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MESOPOROUS HYBRID MATERIALS IN THE SYSTEM (TEOS-BTPTS)

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Abstract

Polysulfide–functionalized mesoporous were synthesized by using co–condensations of tetraethoxylsilane(TEOS) and bis[3-(triethoxysilyl)propyl]tetra sulfide (BTPTS) in the presence of 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 template for improving the porosity of the hybrid gels. In this work we synthesized samples with different BTPTS amounts in acidic media. The final materials were soaked for 24 hours in ethanol and HCl for removing of P123. In this work we investigate the materials structure before and after extraction of the surfactant and the functional group amount incorporated in the silica framework. For this aims we used thermo gravimetric analysis (DTA/TG), Fourier–transform infrared spectroscopy (FT-IR), and elemental analysis.

Key words: *Sol-gel, Hybrid Mesoporous Materials*

1. 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 ,and separation et al. The incorporation of functional groups into mesoporous silica is the basis for their potential applications. The mesoporous silica functionalized with organic groups have been approved to be efficient adsorbents, acid–base catalysts, host materials for biomolecules,and the drug delivery.Generally, the grafting and co-condensation method could be used to prepare the 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 mesoporous silica [2–4]. Because the PMOs are synthesized from bridged organosilane molecules $(RO)_3Si–R–Si(OR)_3$ [R = organic group], they exhibit advantages of higher amounts incorporation of organic groups and uniform distributions of organic groups compared with the hybrid mesoporous silica synthesized using co-condensation and grafting method (the content of organic group is limited to less than 25 mol %for the hybrid mesoporous silica synthesized using the co-condensation of $Si(OR)_4$ and $(RO)_3SiR$, the distributions of the organic groups is not uniform for the hybrid mesoporous silica synthesized by 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 opportunity to introduce other functional groups through organic chemical transformation [1, 5] this allows for the design of hybrid mesoporous silica with well-define 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 mesoporius channels and their potential application as adsorbents to remove Hg^{+2} and phenol from waste water. 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 not only provide extra anchoring sites for the adsorption of organic pollutants such as phenol, but also endow mesoporous materials with high hydrothermal stability. The dependence of mesoporous structure and the hydrothermal stability of mesoporous materials on thioether concentration in framework have been established [10].

For synthesize large-pore mesoporous organosilicas, Jain liu and coworkers reported an example of structural control over 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, pH4.4). At low concentrations, the hydrophobic group in TESPTS can penetrate into the core of the surfactant 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 order 2D hexagonal structure, vesicle like structure, mesostructure cellular foams (MCFs), or a mixed phase of hexagonal/vesicle and MCFs/vesicle structure can be obtained. The latter material exhibit a bimodal pore structure [11]. Thioeher groups (-S-) show highly selective adsorbents for Hg^{2+} and were conveniently separated from waste water [12]. At this moment haven't reported so many paper about comparing this materials before and after extraction of the surfactant

The aim of the paper is to be investigated the structure of the materials befor and after P123 extraction, and also the thioether amount of organic group incorporated in the framework after the polymer extraction

2. **MATERIALS AND METHODS**

2.1. Materials

Tri-block copolymer Pluronic P123, 1, 4-Bis (triethoxysilyl) propane tetrasulfide (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 analytical grade.

2.2. Preparation method

The precursor sols were prepared by the following procedures. A total of 1.2 g of P123 and 3.5g of potassium chloride was dissolved in 10 g of distilled water and 52ml of 2M hydrochloric acid and magnetically stirred at room temperature till complete dissolving to obtain a homogenous solution. Then 2.64ml of Xylene was added into the surfactant solution with stirring for 1 h then 2.64ml of TEOS was added and also stirring for 1 h. Then different quantities of the organosilane precursor (BTPTS) were added with contentious stirring at 40 ± 0.1 °C for 1h. the resultant slurry was dried at 100 °C for 24h .the surfactant was extracted using an ethanol/HCL extraction method by soaking 1.0 g. of solid in 150ml ethanol containing 1.7 ml of concentrated 37% HCl at 50 °C for 24h.

Table (1) Sample composition

Sample	P123 [g]	HOH [ml]	KCl [g]	2MHCl [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

2.3. Characterization

The Thermo gravimetric analysis (TGA) was performed on PT1600 TG-DTA/DSC (STA Simultaneous Thermal Analysis) LINSESIS Messgerat Gmbh, Germany Instrument at a heating rate of 10 °C min-1 under a flow of air. Fourier-transform infrared spectroscopy (FTIR) of KBr powder pressed pellets was recorded on (Varian 660-IR spectrometer). The sulfur contents of the extracted samples were analyzed quantitatively by Elemental analyses on an (Elemental analyzer SPA Euro Vector EA 3000).

3. RESULTS AND DISCUSSIONS

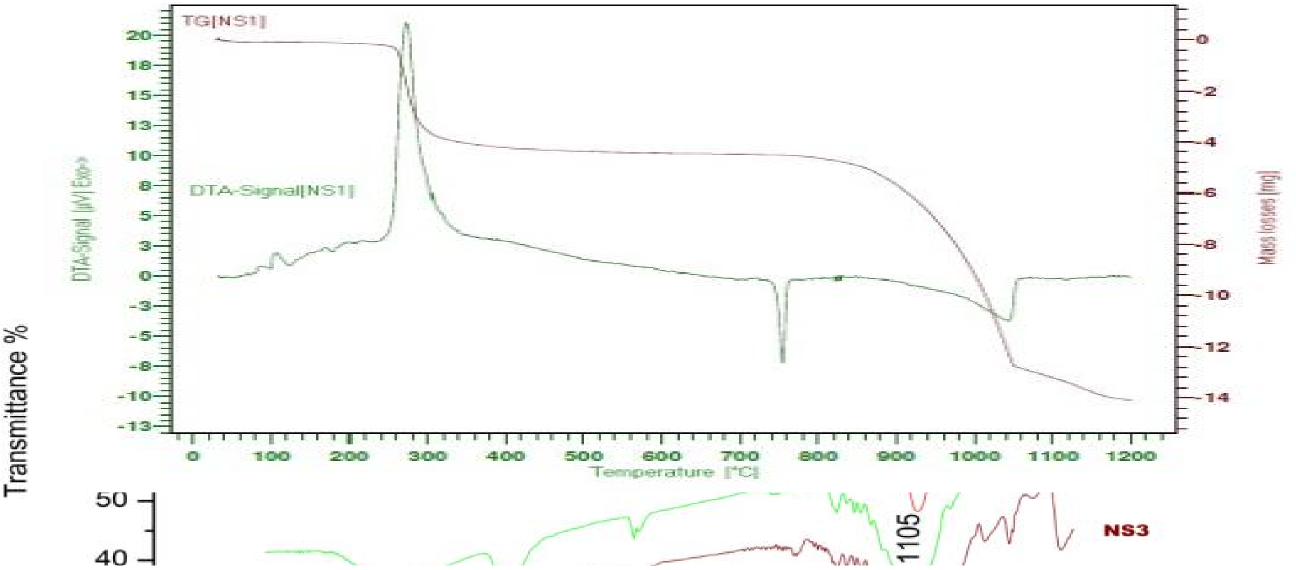
3.1. Characterization of tetra sulfide functionalized adsorbents

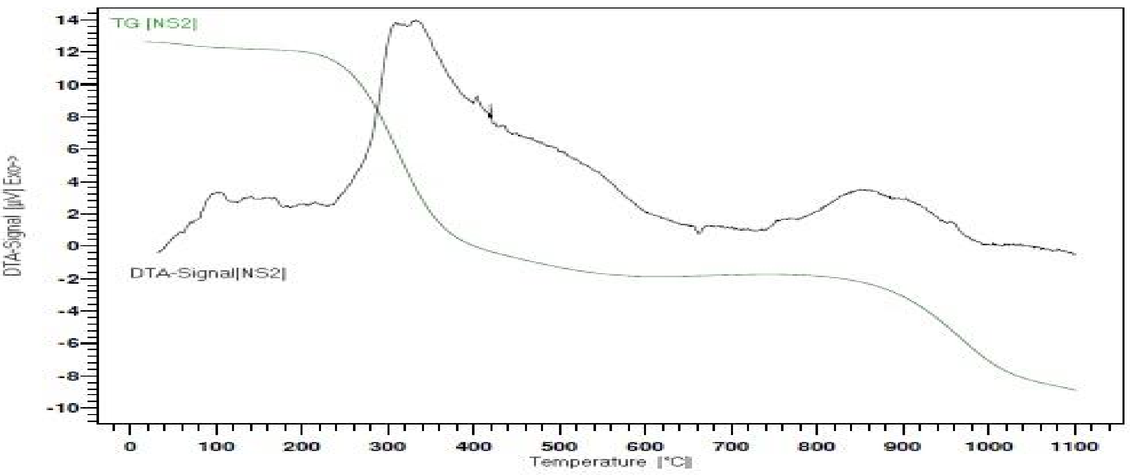
Common to all samples (before and after extraction) are the bands around 1220, 1070, 794, and 471 cm^{-1} assigned to the typical Si–O–Si stretching and bending vibrations of condensed silica network and the peaks around 960 cm^{-1} corresponding to non-condensed Si–OH groups [13, 14]. The broad band around 3400 cm^{-1} and the strong peak around 1630 $cm^{-}1$ are due to the stretching and bending vibrations of adsorbed H_2O. The absorption peak of C–H (2900–3000 cm^{-1}), C–C, C–H_2 (1300–1500 cm^{-1}), and S–S, S–C bonds (520–720 cm^{-1}) appears indicating that (BTPTS) has been successfully incorporated into the porous walls [15] (Figure.1).

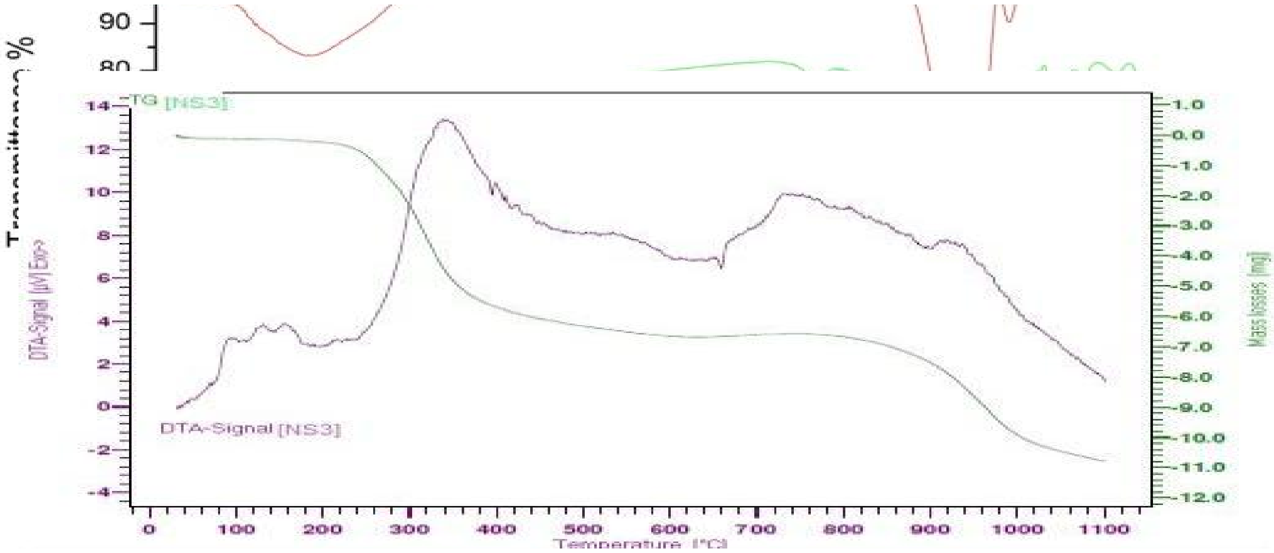
Elemental analysis show incresing of sulfur in synthsized samples after extraction of the copolymer this mean that we have not dissolving of sulfur during the extraction and also with increasing the amount of precursor increasing the amount of sulfur that’s mean there is no saturation of sulfur. The TG profiles (Figure 2&3) of the sample before and after surfactant extraction the 5% weight loss at temperature lower than 100 °C is attributed to the loss of small amount of adsorbed water. The weight loss at 250-450 °C decreased after the extraction of P123 for all sampls.Sample S1 in this tempruture region show weight loss 14% and the same sample befor extraction (NS1) is 28% is mainly due to the decomposition of copolymer surfactant.. in another papre was reported that in the temprature region (500-700 °C) aquir wegiht loss due to the decompostion of the organic groupin the framework [16]. The absent of weight loss in this temprature region in our DTA-TG spectra prove that the synthesized hybrid materials show good thermal stability. higher thermal stability to 900°C , above this temperature ocure decomposition of the hybrid network

Table (2) Elemental analysis of the samples b8efore and after surfactant Extraction

Sample	Sulfur content(%)	
	Before	After
S1	-------------	------------
S2	3.933	4.785
S3	4.692	7.909


TG[NS1]
DTA-Signal[NS1]
DTA-Signal [µV] Exo->
Mass losses [mg]
Temperature [°C]
20
18
15
13
10
8
5
3
0
-3
-5
-8
-10
-13
0
-2
-4
-6
-8
-10
-12
-14
0 100 200 300 400 500 600 700 800 900 1000 1100 1200
Transmittance %
50
40
1105
NS3


TG [NS2]
DTA-Signal[NS2]
DTA-Signal [µV] Exo->
Temperature [°C]
14
12
10
8
6
4
2
0
-2
-4
-6
-8
-10
0 100 200 300 400 500 600 700 800 900 1000 1100


Transmittance %
90
80
TG [NS3]
DTA-Signal [NS3]
DTA-Signal [µV] Exo->
Mass losses [mg]
Temperature [°C]
14
12
10
8
6
4
2
0
-2
-4
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
-12.0
0 100 200 300 400 500 600 700 800 900 1000 1100

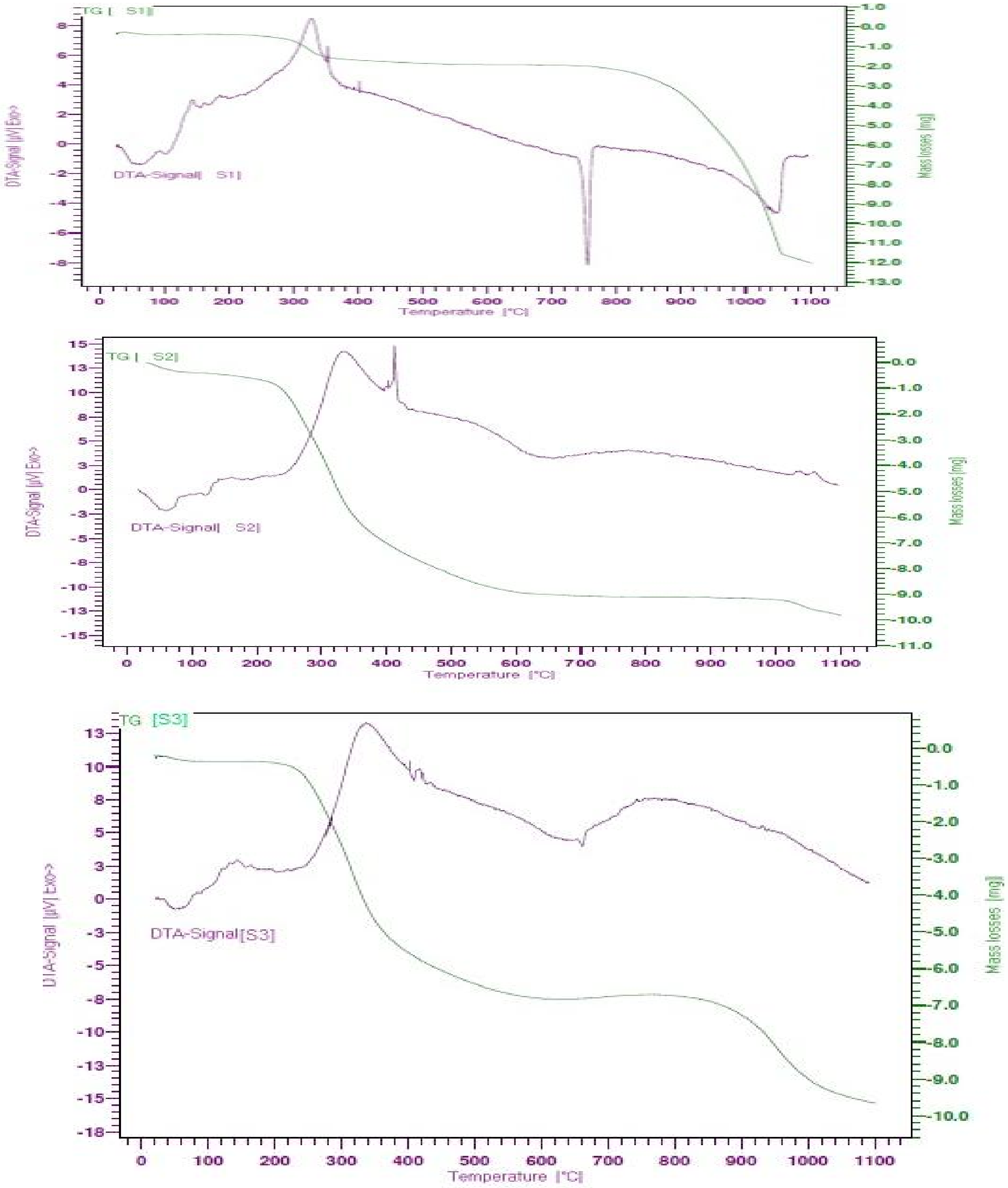


Figure (3) **TG** and DTG profiles of synthesized sample after extraction S1, S2and S3 respectively.

4. CONCLUSIONS

Sucseful was synthesized thermal stabel hybrid thioether-bridged materials. This was confirm by the FT-IR and Elemental analysis, they shows the presense of organic and thioester group incorporetd in the final hybrid network. The sucseful incorporation of the hydrophobic thioeter group improves the thermal stabilty of the obtained organic-inorganic hybrid materials. 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 thioether bridged group has been successfully incorporated in silica framework this confirm that our materials are organic-inorganic hybrid materials. The elemental analysis show increasing in sulfur content after extraction of the copolymer and also that have not saturation of sulfur with incresing the concentration of BTPTS in the composion of the sample.

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