Bulgarian Chemical Communications, Volume 47, Number 1 (pp. 276–282) 2015

Synthesis and characterization of poly sulfide-functionalized hybrid mesoporous silica

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Received December, 2014; Revised January, 2015

Poly sulfide-functionalized materials were synthesized by co- condensations of bis[3-(triethoxysilyl)propyl]tetrasulfide (BTPTS) and 1,2-bis(triethoxysilyl)ethane (BTESE) in the presence of the non-ionic 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. Samples were synthesized 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 investigated the influence of the BTPTS amounts on the structure and morphology of the materials after extraction of the surfactant. Samples were characterized by thermo gravimetric analysis (DTA/TG), Fourier–transform infrared spectroscopy (FT-IR), Nitrogen adsorption-desorption measurement (BET), Scanning electron microscopy (SEM), ^{13}C CP MAS NMR, ^{29}Si MAS NMR analysis and elemental analysis. The results from ^{13}C CP MAS NMR, ^{29}Si MAS NMR, and FT-IR showed that the materials are hybrid organic-inorganic materials. BET and SEM results showed that BTPTS amounts have a significant influence on the morphology and texture parameters of the final materials. the surface area and pore volume decreased by increasing BTPTS amounts; which make the hybrid network to be more flexible and resistant against degradation. DTA/TG results showed that, increasing the amount of BTPTS, the thermal stability of the gel materials decreased.

Key words: Hybrid material, Mesoporous, Template, Thioether bridging group.

INTRODUCTION

Development of organic–inorganic mesoporous hybrid materials is currently an area of extensive research, particularly with regard to potential applications such as adsorption, biotechnology, host–guest chemistry, chromatography, catalysis, sensor technology and gas storage [1–5]. The use of hybrid materials comprised of organic and inorganic building blocks aims to combine the advantages of both components within the solid, making possible production of materials with high mechanical, structural and hydrothermal stability of inorganic materials, with the flexibility and functionality typical of organic compounds. Many different precursors and synthetic routes have been used to prepare hybrid mesoporous materials [5, 6–11]. Organic chain bridging groups originating from methane, ethane, ethylene, as well as small organic aromatic ones such as thiophene, xylene, benzene and biphenylene have successfully been incorporated into the periodic mesoporous organosilicas (PMOs) [12]. The materials synthesize with thioether functionalized precursor exhibit high adsorption affinity for heavy metal ions [13]. Hydrophobic alkyl chains of thioether functionality may not only provide extra anchoring sites for the adsorption of organic pollutants such phenol, but also endow mesoporous material with high hydrothermal stability [8]. The presence of ethylene bridges in the framework has a high impact on the structure-adsorption characteristics properties of the final materials [14]. Properties and structures of the final mesoporous materials depend on synthesis conditions, such as temperature, acidity of the media, reagents and nature of organic groups as well as the homogenous distribution of organic groups in the silica framework [15]. In the meantime, the variability of PMOs was further extended by the construction of bi-functional PMOs through co-condensation reactions of either bridged bis-(trialkoxysilyl)-organo-silanes $[(R'O)_3Si–R–Si(O')_3]$ and terminal organotrialkoxysilanes $[(R'O)_3SiR'']$ in the presence of an appropriate structural directing agent (SDA),

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or by using a mixture of two or more bridged bis-(trialkoxysilyl) precursors which will co-condense also in the presence of a SDA. In the first case, the resulting bi-functional PMOs consist of a combination of bridging organic units and terminal organic units, their end groups inside the pores can be used for further chemical reactions. In the latter case, the PMOs consist of two (or more) different organic bridges that are incorporated within the framework of the pore walls [16]. On basis of the literature data our motivation is to synthesize bifunctional hybrid materials by co-condensation between BTPTE and BTESE precursors, and to study the influence of BTPTS on the structure and morphology characteristic of the final hybrid gel materials. Most of previous research presented the results about hybrid materials synthesized with low amount of BTPTS precursor [8, 13, 17, 18, 25, 28]. From a practical point of view it is interesting to investigate the influence of high concentration of BTPTS on the homogeneity and the final materials structure.

EXPERIMENTAL

Materials

Bis-[3-(triethoxysilyl)propyl]tetrasulfide BTPTS 90% $(CH_3CH_2O)_3Si(CH_2)_3S–S–S–S(CH_2)_3Si–(OCH_2CH_3)_3)$, and 1,2-bis(triethoxysilyl)ethane BTESE 96% $[-CH_2Si(OC_2H_5)_3]_2$, were purchased from Aldrich Were used as the bridged organosilica sources. Pluronic P123 $(EO_{20}PO_{70}EO_{20})$ (Mw=5800) (Aldrich), HCl (aqueous, 36%), KCl and Xylene and Ethanol were used as the structure-directing agent, acid source, pore improving, swelling agent and template extraction respectively all chemicals used without further purification.

Method of Preparation

The way of preparing of the samples was described in the previous work [19]. The samples were prepared as follow: 1.2 g of P123 and 3.5 g of KCl were dissolved in 10 ml of distilled water and 52 ml of 2M hydrochloric acid and then magnetically stirred at room temperature until complete dissolution to obtain a homogenous solution. 2.64 ml of Xylene were added into the surfactant solution with stirring for 1hour followed by addition of 2.64 ml of BTESE and again stirring for 1h. Finally, different quantities of BTPTS were added with continuous stirring at 40 ± 1 °C for 1h as shown in Table 1. The resultant slurry was dried at 100 °C for 24 h; the surfactant was extracted by soaking 1.0 g of the dried gel in 150 ml ethanol, containing 1.7 ml of HCl 36%, at 50 °C for 24h.The way of extraction of P123 was preferred than the knowing approaches in the literature [20, 21, 25, 30] because the approach save the organic functional group in the final materials [19].

Characterization

The thermo gravimetric analysis (TGA) was performed on (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 (FT-IR) 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). The morphology of the samples was observed by scanning electron microscopy (SEM) the images were recorded on a Hitachi S-4100 scanning electron microscope with an acceleration voltage of 15 kV. ^{13}C (100.61MHz) cross-polarization magic angle spinning (CP MAS) and ^{29}Si (79.49 MHz) MAS solid-state NMR experiments were recorded on a (9.4 T) Bruker Avance 400 spectrometer. The experimental parameters for ^{13}C CP MAS NMR experiments: 9 kHz spin rate, 5 s pulse delay, for ^{29}Si MAS NMR experiments: 5 kHz spin rate, 60s pulse delay. Pore size distributions were determined based on the Barrett-Joyner-Halenda (BJH) desorption curve [22].

Table 1. Samples composition of (M1, M2, M3 and M4)

Sample	P123 [g]	H_2O [ml]	KCl [g]	2M HCl [ml]	Xylene [ml]	BTESE [Mol%]	BTPTS [Mol%]
M1	1.2	10	3.5	52	2.64	75.4	24.6
M2	1.2	10	3.5	52	2.64	47.7	52.3
M3	1.2	10	3.5	52	2.64	38	62
M4	1.2	10	3.5	52	2.64	31.3	68.7

RESULTS AND DISCUSSION

FT-IR spectrum of samples in Fig. 1 showed the absorption bands at 3458 and 1635 cm^{-1} are assigned to OH groups due to the surface silanol groups and the remaining adsorbed water molecules. The band at 911 cm^{-1} is assigned to Si–OH stretching. The absorption bands at 2927 and 1411 cm^{-1} are assigned to CH_2 groups of BTPTS and BTESE or residual amounts of P123 after extraction [23]. A broad peak noted at 1105 cm^{-1} and 465cm^{-1}, due to the siloxane vibrations and bending vibrations of Si-O-Si groups [24]. The presence of –S–S– and –S–C– bonds are attributed to the vibration bands at 694 cm^{-1} and at 580 cm^{-1} respectively [25], indicating that BTPTS has been successfully incorporated into organic silica based framework.

Table 2 shows the elemental analysis. All samples have sulfur which confirms FT-IR analysis, by increasing the amounts of BTPTS the amounts of sulfur content increase and the co-condensation reaction with BTESE occurs successfully.

^{29}Si MAS NMR measurements are shown in Fig. 2. The signals at –58.5, –66.0 ppm are assigned as T^2 ((C–$Si(OSi)_2(OH)$)), and T^3 (C– $Si(OSi)_3$), respectively, [26]. Results strongly support the presence of Si-C in silica framework, also the absence of $Q^n[Si(OH)_4(OSi)_{4-n}]$ whose signals are usually observed in the range of –92 and –110 ppm, confirms that the C–Si bond cleavage of the BTESE and BTPTS precursors as material has not occurred during co condensation processes and the extraction process of P123 [27] . These results are in a good agreement with FT-IR analysis.

^{13}C CP MAS NMR analysis for sample M1 presented in Fig. 3. The resonances at 12.3, 22.6 and 42.5 ppm in the ^{13}C CP MAS NMR spectrum of sample M1 assign to the ^{1}C, ^{2}C, and ^{3}C carbon atoms of Si–$^1CH_2{}^2CH_2{}^3CH_2$–S–S–S–S–$^3CH_2{}^2CH_2{}^1CH_2$–Si, respectively [28], as tetrasulfide bridging groups are incorporated in the framework. The resonance at 5 ppm assign to ethane carbon atoms in BTESE [29],

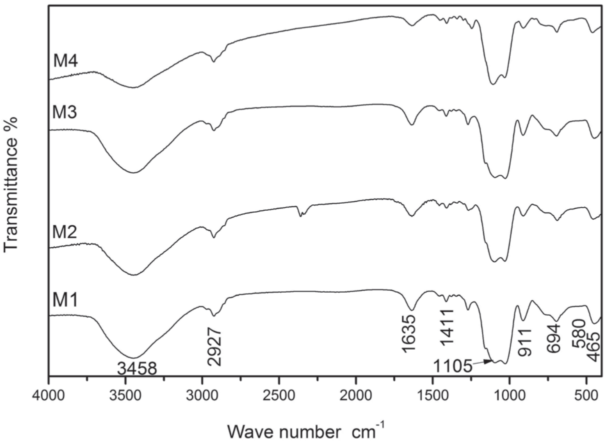

Fig. 1. Infrared spectrum of synthesized samples(M1, M2, M3 and M4)

Table 2. Elemental analysis of samples (M1, M2, M3 and M4)

Sample	Weight (mg)	Sulfur (Wt. %)
M1	1.18	1.47
M2	1.41	21.88
M3	0.70	23.40
M4	2.10	25.83

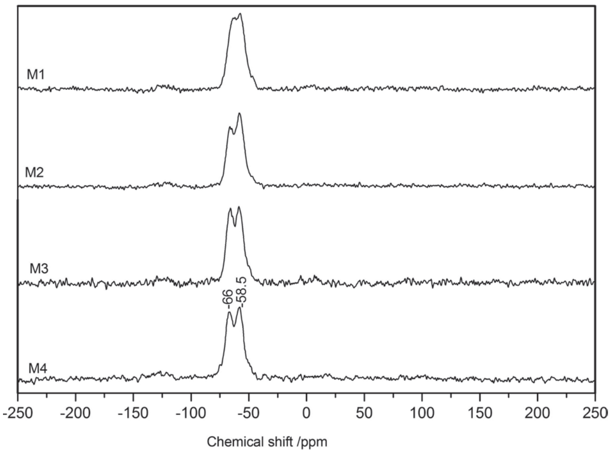

Fig. 2. ^{29}Si MAS NMR spectraof synthesized samples (M1, M2, M3 and M4)

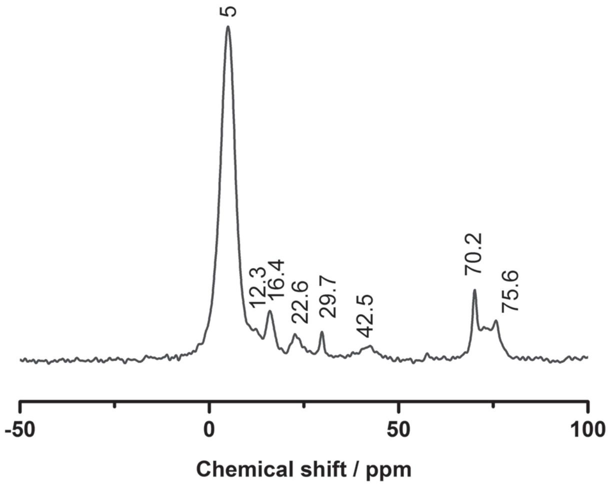

Fig. 3. ^{13} C MAS NMR spectra of the sample M1

which confirm the presence of both bridging groups in the hybrid materials and successful co-condensation process between BTESE and BTPTS. The resonance at 16.4 ppm is attributing to the side-chain carbons of methyl groups of P123, additionally; it could also be assign to carbons of ethoxy groups formed during surfactant extraction [30]. The signals at 70.5 and 75.6 ppm are due to the main-chain carbons of ethylene oxide (EO) and propylene oxide segments of P123 respectively, suggesting incomplete surfactant removal during the extraction process [12].

The thermo-gravimetric analysis was performed under air atmosphere. The weight loss below 150 °C is mainly due to the removal of physically adsorbed water from the materials Fig. 4. The weight loss decrease by increasing the BTPTS amounts. Decomposition of bridging organic group occurs between 300 and 600 °C [31]. Samples M1, M2, M3 and M4 show weight loss 25 wt.%, 42 wt.%, 45 wt.% and 47 wt.% respectively, the weight loss increases as a result of increasing amounts of tetrasulfide functionalized precursor which confirm the incorporation of tetrasulfide organic functional group in silica framework at high BTPTS amount. Weight loss is observed above 600°C, may be attributed to the combustion of residual organic material and/or to the desorption of water resulting from silanol condensation [23].

The N_2 adsorption–desorption isotherms of the materials are presented in Fig. 5. According to IUPAC classification the hysteresis can be clas-

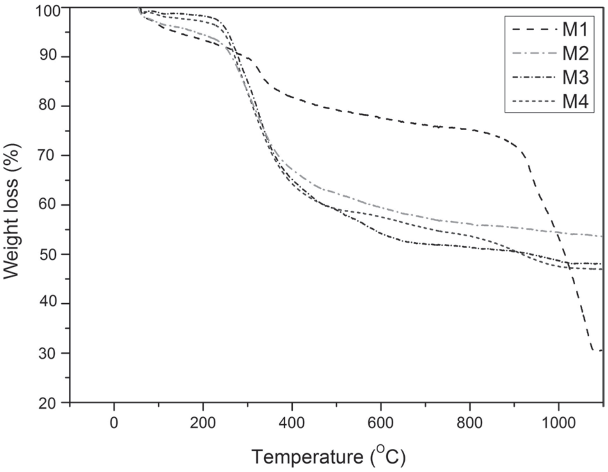

Fig. 4. DTG profiles of synthesized samples (M1, M2, M3 and M4)

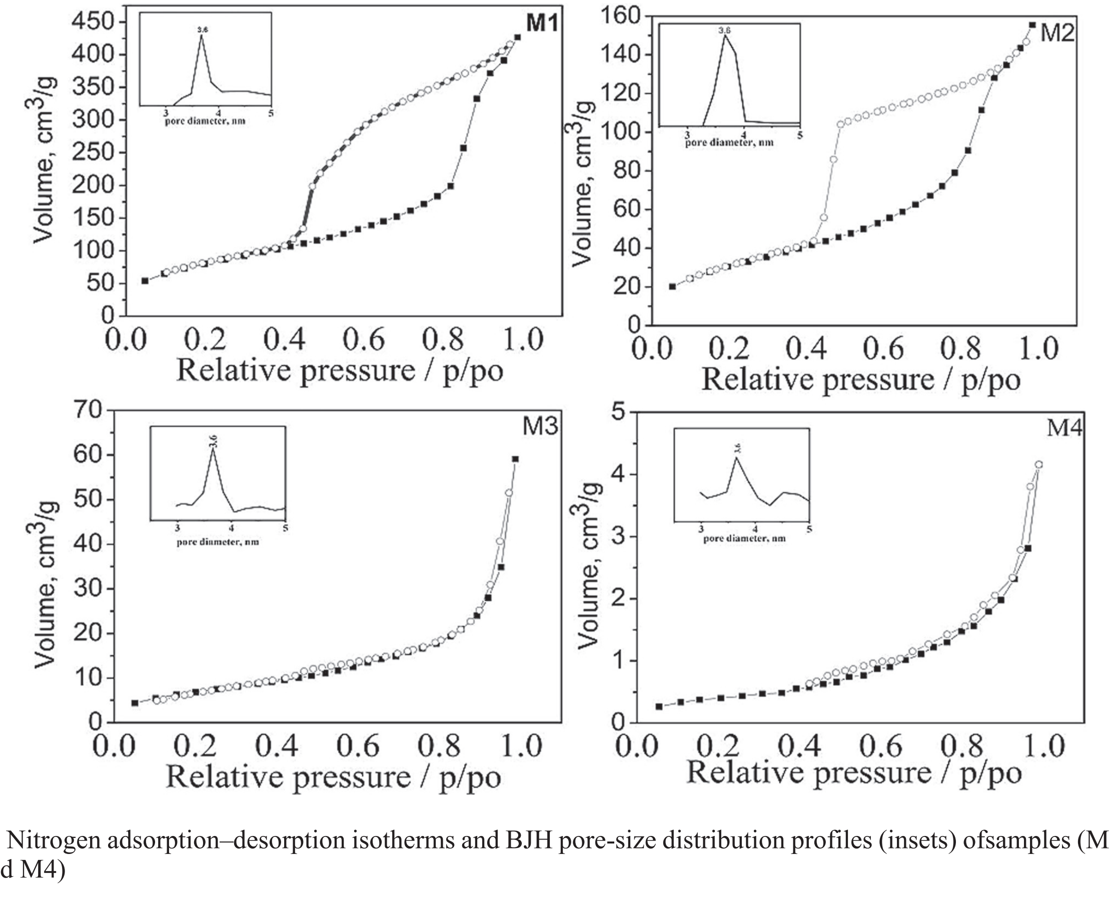

Fig. 5. Nitrogen adsorption–desorption isotherms and BJH pore-size distribution profiles (insets) ofsamples (M1, M2, M3 and M4)

Table 3. Physical and textural properties ofsamples (M1, M2, M3 and M4)

Sample	S_{BET} [m^2/g]	V_{total} [cm^3/g]	$D_{average}$ [nm]
M1	294	0.61	3.7
M2	114	0.22	3.7
M3	26	0.05	3.7
M4	2	0.005	3.6

sified as type IV which is typical for mesoporous structure. Sample M1 and M2 show hysteresis loop type H2 which is typical for ink bottle like pores. The type of hysteresis loop of sample M3 and M4 is H3 characteristic for slit like pores [32]. These results show that increasing the BTPTS amount lead to changes in the pore shapes. The textural parameters are shown in Table 3. By increasing the content of tetrasulfide functionalized precursor occur significant changes in surface area and pore volume, whereas the pore size for all samples almost the same. This can be explained by the flexibility of the silica network with increasing the amount of BTPTS, which prevent the hybrid framework from collapse during the surfactant extraction and during the drying process. The presence of residuals amount of P123 in the pores which was confirm by ^{13}C CP MAS NMR is the main reason for the close values of the pore size.

SEM images of samples presented in Fig. 6 display homogenous structure. The images show significant change in the morphology of the materials with increasing amount of BTPTS. Sample M1 shows particle like structure with particle size between 100–200 nm. Sample M2 shows the formation of smoother surface with particle size around 300 nm. Sample M3 shows particles aggregate with size around 500 nm. Sample M4 shows the smoothest surface than the other. These results confirm the results from BET analyses which show the decreasing of the textural characteristic with increasing the BTPTS amount.

CONCLUSION

Co-condensation reaction with high amount of BTPTS precursor are carried out successfully and the materials are homogeneous, the synthesized gels are tetrasulfide functionalized organic-inorganic hybrid mesoporous materials. The presence of the bands at 694 and 580 cm^{-1} in FT-IR spectra confirm the

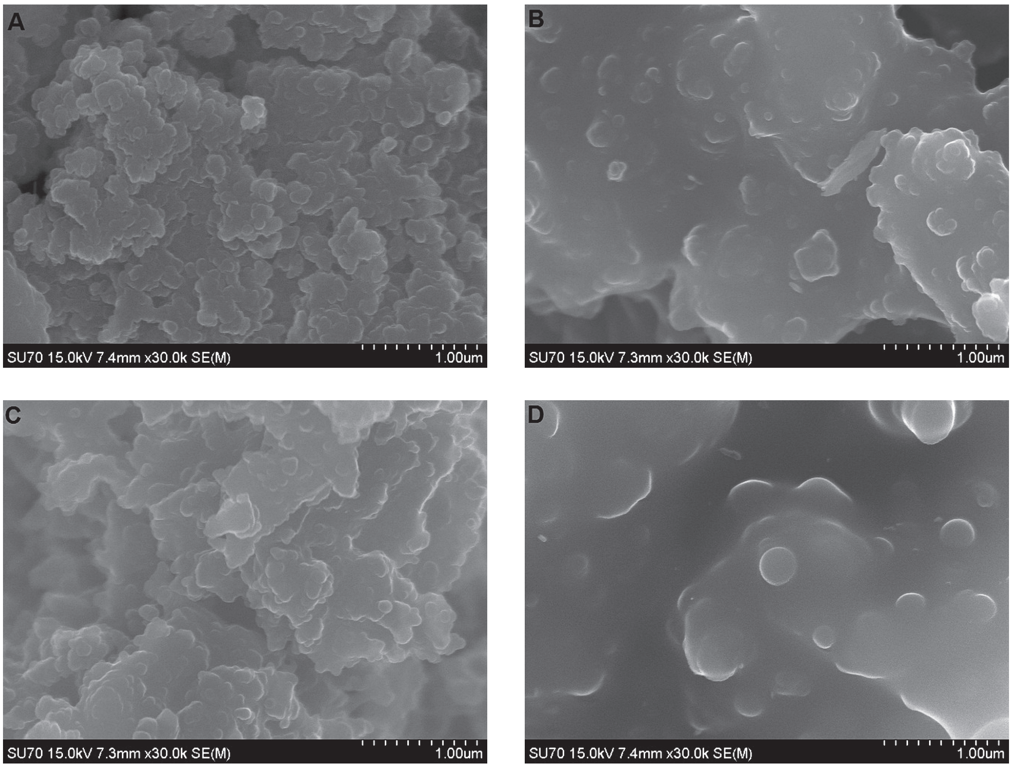

Fig. 6. SEM images of samples (M1, M2, M3 and M4)were A=M1, B=M2, C=M3, D=M4

incorporation of sulfur in the final hybrid structure and also the bands at 2927 and 1411cm^{-1} confirm the incorporation of bridging groups in silica network without occurrence decomposition during drying and extraction processes. ^{13}C CP MAS NMR confirms the presence of the bridging groups CH_2-CH_2 and –CH_2-CH_2-CH_2-S-S-S-S-CH_2-CH_2-CH_2– from both precursors in the final structure. Surface of gels become smoother, by increasing BTPTS amounts, surface area and pore volume decrease and pore size almost the same. The shape of the pores is changing from type H2 typical for ink-bottle to H3 typical for slit-like shape. These observed changes are result of increased flexibility of the final hybrid network with the increasing the amount of BTPTS. The final hybrid materials show characteristic applications as adsorbent of organic pollutants and days from waste water.

Acknowledgements: *This study was financially supported by the Erasmus Mundus MEDASTAR (Project Number: 2011-405/001-002-EMA2). And the silicate technology department of the University of Chemical Technology and Metallurgy Sofia, Bulgaria.*

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СИНТЕЗ И ХАРАКТЕРИЗИРАНЕ НА ПОЛИСУЛФИД ФУНКЦИОНАЛИЗИРАНИ ХИБРИДНИ МЕЗОПОРЕСТИ СИЛИЦИЕВО-ДИОКСИДНИ МАТЕРИАЛИ

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Постъпила декември, 2014 г.; приета януари, 2015 г.

(Резюме)

Синтезирани са полисулфид функционализирани материали чрез съкондензация на бис[3-(триетоксисилил) пропил]тетрасулфид (BTPTS) и 1,2-бис(триетоксисилил)етан (BTESE), в присъствие на нейонно повърхностно активно вещество (ПАВ) триблок съполимер полиетилен гликол-блок-полипропилен гликол-блок-полиетилен гликол ($EO_{20}PO_{70}EO_{20}$), Pluronic P123. ПАВ е използвано като шаблон за подобряване порестостта на хибридните гели. Образците са синтезирани с различни количества BTPTS в кисела среда. Крайните материали са накиснати за 24 часа в разтвор на етанол и HCl за отстраняване на Pluronic P123.

В настоящата работа ние изследваме влиянието на количеството на BTPTS прекурсора върху структурата и морфологията на материалите след екстракция на ПАВ. Образците са охарактеризирани с Диференциално термичен и Термогравиметричен анализи (DTA/TG), Инфрачервена спектроскопия с Фурие трансформация (FT-IR), Азот адсорбционно–десорбционен анализ (БЕТ), Сканираща електрнна микроскопия (СЕМ), Ядрено магнитен резонанс на ядра ^{13}C (^{13}C CP MAS NMR) и ^{29}Si (^{29}Si MAS NMR) и елементен анализ. Резултатите от ^{13}C CP MAS NMR, ^{29}Si MAS NMR и FT-IR показаха, че материалите са хибридни органо-неорганични. БЕТ и СЕМ резултатите показаха, че количеството на BTPTS оказва съществено влияние върху морфологията и стойностите на текстуралните характеристики на крайните материали. Стойностите на свободната повърхност и обемът на порите се понижават с повишаване количеството на BTPTS прекурсора, придаващ на хибридната мрежа по-голяма гъвкавост и устойчивост на разрушаване. Резултатите от DTA/TG показаха, че с повишаване количеството на BTPTS термичната стабилност на гелните материали се понижава.