matrix. Thermal analysis indicated that the condensation degree increases with the molar ratio diol/TEOS until a certain value. The thermal decomposition of the organic chains bonded within the silica network in the temperature range 250–320 °C, leaded to a silica matrix with modified morphology. The adsorption–desorption isotherms type is different for the samples with and without diol. Thus, the specific surface areas have values $<11\ m^2/g$ for the samples without diol and $>200\ m^2/g$ for the samples with diols, depending on the annealing temperature.

Keywords Hybrid · Polyol/TEOS · Thermal analysis

Introduction

The preparation and characterization of nanocomposites are intensively investigated for their potential applications in obtaining magneto-optical devices, in catalysis, ferrofluids, environmental protection, medicine [1–5]. Important are the obtaining and maintaining of a material at nanometric scale with performant properties. One of the preparation methods that provide a control on the morphological and chemical properties is the sol–gel processing by using amorphous silica as inorganic matrix [6].

The preparation of the silica matrix presumes hydrolysis and condensation reactions that lead to the formation of $\equiv$Si–O–Si$\equiv$ units [6]. These processes are influenced by a series of parameters: catalysts (acid, basic), solvent, temperature, pH, molar ratio H_2O:Si. Catalysts can influence the hydrolysis and condensation mechanisms as well as the structural evolution of the gels, leading to aggregates of monomer–cluster or cluster–cluster type. The rate of the hydrolysis and condensation reaction is influenced until the gelation point by temperature, solvent, pH. The ulterior maturation process leads to the modification of the gels structure in time [6]. The sol–gel method used for the obtaining of organic–inorganic hybrid matrices is of great interest for science and technology [7]. Practically, inorganic precursors (alkoxides of silica) and organic polymers (polyethylene glycol, polyvinyl alcohol) [8, 9] are mixed to obtain a ‘hybrid’ solid matrix. The hybrids thus formed can be used in different forms, such as monolithic blocks, thin films, fibres and coatings on different substrates.

In the composites whose organic components have polar groups, the inclusion of ionic interactions [10] or the formation of hydrogen bonds between components of the system [11] is important for understanding the nature of synthesized materials.

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In our previous papers we have studied the preparation of some hybrid matrices tetraethylorthosilicate (TEOS)–diols (ethylene glycol (EG), propane diol (1,2 PG and 1,3 PG)). The studies have evidenced that diols (HO–$(CH_2)_2$–OH and HO–$(CH_2)_3$–OH) present in the system $Si(OC_2H_5)_4$–H_2O in acid catalysis (H^+) chemically interact with the ≡Si–OH groups during the gelation (hydrolysis–condensation). By thermal treatment of the hybrid gels one can obtain silica matrices with modified morphologies depending on the diols nature [12, 13].

In this paper we present the study on the influence of the molar ratio TEOS-EG and TEOS-1,3 PG on the chemical interaction between ≡Si–OH and OH–C≡ during the formation of the silica matrix. We have also studied the influence of the diols nature on the matrices morphology obtained by thermal treatment of the gels.

Experimental

Synthesis

The materials used for the gels synthesis were of analytical grade purity (Merck): ethylene glycol (EG), 1,3 propane diol (1,3 PG), absolute ethanol, tetraethylorthosilicate (TEOS), concentrated HNO_3.

The synthesis of the hybrid matrices was performed by addition of an ethanolic TEOS solution, at room temperature, under intense magnetic stirring to the acidulated ($c(HNO_3) = 0.01$ mol L^{-1}) diol hydroalcoholic solution. The resulted clear solution was maintained under stirring another 30 min, after which it was left for gelation at room temperature.

Table 1 Characteristics of the synthesized samples

Sample	Diol	Molar ratio TEOS:Diol:H_2O	t_{gel} (h)
1	EG	1:0.25:4	140
2		1:0.50:4	144
3		1:0.75:4	170
4		1:1.00:4	170
5		1:1.25:4	180
6		1:1.50:4	180
7	1,3 PG	1:0.25:4	140
8		1:0.50:4	230
9		1:0.75:4	240
10		1:1.00:4	235
11		1:1.25:4	235
12		1:1.50:4	300

There were synthesized 12 gels with the two diols (EG, 1,3 PG) at different molar ratios. The characteristics of the synthesized samples are presented in Table 1.

After gelation, the obtained gels were crushed and dried at 40 °C for 2 h. The dried gels were thermally treated at 200 °C and 500 °C.

Characterization techniques

The samples from 40 °C and 200 °C were characterized by thermal analysis (TG, DTA coupled with evolved gas analysis (EGA)) on a Diamond Perkin Elmer thermobalance and FT-IR spectrometry using Shimadzu Prestige-21, in KBr pellets, in the domain 400–4000 cm^{-1}. Specific surface areas were measured for the samples thermally treated at 400 °C using a Micromeritics ASAP 2020.

Results and discussions

Figure 1(a, b) exhibits the thermal curves of the gels synthesized with EG (a) and 1,3 PG (b) for a molar ratio TEOS:diol = 1:1, dried at 40 °C.

The mass loss up to 250 °C corresponds to the elimination of absorbed water, to the condensation reaction and to the unbounded diols (EG and 1,3 PG) and it was evidenced by EGA. The strong exothermic effect in the range 300–320 °C corresponds to the burned organic chains chemically bounded in the matrix. All synthesized samples have shown similar thermal behaviour.

The FT-IR spectrometry has evidenced the presence of diols within the matrix. Figure 2 presents the FT-IR spectra of the gels obtained at 40 °C and 200 °C, with EG (a) and 1,3 PG (b) for a molar ratio TEOS:diol = 1:1. The gels thermally treated at 40 °C (Fig. 2a, b spectra 1) exhibit the bands corresponding to the diols present within the gels pores: ν(C–OH) H-bonded (3400 cm^{-1}) and free (1100–900 cm^{-1}), ν(CH) (3000–2800 cm^{-1}; 1300–1400 cm^{-1}) and ν(C–C) 877 cm^{-1}. At this temperature the silica network is not very well formed and its characteristic bands are overlapped by the diols bands. The FT-IR spectra of the gels at 200 °C (Fig. 2a, b spectra 2) that contain only the diols chemically bounded within the matrix, evidence a better formed silica network (bands at 450 cm^{-1}, 570 cm^{-1}, 794 cm^{-1}, 960 cm^{-1}, 1080 cm^{-1}, 3440 cm^{-1}). In the range 2800–3000 cm^{-1} the spectra present bands of the organic chains chemically bounded within the matrix.

In order to evidence the influence of the molar ratio diol:TEOS on their chemical interaction during the formation of the hybrid matrix, all gels (Table 1) were thermally treated at 200 °C, 2 h. Under these conditions, volatiles and unbounded diol are eliminated (Fig. 1). Figure 3 presents the thermal curves of the silica matrix synthesized without

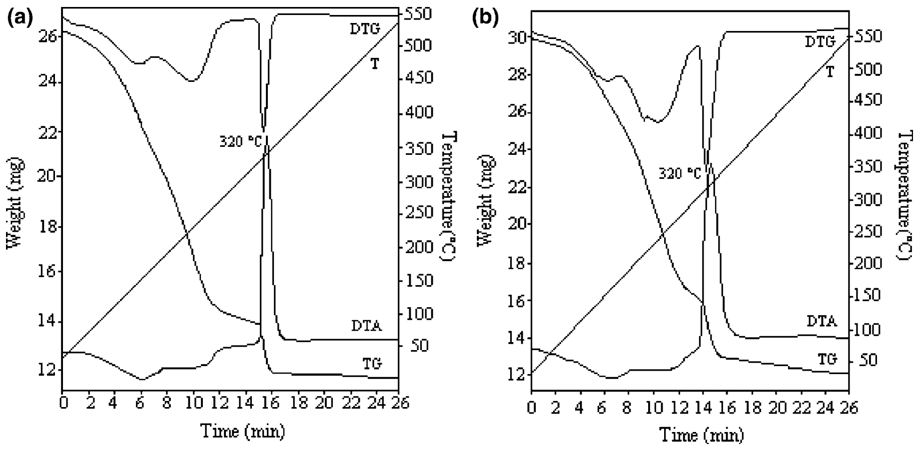

Fig. 1 Thermal curves of the gels with EG (**a**) and 1,3 PG (**b**) dried at 40 °C

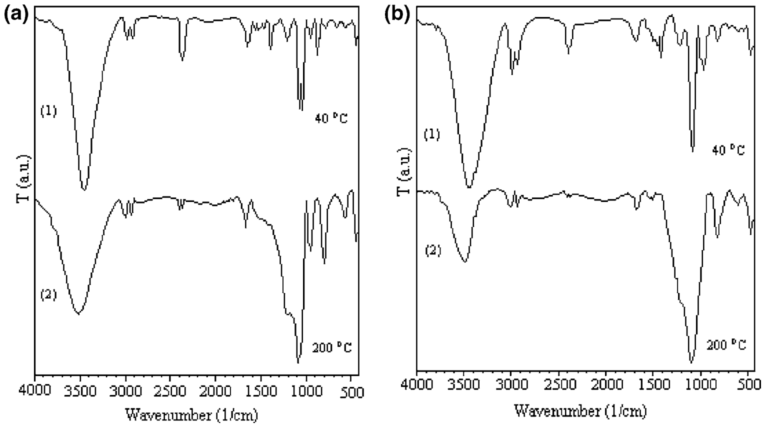

Fig. 2 FT-IR spectra of the samples with EG (**a**) thermally treated at 40 °C (1) and 200 °C (2) and 1,3 PG (**b**) thermally treated at 40 °C (1) and 200 °C (2)

diols, thermally treated at 200 °C. The TG curve shows a mass loss associated to an endothermic effect at 150 °C attributed to the elimination of water and condensation products. The slow mass loss up to 300 °C is due to the evolution of the poly-condensation process. The exothermic process from 360 °C with mass loss, corresponds to the burning of the matrices residual groups (–OC_2H_5), according to EGA.

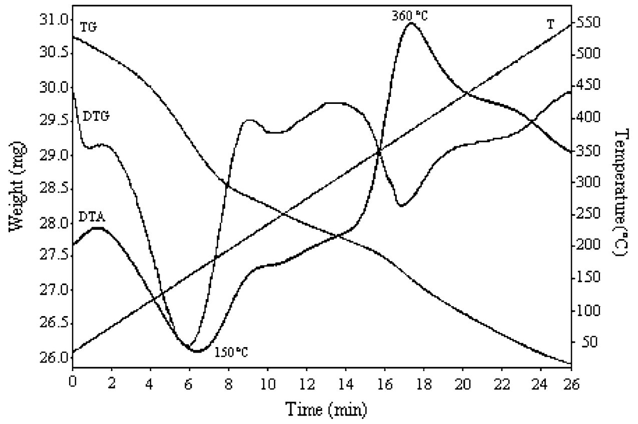

Fig. 3 Thermal curves of the silica matrix without diols thermally treated at 200 °C

Figure 4 presents the thermal curves of the gels with EG (a) and 1,3 PG (b) for a molar ratio TEOS:diol = 1:1 thermally treated at 200 °C. From the thermal curves, we can observe that both gels exhibit similar thermal processes. The mass loss up to 280 °C corresponds to the elimination of the adsorbed water and to the diol from the pores of the xerogel. The high rate mass loss in the range 280–350 °C associated to a pronounced exothermic effect corresponds to the oxidative burning of organic fragments chemically bounded within the silica matrix. In case of 1,3 PG the higher mass loss may be attributed to the longer organic chain, compared to EG, or to a higher interaction degree. The evolved gas analysis (EGA) has evidenced, in this temperature range, a massive presence of CO_2 as well as of some partial oxidation products (HCOOH for EG and HCOOH, CH_3CHO for 1,3 PG). The exothermic effect from ~450 °C is attributed to the burning of residual carbon.

All gels synthesized with the two diols according to Table 1 have presented a similar thermal behaviour. Based on the mass losses from the range 300–400 °C

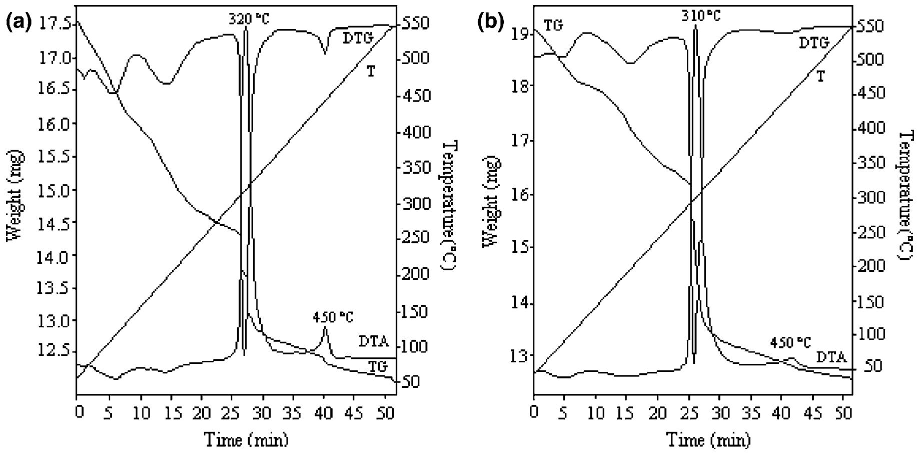

Fig. 4 Thermal curves of the gels with EG (**a**) and 1,3 PG (**b**) thermally treated at 200 °C

Table 2 Results for the samples of different compositions synthesized with EG

Molar ratio TEOS:EG	m_i (mg)	Δm (mg) 250–400 °C	$m_{\mathrm{residueSiO_2}}$ (mg) 600 °C	Mols EG chemically bounded	Mols TEOS	Experimental molar ratio TEOS:EG
1:0.25	22.61	2.19	17.34	0.0498	0.289	1:0.17
1:0.50	20.86	2.23	15.08	0.0507	0.251	1:0.20
1:0.75	21.69	2.47	15.43	0.0561	0.257	1:0.22
1:1.00	17.52	1.96	12.14	0.0445	0.202	1:0.22
1:1.25	22.43	2.70	15.51	0.0614	0.259	1:0.23
1:1.50	18.05	1.95	12.26	0.0443	0.204	1:0.22

Table 3 Results for the samples of different compositions synthesized with 1,3 PG

Molar ratio TEOS:1,3 PG	m_i (mg)	Δm (mg) 250–400 °C	$m_{\mathrm{residueSiO_2}}$ (mg) 600 °C	Mols 1,3 PG chemically bounded	Mols TEOS	Experimental molar ratio TEOS:EG
1:0.25	13.98	1.90	10.24	0.0328	0.171	1:0.19
1:0.50	15.55	2.62	10.74	0.0452	0.179	1:0.25
1:0.75	15.79	2.86	10.53	0.0493	0.176	1:0.28
1:1.00	19.15	3.44	12.57	0.0593	0.209	1:0.28
1:1.25	16.19	3.03	10.47	0.0522	0.175	1:0.29
1:1.50	16.20	2.85	10.49	0.0491	0.175	1:0.28

corresponding to the organic chains bounded within the matrix and the residue from 600 °C (SiO_2), we have estimated the molar ratio diol (bounded): TEOS, for each gel. Tables 2 and 3 present the results obtained for the gels of different compositions (according to Table 1) synthesized with the 2 diols:EG (Table 2) and 1,3 PG (Table 3).

According to the results of thermal analysis we can observe that until the ratio 1:0.75, the quantity of the chemically bounded diol within the matrix increases with the increase of the molar ratio diol:TEOS. For higher ratios we can observe that the quantity of chemically bounded diol remains almost constant (Fig. 5). This can be explained by the fact that the reaction between the groups $\equiv$Si–OH develops faster than the reaction between the groups $\equiv$Si–OH and OH–C$\equiv$. The gelation times increase slowly up to the ratio 1:0.75 and afterwards remain almost

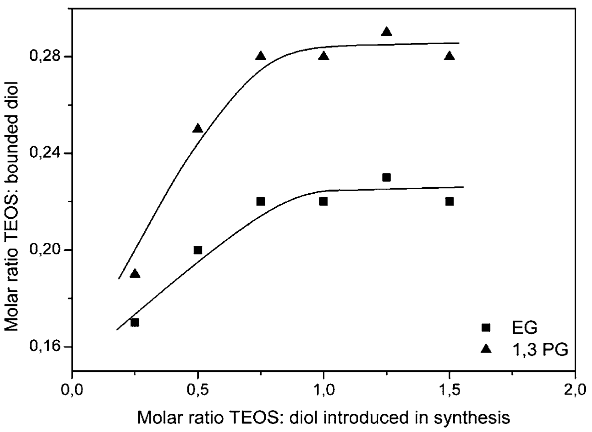

Fig. 5 Dependence between theoretical and experimental molar ratio TEOS:diol

constant making more difficult the condensation of diol groups. For the same ratio diol:TEOS introduced in synthesis, the quantity of the chemically bounded diol is higher in case of 1,3 PG.

From the presented ones, the thermal analysis has evidenced that the studied diols similarly interact with the ≡Si–OH groups during the formation of the silica network leading to organic–inorganic hybrid materials. The interaction of diols with ≡Si–OH groups of the matrix can be represented as follows:

$$\equiv \mathrm{Si{-}OH} + \mathrm{HO{-}(CH_2)_n{-}OH} + \mathrm{HO{-}Si} \equiv \rightarrow$$
$$\equiv \mathrm{Si{-}O{-}(CH_2)_n{-}O{-}Si} \equiv + 2\ \mathrm{H_2O}\ n = 2, 3$$

The interaction degree of the diols is also influenced by the higher rate of the poly-condensation reaction:

$$\equiv \mathrm{Si{-}OH} + \mathrm{HO{-}Si} \equiv \rightarrow \equiv \mathrm{Si{-}O{-}Si} \equiv + \mathrm{H_2O}.$$

The increasing of the gelation time facilitates the interaction of diol with the Si–OH groups leading to a higher condensation degree. The longer gelation times observed in case of the gels with 1,3 PG explain the higher degree of chemical interaction of this diol with the Si–OH groups.

The length of the organic chain (*n* value) may influence the morphology of the silica matrix resulted by thermal decomposition of the hybrid matrices. This results from the specific surface area measurements of the gels with diol:-TEOS molar ratio of 1:1 for the gels with EG and 1,3 PG. The obtained values for the gels 4 and 10 annealed at 400 °C were, expressed in m^2/g: 256 and 337, compared to 11 m^2/g for the gel without diol. In Figs. 6 and 7 are presented the low temperature nitrogen adsorption–desorption isotherms for the samples without diol and with 1,3 PG (TEOS:1,3 PG = 1:1) annealed at 600 °C. The evolution of the adsorption–desorption isotherms of the two samples is significantly different. In case of the sample without diol the shape of the isotherm is close to type II isotherms characteristic for nonporous solids. This fact explains the low value of the specific surface area: ~1 m^2/g.

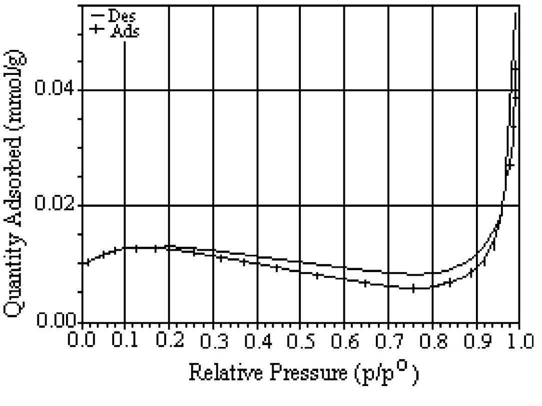

Fig. 6 Low temperature nitrogen adsorption–desorption isotherm for the samples without diol

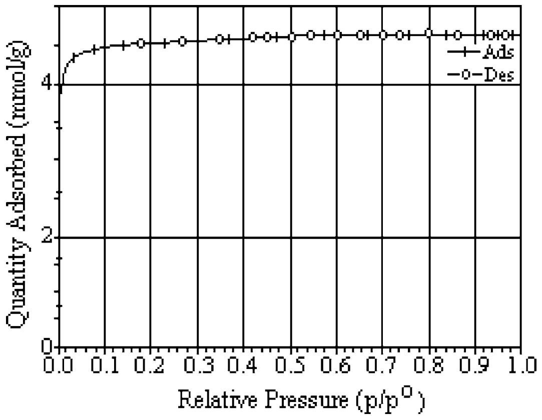

Fig. 7 Low temperature nitrogen adsorption–desorption isotherm for the sample with 1,3 PG

In case of the sample with 1,3 PG the shape of the isotherm is close to the type I isotherms characteristic for the micro-porous materials (average pore width <2 nm). The specific surface area is influenced by the presence of the diol during the gelation process. Thus, the obtained value was 329 m^2/g.

Conclusions

The paper has studied the chemical interaction between diol, ethylene glycol or 1,3 propanediol and the Si–OH groups from the silica network, during gelation. Thermal analysis of the synthesized gels has evidenced that the quantity of the chemically bounded diol increases with the increasing of the diol:TEOS molar ratio until a certain value, than remains constant. In the case of 1,3 PG the degree of condensation in the silica network was higher, due to the longer gelation times of the corresponding gels.

The thermal treatment of the hybrid gels leads, after thermal degradation of the organic chains, to silica matrices with modified morphology: higher surface area values and micro-porous structure.

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