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THIOETHER FUNCTIONALIZED HYBRID MATERIALS

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ABSTRACT

Thioether-functionalized materials were synthesized by co-condensations of bis[3-(triethoxysilyl)propyl]tetra sulfide (BTPTS) and tetraethoxylsilane (TEOS) in the presence of the nonionic surfactant triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) ($EO_{20}PO_{70}EO_{20}$), Pluronic P123. The surfactant was used as a template for improving the porosity of the hybrid gels. In this work we synthesized samples with different amounts of BTPTS in acidic media. The final materials were soaked for 24 hours in ethanol and HCl for removing P123. In this work we investigate structure of the materials and the functional group amount incorporated in the silica frame work after extraction of the surfactant. For this purpose we used thermo gravimetric analysis (DTA/TG), Fourier–transform infrared spectroscopy (FT-IR), ^{29}Si MAS NMR and element analysis.

On the bais of these results it was confirmed that the materials were organic inorganic hybrid materials and they are thermally stable to 900°C, which was the result of the incorporation of a hydrophobic thioester group in the silicate frame work.

Keywords: sol-gel, hybrid materials, surfactant.

INTRODUCTION

The mesoporous silica with high surface area, large pore volume and tunable pore size has attracted great research attention in the fields of catalysis, adsorption separation, etc. The incorporation of functional groups into mesoporous silica is the basis for their potential applications. The mesoporous silica, functionalized with organic groups, have been proved to be efficient adsorbents, acid-base catalysts, host materials for biomolecule and drug delivery. Generally, the grafting and co-condensation method can be used to prepare hybrid mesoporous silica containing the organic groups. Great success has been achieved for the synthesis of organic group functionalized mesoporous silica by employing these methods [1]. In the late 1990s, the appearance of periodic mesoporous organosilicas (PMOs) provides an alternative method for the synthesis of hybrid mesoporoussilica [2 - 4]. Because the PMOs are synthesized from bridged organosilane molecules $(RO)_3Si–R–Si(OR)_3$, (R = organic group), they exhibit the advantages of having amounts of incorporated organic groups and uniform distribution of organic groups, as compared with the hybrid mesoporous silica, synthesized by co-condensation and grafting. The content of organic groups is limited to less than 25 mol% for the hybrid mesoporous silica, synthesized with the co-condensation of $Si(OR)_4$ and $(RO)_3SiR$; the distribution of the organic groups is not uniform for the hybrid mesoporous silica, synthesized by the grafting method. In addition to the above mentioned advantages, the organic groups bridged in the mesoporous wall of PMOs can modify the chemical/physical properties of the PMOs as well as provide an opportunity to introduce other functional groups through

organic chemical transformations [1, 5]. This allows for the design of hybrid mesoporous silica with well defined functionality, flexibility, and intrapore surface properties, i.e. hydrophobicity/hydrophilicity, etc. [7 - 9]. The synthesis of thioether-bridged mesoporous materials with extensive void defects in the mesoporous channels defines their potential application as adsorbents for removal of Hg^{+2} and phenol from wastewater. Thioether ($-CH_2CH_2CH_2$-S-S-S-S-$CH_2CH_2CH_2$-) functionalities exhibit high adsorption affinity for heavy metal ions and hydrophobic alkyl chains of thioether functionality may provide not only extra anchoring sites for the adsorption of organic pollutants such as phenol, but also endow mesoporous materials with a high hydrothermal stability. The dependence of mesoporous structure and the hydrothermal stability of the mesoporous materials on thioether concentration in framework have been well established [10].

For synthes of large pore mesoporous organosilicas, Jain Liu et al. reported an example of structural control over the mesoporous organosilicas through co-condensation of bis[3-(triethoxysilyl)propyl]tetra sulfide, TESPTS and TMOS in the presence of a triblock copolymer template (P123) in an acetic acid/sodium acetate buffer solution (HAc-NaAc, pH 4.4). At low concentrations, the hydrophobic group in TESPTS can penetrate into the core of the surfactants. As a result the curvature of the interface can be adjusted by simply employing different amounts of TESPTS in the initial gel mixture. More specifically, large amounts of TESPTS can form emulations with P123 solutions during the synthetic process. Depending in the molar fraction of TESPTS, an ordered 2D hexagonal structure, a vesicle like structure, mesostructure cellular foams (MCFs), or a mixed phase of hexagonal/vesicle and MCFs/vesicle structures can be obtained. The latter material exhibit a bimodal pore structure [11]. Thioeher groups (-S-) are highly selective adsorbents for Hg^{2+} and are conveniently separated from wastewater [12]. Up to now there are not many papers about comparing these materials, before and after the extraction of the surfactant.

The aim of this paper is to investigate the structure of the materials and the amount of thioether organic groups incorporated in the framework after the P123 polymer extraction.

EXPERIMENTAL

Materials

Tri-block copolymer Pluronic P123, 1,4-Bis (triethoxysilyl) propanetetrasulfide (BTPTS, $(CH_3CH_2O)_3Si(CH_2)_3S$–S–S–$S(CH_2)_3Si(OCH_2CH_3)_3$), xylene, HCL and tetraethyl orthosilicate (TEOS) were purchased from Aldrich and used without further purification. All other chemicals used were of an analytical grade.

Preparation method

The precursor sols were prepared by the following procedures. A total of 1.2 g of P123and 3.5 g of potassium chloride were dissolved in 10 g of distilled water and 52 ml of 2M hydrochloric acid, and magnetically stirred at room temperature until complete dissolution to obtain a homogenous solution. Then 2.64 ml of xylene were added into the surfactant solution with stirring for 1 h followed by addition of 2.64 ml of TEOS and again stirring for 1 h. Then different quantities of the organosilane precursor (BTPTS) were added with continuous stirring at 40 ± 0.1°C for 1 h the resultant slurry was dried at 100°C for 24h, the surfactant was extracted by soaking 1.0 g of solid in 150 ml ethanol, containing 1.7 ml of concentrated HCl, at 50°C for 24 h.

Table1. Sample composition.

Sample	P123 [g]	HOH [ml]	KCl [g]	2M HCl [ml]	Xylene [ml]	TEOS [ml]	BTPTS [ml]
S1	1.2	10	3.5	52	2.64	2.64	1.16
S2	1.2	10	3.5	52	2.64	2.64	3.9
S3	1.2	10	3.5	52	2.64	2.64	7.8

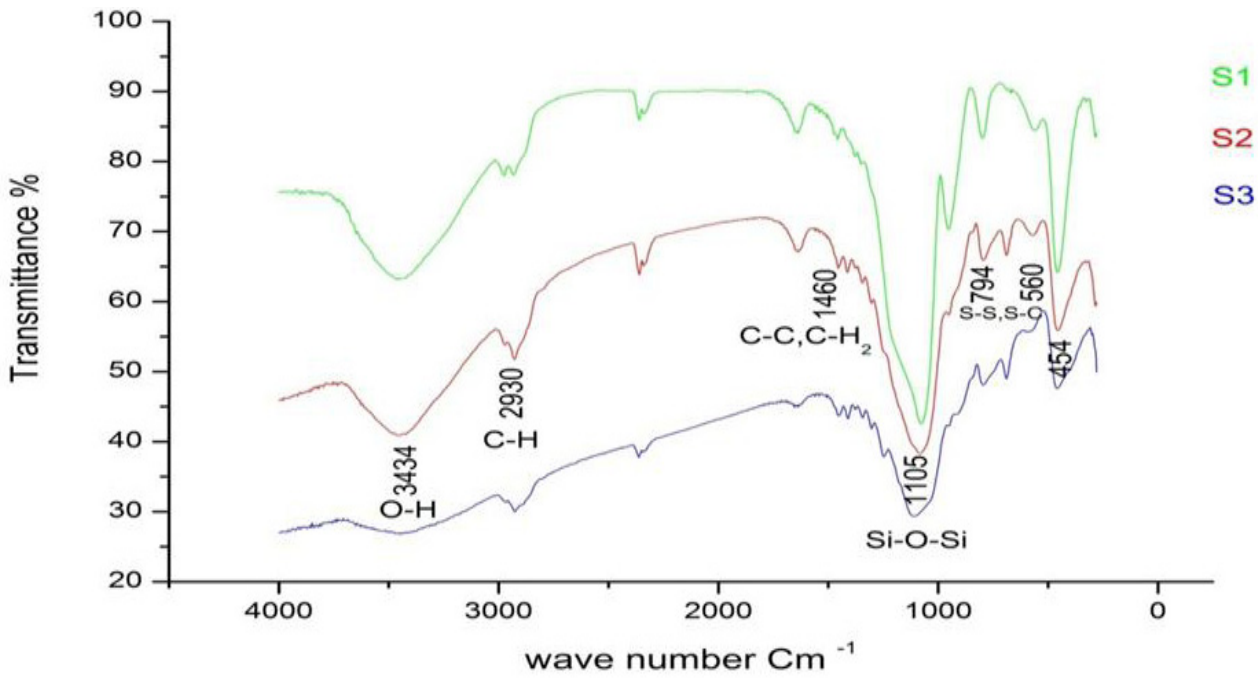

Fig. 1. Infrared spectrum of the samples after extraction, (S1, S2 and S3).

Characterization

The thermo gravimetric analysis (TGA) was performed on a PT1600 TG-DTA/DSC (STA Simultaneous Thermal Analysis) LINSESIS Messgerat Gmbh, Germany Instrument with a heating rate of 10°C min^{-1}, under a flow of air. Fourier-transformation infrared spectroscopy (FTIR) of KBr powder pressed pellets was recorded on (Varian 660-IR spectrometer). The sulfur content of the extracted samples was analyzed quantitatively by elemental analyses (Elemental analyzer SPA Euro Vector EA 3000). 29Si solid-state NMR spectra were recorded at 79.49 MHz on a (9.4 T) Bruker Avance 400 spectrometer. 29Si magic angle spinning MAS NMR spectra were measured with a 40 ms 1H 90º pulse, speed of rotation 50 kHz, and a delay of 60 seconds.

RESULTS AND DISCUSSION

The results from the FT-IR analyses are shown in Fig. 1. Common for all samples after extraction, are the bands around 1220, 1070, 794, and 471 cm^{-1}, assigned to the typical Si–O–Si stretching and bending vibrations of the condensed silica network and the peaks around 960 cm^{-1} corresponding to Si–OH groups [13, 14]. The presence of Si-OH group means that we have not achieved full condensation of the precursors. The broad band around 3400 cm^{-1} and the strong peak around 1630 cm^{-1} are due to the stretching and bending vibrations of adsorbed H_2O on the synthesized materials. The absorption peaks in the range 2900–3000 cm^{-1}, 1300–1500 cm^{-1}, and 520–720 cm^{-1}correspond to C-H, C-C and

Table 2. Elemental analysis of the samples after surfactant extraction.

Sample	Sulfur content(%)
S1	----------
S2	4.785
S3	7.909

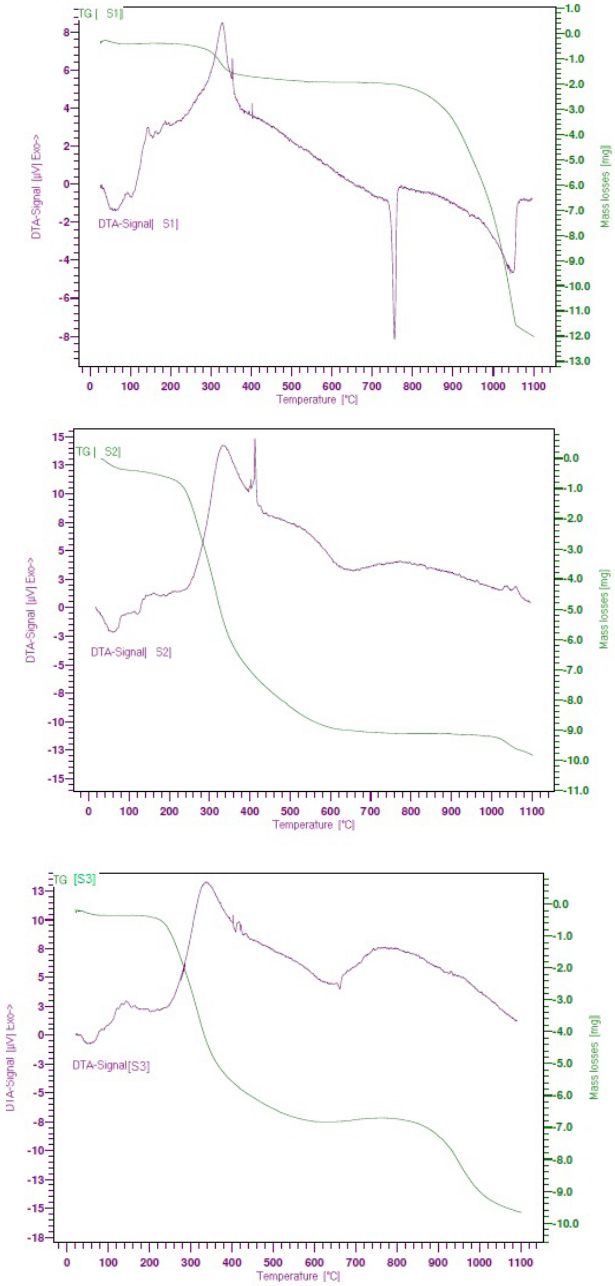

Fig. 2. TG and DTG Curves of the synthesized samples after extraction (S1, S2 and S3).

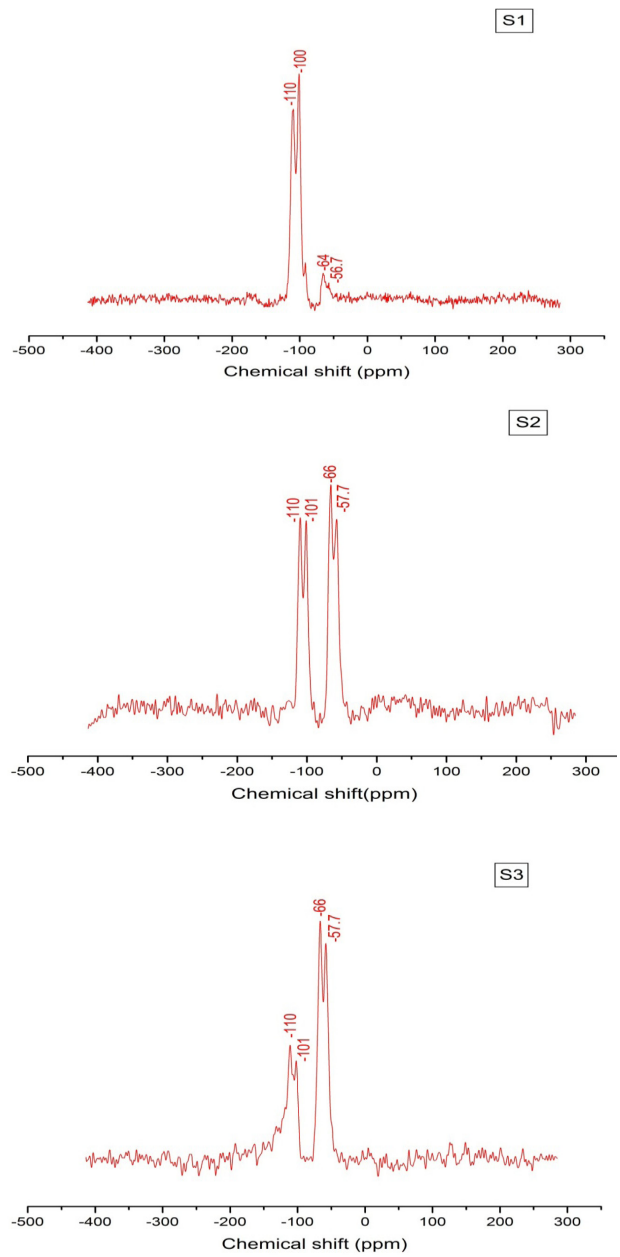

Fig. 3. ^{29}Si MAS NMR spectra of the samples after extraction (S1, S2 and S3).

CH_2, S–S and S–C, respectively. The appearance of this band confirms the incorporation of the organic precursor (BTPTS) in the inorganic silica framework [15]. The absorption peaks, typical for C-H, C-C and CH_2 groups, show the presence of a surfactant in the pores, i.e. - a not completed extraction of the surfactant P123.

In Table 2 are shown the results from elemental analysis. They suggest an increase of a sulfur in the synthsized samples after extraction of the copolymer. This means that there is no dissolving of sulfur during the extraction and with increasing the amount of precursor and the amount of sulfur, there is no saturation of sulfur.

The TG curves of the samples, after surfactant extraction, show 5 % mass loss at temperature lower than 100°C. This is attributed to the loss of a small amount of adsorbed moisture. The mass loss at the temperature

region 250-450°C is 14 %, mainly due to the decomposition of residual surfactant. In another study in the temprature region 500-700 °C the mass loss due to the decompostion of the organic group in the framework was reported, Fig. 2 [16].

The absence of mass loss in this temprature region in our DTA-TG curves proves that the synthesized hybrid materials show good thermal stability to 900°C. Above this temperature decomposition of the hybrid network occurs. Fig. 3 shows ^{29}SiMAS NMR spectra of the synthesized hybrid materials. The signals of -110 ppm and -101 ppm correspond to the resonances of $Si(OSi)_4$(Q4) and $(OH)Si(OSi)_3$ (Q3), respectively, implying a high degree of condensation between the precursors. These results confirm the results from the FT-IR analysis that also show the presence of Si-OH group at 960 cm^{-1}. The signals at -57 ppm and -66 ppm correspond to $(SiO)_2(OH)SiC$ .and $[(SiO)_3SiC]$, respectively [17]. These groups are typical for the organic precursor. The results again confirm the FT-IR results where absorption peaks, typical for the organic precursor and Si-OH groups appear as well.

CONCLUSIONS

Thermally stable hybrid thioether-bridged materials are successfully synthesized. This was confirmed by FT-IR and element analysis, which show the presense of organic and thioester group incorporeted in the final hybrid network.This confirms that our materials are organic-inorganic hybrid materials. The successful incorporation of the hydrophobic thioether group improves the thermal stabilty of the obtained organic-inorganic hybrid materials. The hydrothermal stability of the mesoporous materials is a result of the hydrophobic nature of the materials, derived from the thioether bridging in the framework. The element analyses show increasing of the sulfur content, after the extraction of the copolymer and also that saturation of sulfur with increasing the concentration of (BTPTS) in the composition of the sample, has not being reached.

Acknowledgements

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