

Scientific paper

# Organic-inorganic Hybrid Gels of Diol-TEOS Type. Synthesis and Study on the Chemical Interaction

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## Abstract

Hybrid inorganic-organic materials, silica – diol, were prepared by the sol-gel process from mixtures of tetraethyl orthosilicate (TEOS) and two diols (1,2-propanediol and 1,4-butanediol), using different molar ratios TEOS: diol, in acidic catalysis. The resulted materials were studied by thermal analysis, FT-IR spectroscopy,  $^{29}\text{Si}$ -NMR and nitrogen adsorption measurements. The thermal analysis of the gels, in air and nitrogen, has clearly evidenced the chemical bonding of the studied diols with the Si-OH groups resulting from the hydrolysis of TEOS, forming hybrid gels. The mass loss registered on TG in the range 250–300 °C, corresponding to the burning of the organic chains from the hybrid network allowed us to calculate the fraction of the bonded diol. This fraction depends on the initial molar ratio TEOS:diol and on the diol's nature. By annealing the hybrid gels at 600 °C we have obtained silica matrices with different textural parameters.

**Keywords:** Sol-gel, diol, inorganic-organic hybrid, thermal analysis

## 1. Introduction

Organic-inorganic materials with well defined morphology and controlled structure at nanometric scale represent an interesting class of materials studied in the last years due to their potential applications in different fields of advanced technology.<sup>1–3</sup> The possibility of using organic compounds in order to modify the inorganic framework has long been recognized as an interesting instrument for the development of new composite materials. One of the possibilities to synthesize hybrid materials was to modify the inorganic network by introducing selected organic groups leading to organic modified silicates (Ormosils).<sup>4,5</sup>

The presence of organic compounds with small molecules, especially diols significantly influences the structure and morphology of the silica matrix, leading to organic-inorganic hybrid materials.<sup>6,7</sup>

During the gelation process, ethylene glycol is capable to form hydrogen bonds with the Si-OH groups resulting from the hydrolysis reaction of  $\text{Si}(\text{OR})_4$ . The strong hydrogen bond network shields the reactive centers ( $\equiv\text{Si-O-}$ ) of the incompletely condensed chains. This prevents the efficient condensation which leads to the forma-

tion of a branched network and produces larger and uniformly distributed micropores within the polymeric network.<sup>8</sup> Glycerol is considered as a special chemical additive because of the three hydroxyl groups in its molecule. The main disadvantage of glycerol is that it remains retained in the pores and it is difficult to remove. Even at high temperatures, it tends to decompose to carbonate than to evaporate.<sup>9</sup>

In literature it is usually considered that the presence of primary –OH groups is responsible for the interaction of organic compounds with silanols containing Si-OH groups resulted during the sol-gel synthesis.<sup>10</sup> This interaction between organic compounds and tetraethyl orthosilicate or its hydrolysis products influences the morphology of the silica matrix and thus, the dispersion and size of the embedded oxidic nanoparticles.

Our previous research on the system TEOS – ethylene glycol –  $\text{H}_2\text{O}$ , in acidic catalysis,<sup>11</sup> has shown that during the formation process of the silica matrix, the diol interacts chemically or by H bonds with the hydrolysis products of TEOS. Furthermore we have shown that independent on the diols nature, the interaction TEOS-diol takes place by the same bond type but the morphology of the silica matrix is modified.<sup>12</sup> The chemical bonding of

the organic chains within the silica gel is influenced by the molar ratio TEOS-diol.<sup>13</sup> The diol-TEOS interaction studies are important for the synthesis of materials with magnetic properties embedded in silica matrix.<sup>14,15</sup> The molar ratio diol-TEOS is essential due to the involvement of the diol in the formation of the hybrid gel.

In this paper we report the synthesis and characterization of the hybrid gels 1,2-propanediol-TEOS and 1,4-butanediol-TEOS, for molar ratios within the range 0.1 ÷ 1.5, in order to establish the optimal interaction ratio diol-TEOS. The study was also focused on the influence of the diols structure (nature) and the elucidation of the interaction mechanism TEOS-diol. The hybrid gels could be used for the obtaining of support materials with modified morphology and for embedding of nanomaterials with catalytic, magnetic and environmental sensing properties.

## 2. Experimental

### 2.1. Synthesis

Reagents used for the synthesis of the hybrid gels were of analytical purity (Merck): 1,2-propanediol (1,2PG), 1,4-butanediol (1,4BG), ethanol (EtOH), tetraethyl orthosilicate (TEOS), concentrated HNO<sub>3</sub>.

The hybrid gels were synthesized by adding, at room temperature, under intense magnetic stirring, of an ethanolic TEOS solution to the hydro alcoholic diol solution, previously acidified with HNO<sub>3</sub> ( $c_{ac} = 0.01$  mol/L). The obtained clear solution was stirred for 30 minutes and was left for gelation at room temperature. Samples were synthesized for different molar ratios diol/TEOS = 0.1, 0.2, 0.5, 1.0, 1.5 and the same molar ratio H<sub>2</sub>O/TEOS (8:1). The composition of the synthesized gels and their characteristics are presented in Table 1.

After gelation, the gels were grinded and dried at 60 °C for 2 hours. The dried gels were thermally treated at 200 and 600 °C. The obtained samples were studied by

thermal analysis (TG, DTA), FT-IR spectrometry, <sup>29</sup>Si-NMR spectrometry on solids. Specific surface areas were measured for the samples thermally treated at 600 °C.

### 2.2. Experimental Techniques

Thermal analysis was performed on a Diamond Perkin Elmer thermobalance, in the temperature range 20–550 °C, with a heating rate of 10 °C /min, using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as reference, in air and nitrogen and on a 1500 MOM Budapest Derivatograph, in air up to 500 °C. FT-IR spectra were recorded with a Shimadzu Prestige-21 FT-IR spectrometer, in KBr pellets, in the range 400–4000 cm<sup>-1</sup>. <sup>29</sup>Si-NMR spectra were taken on a Bruker MSL300 spectrometer at a frequency of 59.53MHz (7.05 T). Chemical shifts were reported in parts per million (ppm) relative to tetramethylsilane (TMS). Textural characteristics of the out-gassed samples were obtained from nitrogen physisorption using a MICROMERITICS ASAP 2020 instrument. Prior to the measurements, the samples were degassed in vacuum at 250 °C. The BET surface area was calculated by using the standard Brunauer-Emmett-Teller (BET) method, while the pore size distributions were calculated applying the Barret-Joyner-Halenda (BJH) method to the desorption branches of the isotherms.

## 3. Results and Discussion

The hybrid gels synthesized with diols were characterized by thermal analysis, in air and nitrogen, up to 550 °C. Figures 1 and 2 present the TG curves registered in air and in nitrogen, for the hybrid gels  $G_{1,2PG}^{1.0}$  and  $G_{1,4BG}^{1.0}$  thermally treated at 200 °C.

The mass losses registered in air up to 250 °C correspond to the elimination of the adsorbed water and volatile compounds of the poly-condensation (EtOH, H<sub>2</sub>O) as well as to the evaporation of the diol from the matrices po-

**Table 1.** Characteristics of the synthesized gels (TEOS: Diol: H<sub>2</sub>O)

Sample	Diol	Quantity (mols)		H <sub>2</sub> O	EtOH	Molar ratio TEOS:Diol:H <sub>2</sub> O	t <sub>g</sub> (hours)
		TEOS	Diol				
$G_{1,2PG}^{0.1}$	1,2 PG	0.05	0.005	0.4	0.12	1:0.1:8	130
$G_{1,2PG}^{0.2}$	1,2 PG	0.05	0.010	0.4	0.12	1:0.2:8	140
$G_{1,2PG}^{0.5}$	1,2 PG	0.05	0.025	0.4	0.12	1:0.5:8	144
$G_{1,2PG}^{1.0}$	1,2 PG	0.05	0.050	0.4	0.12	1:1.0:8	154
$G_{1,2PG}^{1.5}$	1,2 PG	0.05	0.075	0.4	0.12	1:1.5:8	168
$G_{1,4BG}^{0.1}$	1,4 BG	0.05	0.005	0.4	0.12	1:0.1:8	140
$G_{1,4BG}^{0.2}$	1,4 BG	0.05	0.010	0.4	0.12	1:0.2:8	148
$G_{1,4BG}^{0.5}$	1,4 BG	0.05	0.025	0.4	0.12	1:0.5:8	130
$G_{1,4BG}^{1.0}$	1,4 BG	0.05	0.050	0.4	0.12	1:1.0:8	264
$G_{1,4BG}^{1.5}$	1,4 BG	0.05	0.075	0.4	0.12	1:1.5:8	288

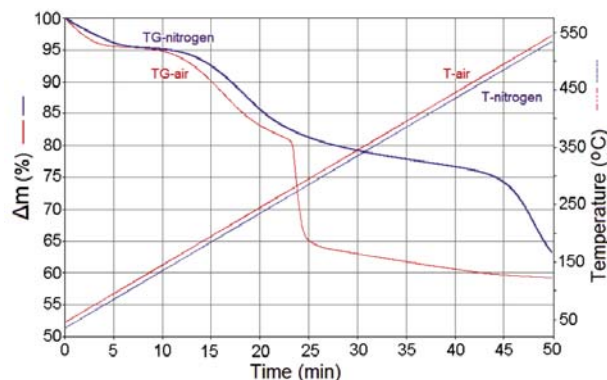


Fig. 1. TG curves in air and nitrogen of gel  $G_{1,2PG}^{0.1}$  thermally treated at 200 °C

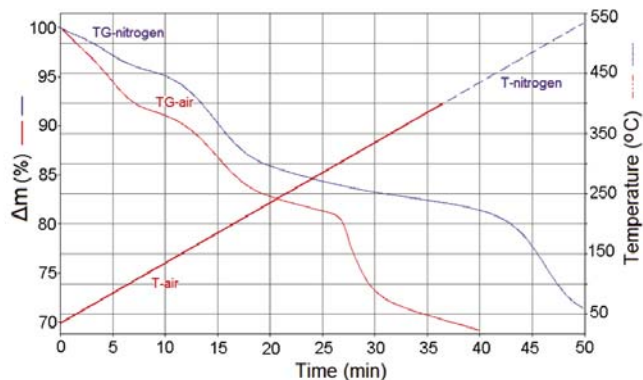


Fig. 2. TG curves in air and nitrogen of gel  $G_{1,4BG}^{1.0}$  thermally treated at 200 °C

res. The process that occurs with mass loss in the range 250–300 °C corresponds to the oxidative decomposition (burning) of the organic chains chemically bonded within the silica network. The slow mass loss registered up to 550 °C can be assigned to the evolution of the silica matrix poly-condensation.

In nitrogen, the evolution of the TG curves up to 250 °C is similar to the one registered in air. In inert atmosphere the thermal decomposition of the organic chains takes place in the range 450–500 °C. The shifting of the thermal process towards higher temperatures confirms the chemical interaction between the diol and the Si–OH groups. The corresponding mass losses registered in this range are identical with the ones registered in the range 250–300 °C, in air.

From the obtained thermal data, it results that up to ~250 °C we have a hybrid diol-silica gel. According to these data, all initial gels (Table 1) have been thermally treated at 200 °C (in order to eliminate the adsorbed water and the volatiles from the pores). The as obtained hybrid gels have been studied by thermal analysis in air up to 500 °C.

Figures 3 and 4 present the TG and DTA curves obtained in air for the hybrid gels heated at 200 °C, synthesized with 1,2PG and 1,4BG for different molar ratios diol:TEOS (Table 1). The mass losses registered in the range 250–400 °C, assigned to the oxidative decomposition of the organic chains bonded within the network depend on the initial molar ratio diol:TEOS and on the diols nature. At low initial molar ratio diol:TEOS (0.1, 0.2) the oxidative decomposition of the organics is shifted towards higher temperatures (300–400 °C) due to the dispersion of the organic chains bonded within the network and to the difficult air diffusion within the pores. For higher molar ratios diol:TEOS = 0.5, 1.0, 1.5, this process takes place at lower temperatures, in the same range (250–300 °C) and the mass losses are close to each other. For all samples, the oxidative decomposition of the organic chains generates on the DTA curve a corresponding exothermic effect.

Table 2 presents the results of the thermal analysis for the hybrid gels. The amount of the diol bonded within the hybrid gels, was calculated from the mass losses in the temperature range 250–400 °C corresponding to the burning of the organic chain  $\text{Si-O-R-O-Si} \rightarrow \text{Si-O-Si} + [\text{OR}]$ , whe-

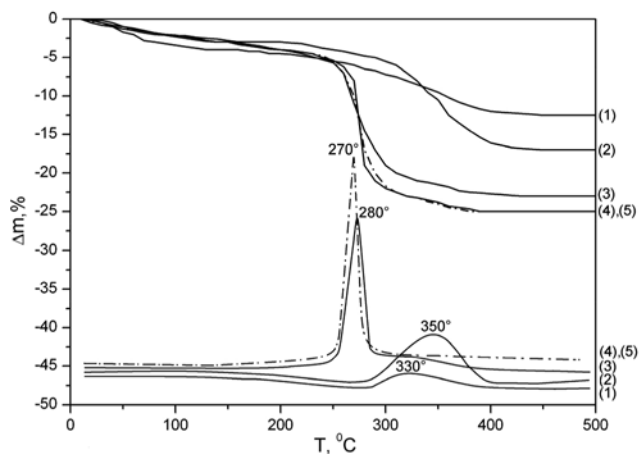


Fig. 3. TG and DTA curves of the hybrid gels:  $G_{1,2PG}^{0.1}$  (1),  $G_{1,2PG}^{0.2}$  (2),  $G_{1,2PG}^{0.5}$  (3),  $G_{1,2PG}^{1.0}$  (4),  $G_{1,2PG}^{1.5}$  (5)

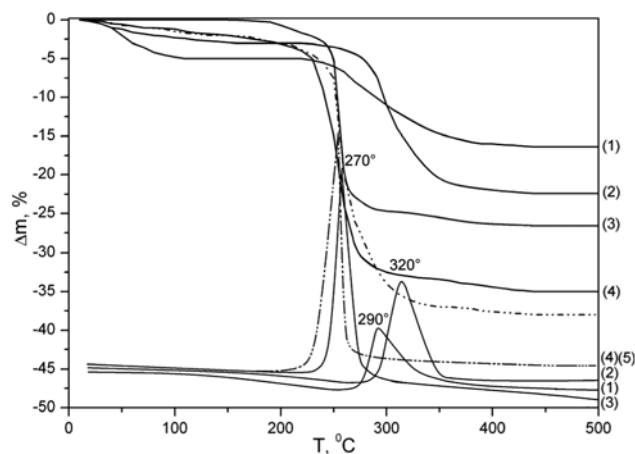


Fig. 4. TG and DTA curves of the hybrid gels:  $G_{1,4BG}^{0.1}$  (1),  $G_{1,4BG}^{0.2}$  (2),  $G_{1,4BG}^{0.5}$  (3),  $G_{1,4BG}^{1.0}$  (4),  $G_{1,4BG}^{1.5}$  (5)

Table 2. Mass losses registered at thermal analysis of the hybrid gels

Sample	mols TEOS	$\Delta m_i$ % 20–500 °C	$\Delta m$ % 250–400 °C	$m_{\text{residue SiO}_2}$ (%) 500 °C	mols OR chemically bounded	Initial molar ratio Diol:TEOS	Experimental molar ratio Diol:TEOS
$G_{1,2PG}^{0.1}$	1.50	12	7	88	0.12	0.10	0.08
$G_{1,2PG}^{0.2}$	1.40	16	14	84	0.24	0.20	0.17
$G_{1,2PG}^{0.5}$	1.28	23	18	77	0.31	0.50	0.24
$G_{1,2PG}^{1.0}$	1.25	25	20	75	0.34	1.00	0.27
$G_{1,2PG}^{1.5}$	1.25	25	20	75	0.34	1.50	0.27
$G_{1,4BG}^{0.1}$	1.40	16	11	84	0.15	0.10	0.10
$G_{1,4BG}^{0.2}$	1.30	22	17	78	0.23	0.20	0.18
$G_{1,4BG}^{0.5}$	1.21	27	25	73	0.34	0.50	0.28
$G_{1,4BG}^{1.0}$	1.08	35	31	65	0.43	1.00	0.40
$G_{1,4BG}^{1.5}$	1.03	38	34	62	0.47	1.50	0.46

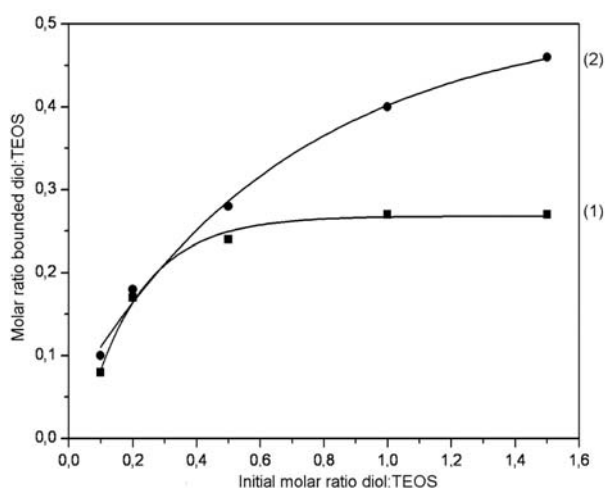


Fig. 5. Dependence of bounded diol: TEOS molar ratio with the initial diol:TEOS for: 1,2PG (1) and 1,4BG (2)

re  $R = -\text{CH}(\text{CH}_3) - \text{CH}_2 -$  or  $R = -(\text{CH}_2)_4 -$ ) and the residual mass at 500 °C (considered as  $\text{SiO}_2$ ).

Figure 5 presents the dependence between the amount of chemically bonded diol and the diol amount introduced in synthesis.

The dependences show that the diols are chemical interacting at low molar ratios diol : TEOS ( $< 0.5$ ). For molar ratios higher than 1.0 the interaction diol-TEOS becomes insignificant.

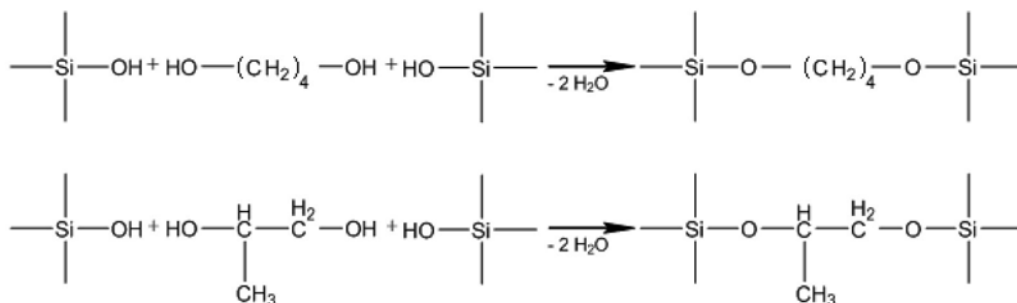
The hydrolysis-condensation reactions and the interaction of the silanol groups ( $\equiv\text{Si-OH}$ ) with the  $-\text{OH}$  groups of the diols take place concurrently. By introducing low amounts of diol, we can presume that the interaction process develops with a higher rate once the gel is formed. At higher diol concentration, the interaction is limited in time by the progress of the hydrolysis-condensation reactions (gelation).

The evolution of the presented curves (Fig.5) shows that the nature of the diol influences the interaction process.

We can propose an interaction mechanism, according to the schemes below, which shows that both hydroxyl groups ( $-\text{OH}$ ), independent on their nature, participate at the formation process of the hybrid gels.

The interaction results and the proposed mechanism suggest that a linear diol favors the chemical bonding while a branched diol is more sterically hindered to interact with TEOS.

FT-IR spectrometry has also evidenced the presence of the diols chemically bonded within the silica gel. Fig-



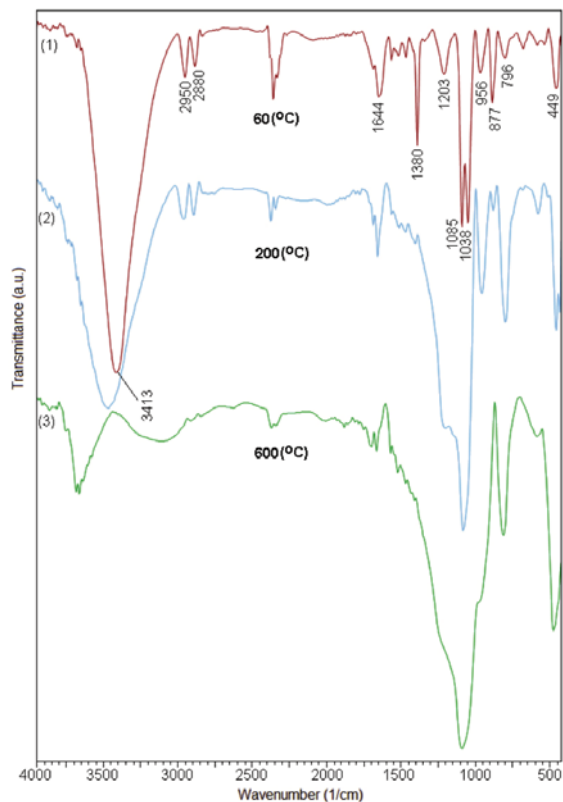


Fig. 6. FT-IR spectra of the hybrid gel  $G4^{1.0}_{1,2PG}$  thermally treated at 60 (1), 200 (2) and 600 °C (3)

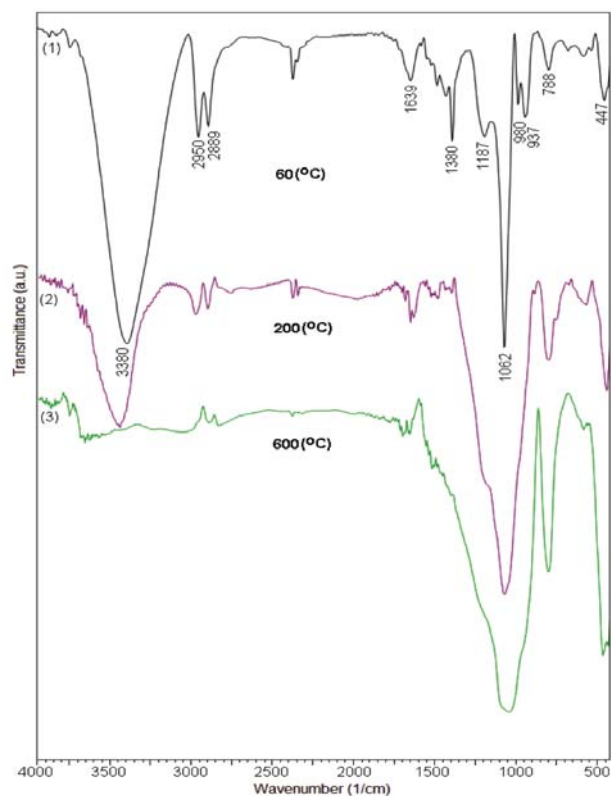


Fig. 7. FT-IR spectra of the hybrid gel  $G4^{1.0}_{1,4BG}$  thermally treated at 60 (1), 200 (2) and 600 °C (3)

res 6 and 7 present the FT-IR spectra of the hybrid gels  $G_{1,2PG}^{1.0}$  and  $G_{1,4BG}^{1.0}$  dried at 60 °C and thermally treated at 200 and 600 °C.

The hybrid gels dried at 60 °C (spectrum 1) present the bands characteristic for the silica gel and for the chemically bonded diol:  $\nu(\text{C-OH}) - \text{H}$  bonds ( $3400 \text{ cm}^{-1}$ ) and the free diol within the gels pores:  $\nu(\text{C-OH})$  ( $1100\text{--}900 \text{ cm}^{-1}$ ),  $\nu(\text{CH})$  ( $3000\text{--}2800 \text{ cm}^{-1}$ ;  $1300\text{--}1400 \text{ cm}^{-1}$ ) and  $\nu(\text{C-C})$   $877 \text{ cm}^{-1}$ .<sup>16</sup> At this temperature, the silica network

is not well formed and its characteristic bands are overlapped with the bands of the diols.

The FT-IR spectra of the hybrid gels thermally treated at 200 °C (spectrum 2), when the poly-condensation degree of the diols within the matrix is more advanced, the intense bands correspond to the silica matrix (the bands at  $1080 \text{ cm}^{-1}$  (Si-O-Si),  $960 \text{ cm}^{-1}$  (Si-OH),  $794 \text{ cm}^{-1}$  (SiO<sub>4</sub>),  $570 \text{ cm}^{-1}$  (cyclic Si-O-Si),  $450 \text{ cm}^{-1}$  (Si-O)).<sup>17–22</sup> The bands  $\nu(\text{CH})$  in the range  $3000\text{--}2800 \text{ cm}^{-1}$  are still

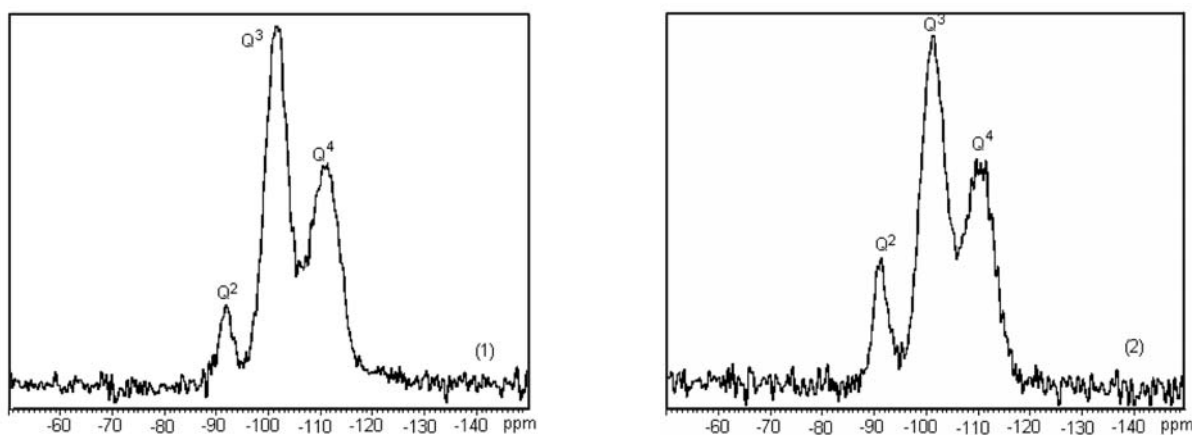


Fig. 8.  $^{29}\text{Si-NMR}$  spectra of the hybrid gels  $G_{1,2PG}^{1.0}$  (1) and  $G_{1,4BG}^{1.0}$  (2) thermally treated at 200 °C

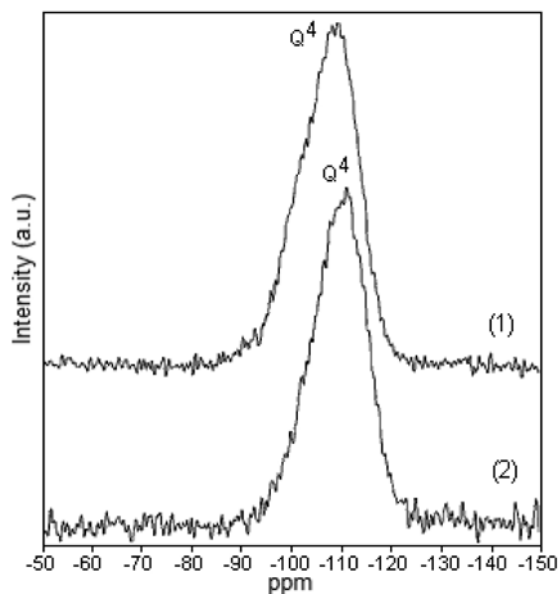


Fig. 9.  $^{29}\text{Si}$ -NMR spectra of the hybrid gels  $G_{1,2\text{PG}}^{1.0}$  (1) and  $G_{1,4\text{BG}}^{1.0}$  (2) thermally treated at 600 °C

present. In the region 1000–1300  $\text{cm}^{-1}$  the Si-O-C vibrations attributed to unreacted alkoxides which are overlapped with the vibrations of other species from the hybrid gel also exist.<sup>23</sup>

Spectrum (3) of the gels treated at 600 °C, when the organic chains of the bonded diols have burned, forming the silica matrix, presents only the bands characteristic for the silica matrix.

The studied gels were also characterized by solid state  $^{29}\text{Si}$ -NMR spectrometry in order to describe the local surrounding of the Si atom within the network. Figure 8 presents the  $^{29}\text{Si}$ -NMR spectra of the hybrid gels  $G_{1,2\text{PG}}^{1.0}$  and  $G_{1,4\text{BG}}^{1.0}$  thermally treated at 200 °C, when the diol is chemically bonded within the matrix.

All NMR spectra have evidenced the presence of the species  $Q^4$  ( $\delta \approx -110$  ppm),  $Q^3$  ( $\delta \approx -100$  ppm) and  $Q^2$  ( $\delta \approx -90$  ppm),  $Q^3$  being predominant. The presence of the

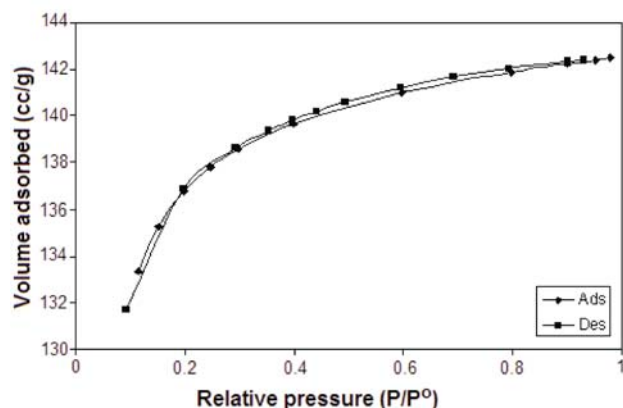


Fig. 10.  $\text{N}_2$  adsorption – desorption isotherms for the gel  $G_{1,2\text{PG}}^{1.0}$

specie  $Q^3$  and especially of  $Q^2$  points to a low poly-condensation degree of the matrix at this temperature (200 °C), which can be explained by the existence of organic chains bonded within the matrices network concordant to thermal analysis results of the hybrid matrices at 200 °C.

By thermal treatment at 600 °C, the combustion of the organic chains of the hybrid matrices with formation of a silica matrix takes place. The  $^{29}\text{Si}$ -NMR spectra of the silica matrices obtained by calcinations at 600 °C are similar. Figure 9 presents the NMR spectra of the matrices  $G_{1,2\text{PG}}^{1.0}$  and  $G_{1,4\text{BG}}^{1.0}$  obtained at 600 °C. The spectra are similar with a shift at -110 ppm corresponding to  $Q^4$  species, indicating a high condensation degree ( $\text{SiO}_2$ ).

The microporous texture of the samples with different diol content was studied by  $\text{N}_2$  adsorption isotherm measurements. The textural properties (BET surface area, pore volume and average pore size) of the silica samples, obtained by annealing at 600 °C of the synthesized gels showed that the presence of the diol in the gels leads to silica matrices with narrow mesopores ( $> 2$  nm at the boundary between meso- and micro-pores). The surface area for the gel  $G_{1,4\text{BG}}^{1.0}$  was 277  $\text{m}^2/\text{g}$ , the pore volume was 0.975  $\text{cm}^3/\text{g}$  and the average pore diameter was 1.87 nm. The values of the textural parameters for the gels synthesized with 1,2PG are indicated in Table 3.

Table 3. Textural characteristics of the  $\text{SiO}_2$  matrices from the BET adsorption isotherm

Sample	Surface area $S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Pore volume $\text{BJH}_{\text{des}}$ ( $\text{cm}^3/\text{g}$ )	Average pore diameter $\text{BJH}_{\text{des}} D_p$ (nm)
$G_{1,2\text{PG}}^{0.5}$	284	0.161	1.97
$G_{1,2\text{PG}}^{1.0}$	396	0.220	3.05
$G_{1,2\text{PG}}^{1.5}$	420	0.241	3.40

All compositions showed the same type of adsorption-desorption isotherms. Figure 10 presents the adsorp-

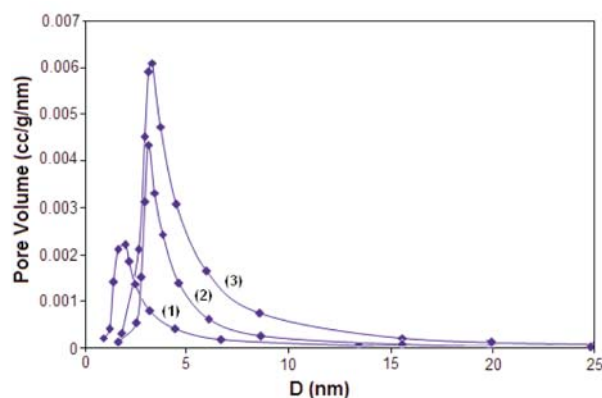


Fig. 11. Pore size distribution for the gels:  $G_{1,2\text{PG}}^{0.5}$ ,  $G_{1,2\text{PG}}^{1.0}$ ,  $G_{1,2\text{PG}}^{1.5}$

tion-desorption isotherm for the gel  $G_{1,2PG}^{1.0}$ . The shape of the isotherm is close to type I, characteristic for microporous materials.<sup>23</sup> The pore size distributions for the gels synthesized with 1,2PG are presented in Fig. 11.

The textural parameters values of the gels synthesized with different diols ( $G_{1,2PG}^{1.0}$  and  $G_{1,4BG}^{1.0}$ ) are due to the structure (branched or linear) of the diols. The surface areas values of the gels  $G_{1,2PG}^{0.5}$ ,  $G_{1,2PG}^{1.0}$ ,  $G_{1,2PG}^{1.5}$  depend on the molar ratio 1,2PG – TEOS.

The presence of diols in the system leads to much higher surface areas compared to the silica gel without diol (surface area of  $\sim 11$  m<sup>2</sup>/g),<sup>25</sup> making these materials appropriate for nanocomposites with controlled properties.

## 4. Conclusions

The paper reports the formation of some hybrid organic-inorganic gels starting from tetraethyl orthosilicate and two diols: 1,2-ethanediol and 1,4-butanediol for a wide range of diol:TEOS molar ratios: 0.1 ÷ 1.5. By thermal analysis in air and nitrogen of the hybrid gels, we have shown that the diols are chemically bonded within the silica network by covalent bonds (Si–O–C) leading to the obtaining of organic-inorganic gels, thermally stable up to  $\sim 250$  °C for both diols and all initial diol:TEOS molar ratio.

At low molar ratios diol:TEOS, the interaction develops faster while for higher initial molar ratios the interaction is inhibited. Thus, the optimal interaction ratio was established at 0.5.

FT-IR and solid state Si-NMR studies on the gels obtained at 200 °C have evidenced a low condensation degree in the hybrid gels due to the chemical bonding of the diols. The matrices resulted at 600 °C indicate a more advanced condensation degree. N<sub>2</sub> adsorption-desorption isotherms of the samples obtained at 600 °C have evidenced the formation of microporous silica. The textural properties of the silica matrices depend on the molar ratio diol: TEOS.

The method used by us allows the obtaining of materials which can be used as templates for nanocomposites.

## 5. Acknowledgment

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## Povzetek

Hibridni anorganski-organski materiali v sistemu silicijev oksid – diol so bili pripravljani po sol-gel postopku iz mešanice silicijevega etoksida (TEOS) in dveh diolov (1,2-propandiol in 1,4-butandiol) v različnih molskih razmerjih TEOS: diol s kislinsko katalizo.

Materiali so bili analizirani s termično analizo, FT-IR spektroskopijo,  $^{29}\text{Si}$ -NMR in meritvami adsorpcije dušika. Termična analiza gelov na zraku in v dušiku je potrdila, da je prišlo do nastanka hibridnih gelov. Na osnovi izgube mase v območju od 250 °C do 300 °C, ki ustreza termičnemu razpadu organskih skupin iz hibridne strukture, je bil izračunan delež vezanega diola. Odvisen je od molskega razmerja TEOS: diol in od vrste diola. Z žarenjem hibridnih gelov pri 600 °C smo pripravili silicijev oksid z različnimi teksturami.