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SYNTHESES OF NANOSTRUCTURED SILICA MEDIATED BY ORGANOGELATORS DERIVED FROM D-SORBITOL

Raluca STAN[1]*, Cristina OTT[2], Sorin ROSCA[3], Alina BADANOIU[4], Stefania STOLERIU[5], Georgeta VOICU[6]

Organogelifianţi derivaţi de D-sorbitol au fost utilizaţi ca matriţă pentru sinteze de silice nanostructurate prin polimerizarea sol-gel a tetraetoxisilicatului. Reacţiile de polimerizare au fost realizate in prezenţa catalizatorului bezilamină. Gelurile rezultate au fost evaporate în vid şi au fost supuse unor analize termice complexe (ATD, TG, DTG) în vederea stabilirii conditiilor optime de tratament termic (temperatură, durată). Structura eşantioanelor de silice rezultate a fost investigată prin microscopie electronică de trasmisie (SEM) cuplată cu EDX .

D-Sorbitol derived organogelators have been used as templates for syntheses of nanostructured silica by the sol-gel polymerization of tetraethoxysilicate. The polymerization reactions were conducted in the presence of benzyl amine as catalyst. The resulting gels were vacuum evaporated and subjected to complex thermal analyses (DTA, TG, DTG) in order to establish the optimum duration and temperature of thermal treatment. The structure of the resulted silica samples was investigated by scanning electron microscopy (SEM) coupled with EDX.

Keywords: nanostructured silica, dibenzylidenesorbitol, tetraethoxysilicate, sol - gel

1. Introduction

Nanostructured materials with well controlled dimensions, composition and cristalinity have been the subject of intense research in the last years, mainly because of their applications in electron emission, mesophysics and manufacture of electronic devices, optoelectronics and sensors. Among these materials,

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[1] Professor, Organic Chemistry Department, POLITEHNICA University of Bucharest, 313, Spl. Independentei, Sect. 6,. 060042, Bucharest Romania, *e-mail: rl_stan@chim.upb.ro

[2] Lecturer, Organic Chemistry Department, POLITEHNICA University of Bucharest, 313, Spl. Independentei, Sect. 6,. 060042, Bucharest Romania

[3] Professor, Organic Chemistry Department, POLITEHNICA University of Bucharest, 313, Spl. Independentei, Sect. 6,. 060042, Bucharest Romania

[4] Reader, Science and Engineering of Oxides and Nanomaterials Department, POLITEHNICA University of Bucharest, 313, Spl. Independentei, Sect. 6,. 060042, Bucharest Romania

[5] Lecturer, Science and Engineering of Oxides and Nanomaterials Department, POLITEHNICA University of Bucharest, 313, Spl. Independentei, Sect. 6,. 060042, Bucharest Romania

[6] Lecturer, Science and Engineering of Oxides and Nanomaterials Department, POLITEHNICA University of Bucharest, 313, Spl. Independentei, Sect. 6,. 060042, Bucharest Romania

different types of silica with controlled morphologies and surfaces received great attention due to numerous uses and technical application in the field of ceramics, catalyst supports, biomaterials and modified electrodes [1]. Several types of nanostructured silica are used as templates for other materials as metal nanoparticles [2] or nanoporous carbon [3].

In order to synthesize these nanostructured materials, sol-gel polymerization of tetraethoxysilicate (TEOS) has been recently employed in the presence of organic molecules acting as structure directing agents (SDA) or templates. Compounds extensively used as SDA are: ionic [4] and non-ionic surfactants [5], fluorous and mixed surfactants [6], liquid crystals [7], amphiphilic block copolymers [8] or mixture of the latter with ionic surfactans [9]. The use of organogelators for nanostructured silica as SDA is limited to several examples of cholesteryl [10], sugar-derived organogelators, [11] and recently, 12-hydroxystearic acid and its sodium salt [12].

In the present paper we present the synthesis of nanostructured silica by sol-gel polymerization of tetraethoxysilicate (TEOS) in the presence of three D-sorbitol based organogelators: 1,3 :2,4-bis-*O*-benzylidene-D-sorbitol (**DBS, 1**), 1,3 :2,4-bis-*O*-*p*-nitrodibenzylidene-D-sorbitol (*p*-**NO_2-DBS, 2**) and 1,3 :2,4-bis-*O*-*p*-aminodibenzylidene-D-sorbitol (*p*-**NH_2-DBS, 3**). The substituted DBS derivatives, *p*-**NO_2-DBS, 2** and *p*-**NH_2-DBS, 3**, respectively are recently synthesized in our group [13].

2. Experimental

Sol-gel polymerization. In a typical procedure 1 equiv. (30 mg, for 1%) organogelator was dissolved with heating and occasional sonication in 3 mL solvent in a capped tube. 5 Equiv. of benzylamine were added to the clear solution, followed by 10 equiv. of TEOS and 50 equiv. of water. The tube was sealed and left at the room temperature for 1 week in order to allow the hydrolytic sol-gel process to proceed untill completion. At the end of the period the resulted translucent gel was dried under reduced pressure (10 torr). The dried xerogels were subjected to two different thermal treatments in air: 1) the samples were kept at 500°C for 2 hours; 2) the samples were first heated at 200°C for two hours and subsequently kept at 500°C for 2 hours.

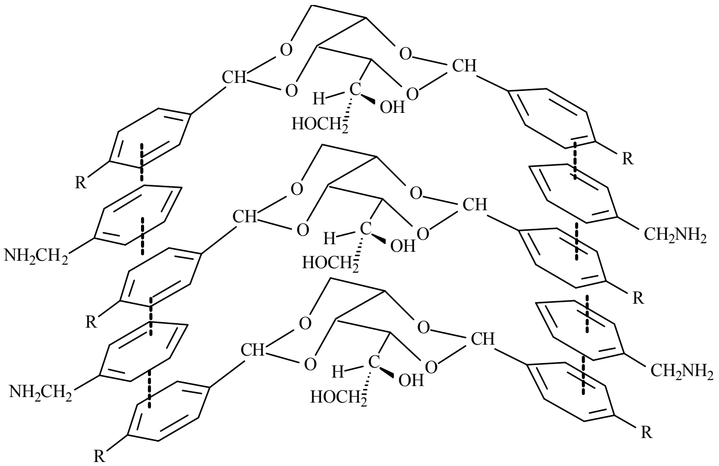
Thermogravimetry (TG) and differential thermal analysis (DTA) of dried xerogels were performed on SHIMADZU DTG-TA-51H device with a heating rate of 10°C/min.

SEM and EDX analyses were performed on Hitachi S2600N scaning electron microscope.

3. Results and discussion

The sol-gel polymerization of TEOS occurs via anionic intermediates, at pH values higher than the isoelectric point of the silica precursor (~ 2) and via cationic intermediates when pH is below the isoelectric point [14]. The templated synthesis takes place when strong interactions between anionic silicate and the organogelator are present. As a result, most of the organogelators which were successfully employed in making nanoporous silica are either cationic or neutral and contain amino functional groups. The transcription-enabling additive benzylamine, which may interact with the phenyl rings from the structure of organogelators through π-π stacking, was successfully utilized for the synthesis of hollow tubular silica [11b, 12], even though the organogelators did not exhibit the structural features enounced above.

Encouraged by these results, we have performed sol-gel polymerizations of TEOS in ethanol and ethylacetate, for different concentrations of organogelators **1-3** (0.2-2% wt/vol) and in the presence of benzylamine as catalyst. Benzylamine interacts with the butterfly-like organogelator molecule by π-π stacking (Fig. *1*), and is consequently intercalated between the organogelators molecules, providing the necesary amino-groups at the gel-fiber surface and stimulating the transcription of gel structure in the obtained silica.



R= H, **1**
NO$_2$, **2**
NH$_2$, **3**

Fig. 1. π-π-Stacking interactions between organogetors **1-3** and benzylamine

Thermogravimetry (TG) and differential thermal analysis (DTA). TG and DTA analysis of dryed xerogel **1** (DBS, 1%, ethanol, 25^{o}C) is presented in Fig. 2. The following effects could be observed:

- the endotherm effect at 134 °C is assumed to result from the humidity loss of the sample and from water loss (water resulted in the TEOS polymerization process). An important weight loss (about 40%) correspond to this effect on the TG curve;
- the exotherm effect at 376°C which is assumed to result from the organic compounds (DBS and benzilamine - traces) combustion. The weight loss (assesed on TG curves) of aprox. 12% is in good agreement with the initial amount of TEOS, DBS and benzylamine in this composition. Similar thermal behavior was recorded for the other compositions with DBS.

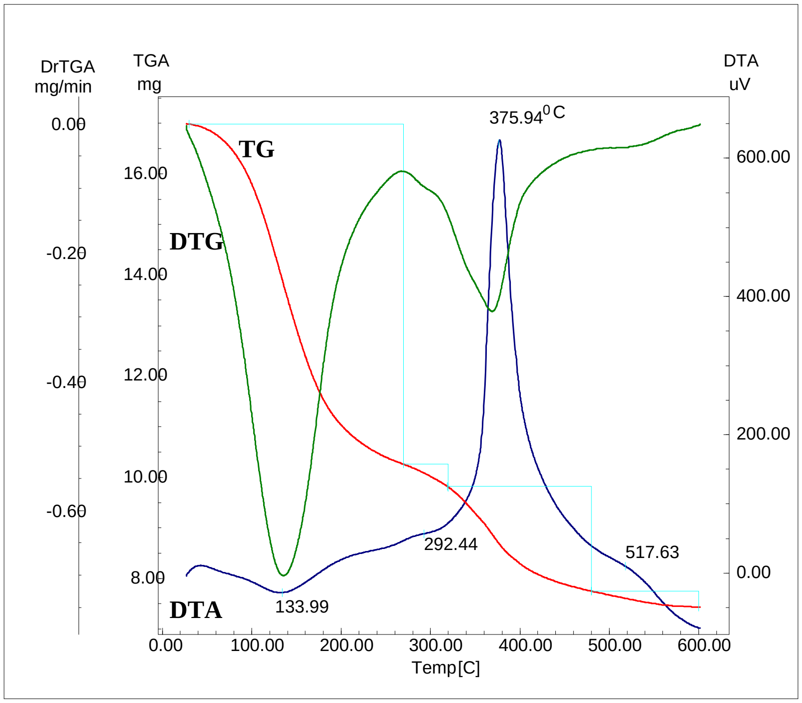


Fig. 2. Thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) curves of xerogel obtained in the presence of DBS (1%, ethanol)

The TG, DTG and DTA curves recorded for the xerogels obtained by TEOS polymerisation in ethanol mediated by **p-NO$_2$-DBS** (a) and **p-NH$_2$-DBS** respectively (b), are presented in *Figure 3.*

The endotherm and exotherm effects recorded on this analysis are similar to those recorded for the DBS xerogel (Fig.2). Nevertheless some differences in the maximum temperature values recorded on DTA curve for the exotherm effect are noticed: with DBS as template, the maximum of the exotherm is recorded at 376°C; in the case of **p-NO_2-DBS** the temperature is lower, 367°C (Fig. 3a) and higher (400°C) in the case **p-NH_2-DBS** (Fig. 3b) respectively.

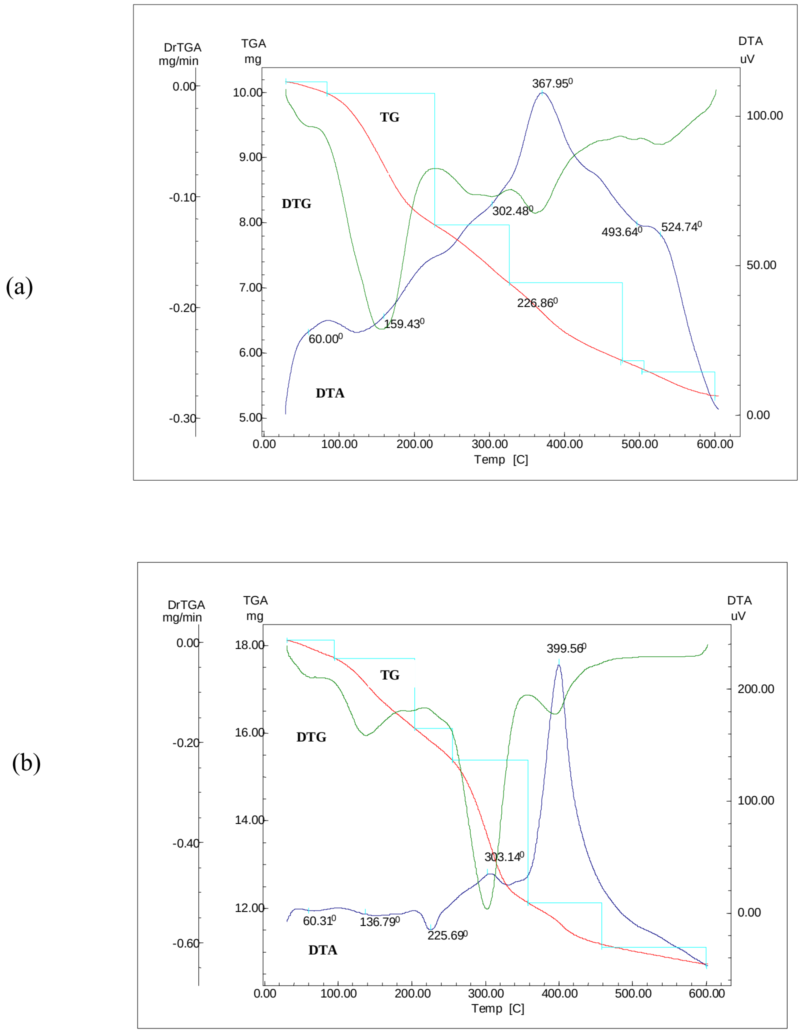


Fig. 3. Thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) curves for xerogels obtained in the presence of **p-NO_2-DBS** (1%, ethanol , a) and **p-NH_2-DBS** (1%, ethanol, b)

These values suggest the fact that these temperatures are not correlated with the molecular weight of the template but with the degree of packing of the fibrils formed by the organogelator in the solvent used for sol-gel polymerization. It is known that, in the case of **DBS** and its methyl derivatives, association occurs mainly by π-π-stacking in order to form fibrils [15]. As previously shown [13], the xerogel formed by **p-NO$_2$-DBS** in ethanol has three dimensional fibrous network with long fibrils with square section around 200 nm due to the voluminous nitro group, whilst in the case of the xerogel obtained from *p*-**NH$_2$-DBS** in ethanol, fibrils are tightly packed probably due to the additional hydrogen bonding induced by the presence of the amino group. Consequently, the organic material from silica gel obtained by sol-gel polymerization of TEOS mediated by loose-packed **p-NO$_2$-DBS** fibrils is degraded at a lower temperature than the one obtained in the presence of **DBS**. In the same manner, the tightly-packed network of **p-NH$_2$-DBS** fibrils used as template increased the temperature of the exothermic effect.

SEM and EDX analysis. The composition of the calcinated samples, from which the organic compounds are removed through combustion, was determined by Energy Dispersive Spectrometry (EDX). As it can be seen from Fig. 4, silicium is the only element detected in the calcinated sample.

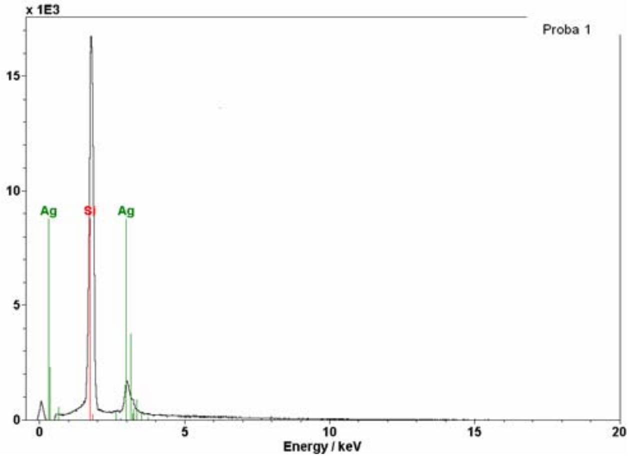
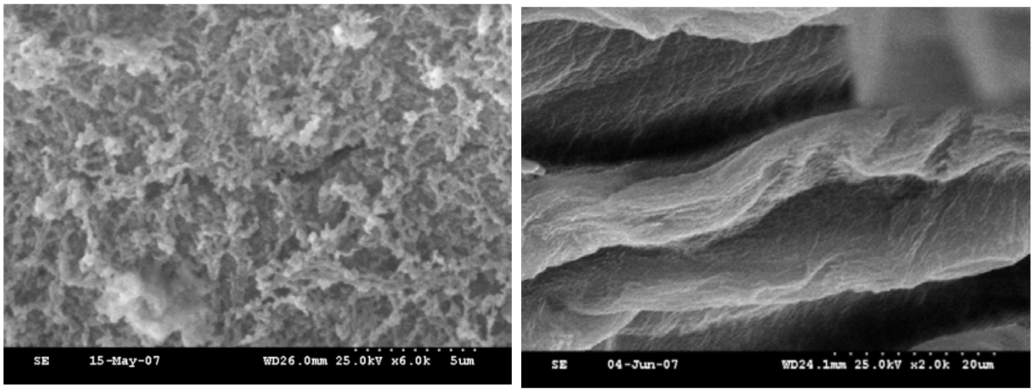


Fig. 4. EDX spectra of the calcinated sample

Visual insights of the microstructure of the calcined samples were obtained by Scaning Electron Microscopy (SEM). Typical SEM pictures of the silica obtained by template sol-gel polymerization of TEOS are presented in Fig. 5.



(a) (b)

Fig. 5. SEM micrographs of xerogel 1 (DBS, 1%, ethanol, 25°C) calcinated:a) 2h at 500°C , b) calcinated 2h at 200°C and subsequently 2 h at 500°C

The silica obtained by calcination at 500°C shows a condensed granular structure with a 300-500 nm average dimension of the grains (Fig. 5a). The general aspect of the material is a colapsed structure, indicating that the template was distroyed before the completion of TEOS polymerization which was adsorbed at the surface of the fibrils. The material obtained by the two steps thermal treatment (2 h at 200°C followed by 2h at 500°C) presents a fibrous structure with aligned fibrils with outer diameters of approx. 10μm (Fig. 5b).

4. Conclusions

Nanostructured silica were synthesized by sol-gel polymerization of TEOS mediated by three organogelators derived from D-sorbitol: 1,3 :2,4-bis-*O*-benzylidene-D-sorbitol, 1,3 :2,4-bis-O-*p*-nitrodibenzylidene-D-sorbitol and 1,3 :2,4-bis-O-*p*-aminodibenzylidene-D-sorbitol, respectively having benzylamine as co-catalyst. The resulting gels were vacuum evaporated and subjected to thermal analyses (DTA, TG, DTG) in order to establish the temperature and the optimum duration of thermal treatment. The structure of the resulted silica samples was assesed by scanning electron microscopy. Thick fibrils or entangled fibrous structure were observed besides normal granular silica.

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