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EFFECT OF FUNCTIONALIZATION CONDITIONS ON LOADINGS OF 3-(TRIMETHOXYSILYL)-1-PROPANOLTHIOL IN HEXAGONAL MESOPOROUS SBA-15

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Abstract. Thiol-functionalized SBA-15 silicas have been directly synthesized by co-condensation of tetraethyl orthosilicate (TEOS) and 3-(trimethoxysilyl)-1-propanolthiol (TSPT) under hydrothermal condition. Mesoporous structure was obtained after the surfactant removal by Soxhlet and reflux ethanol extraction. These materials were characterized by means of powder X-ray diffraction, isotherms of nitrogen adsorption/desorption, thermal analysis, infrared spectroscopy and energy-dispersive X-ray spectroscopy. The initial molar ratio of TEOS to TSPT, the time of adding TSPT to synthesize gel and the Soxhlet and reflux ethanol extraction to obtain thiol-functionalized SBA-15 silicas with high thiol content and highly ordered hexagonal mesostructure were discussed.

1 Introduction

Ordered nanoporous organosilicas constitute a very exciting field in materials chemistry and have numerous potential applications due to their high surface areas, large pore volumes of ordered mesopores and narrow pore size distributions as well as the possibility of easy functionalization [1]. Among them, the SBA-15 materials have become one of the most popular ordered silica nanomaterials due to large mesopores (up to 15 nm), thicker pore walls, presence of irregular interconnecting micropores and higher thermal and hydrothermal stabilities caused by their thicker mesopore walls [2]. SBA-15 materials are synthesized by hydrolysis and condensation of silica precursor under strong acidic conditions by employing the amphiphilic triblock copolymer (usually Pluronic P123) followed by removal of polymeric template by either extraction or calcination at elevated temperatures. Possibility of introduction of different functional groups into the framework or the surface of ordered mesoporous silicas make these materials very attractive for catalytic and adsorption processes, sensing devices and environmental applications [3]. Such hybrid materials are known as ordered mesoporous organosilicas. Such a surface functionalization leads to the materials

differing in the reactivity, pore accessibility and distribution of organic groups. It is particularly important when adsorption applications are considered, especially from the water systems. Among all the surface modifications, thiol-functionalized mesoporous silica [4] has much application potential. Liang and co-workers [5] have reported its wide availability and high capacity to fix Pb^{2+} and Cd^{2+}. Thiol groups can also be incorporated and used to synthesize carbon replicas of the silicas [6].

These groups can be included by post-synthetic grafting or by co-condensation during synthesis. In post-synthetic grafting, a pre-calcined mesoporous silica, partially re-hydrated to generate surface hydroxyls, is reacted with the appropriate alkoxysiloxane, whereas co-condensation involves the addition of both tetraethyl orthosilicate (TEOS) and the functionalised siloxane $(MeO)_3$–Si–X to the synthesis mixture.

In the present work, thiol-functionalized SBA-15 was prepared through co-condensation. The effect of solvents and time of extraction on the removal of template from thiol-functionalized SBA-15 were also discussed.

2 Experiments

Organically-modified molecular sieves were prepared by the co-condensation of trialkoxysilanes and tetraethyl orthosilicate. The general procedure adopted was similar to that reported for SBA-15 [7]. The non-ionic triblock copolymer Pluronic P123 (EO20–PO70–EO20, M_W: 5800; Aldrich) was used as a template and tetraethyl orthosilicate (TEOS, 98% Aldrich) was the silica source. 3-(trimethoxysilyl)-1-propanolthiol (TSPT), $(MeO)_3Si(CH_2)_3SH$ (95%, Merck) was added at molar ratio of Si to S in the range from 19-5.75. The surfactant was dissolved in the hydrochloric acidic media and stirred at 313K. TEOS and TSPT were added simultaneously and the mixture stirred for 24h for the mesostructure formation to take place. Finally the mixture was transferred to a Teflon bottle and hydrothermal treatment applied at 373K for 24h enabling further condensation of the silica framework. The resulting solids were filtered. The samples were denoted as-synthesized SBA-15-SH(x) with x being 19, 11.5, 8.25 and 5.75 implying as molar ratio of TEOS/TSPT. The general procedure was similar to that mentioned above. The molar ratio of TEOS/TSPT was remained at 5.75 while the TEOS is allowed to prehydrolyze for determined minutes. After time spans (t=0, 5, 10, 20, and 30 minutes) since TEOS and P123 were mixed, TSPT was added to synthesize gel. These samples were denoted as as-synthesized SBA-15SHt with t being 0, 5, 10, 20 and 30 minutes.

The template removal from as-synthesized SBA-15SH30 was conducted by Soxhlet ethanol extraction. The part of as-synthesized SBA-15SH30 sample was placed into Soxhlet apparatus and extracted with ethanol for 24, 48 and 72h. The template-removed samples were denoted as extracted SBA-15SH(5.75) and SBA-15SH(8.25)

with the numbers in blanket implying the ratio of TEOS/TSPT in initial synthesized gel.

X-ray diffraction (XRD) patterns were recorded on VNU-D8 Advance Instrument (Bruker, Germany) using Cu Kα radiation (λ = 1.5418Å). N_2 adsorption desorption isotherm measurement was performed at 77K with a surface area and porosimetry analyzer (Ommisorp-100) in the relative pressure (P/P_0) range from about 10^{-3} to 0.99. Samples were degassed at 250^0C for 2h before setting the dry mass and data collection. Specific surface areas are calculated using the Brunauer–Emmett–Teller (BET) model. Pore size distributions are calculated using the BJH model on the adsorption branches. Thermal behaviors of samples were conducted by thermal analysis (TG-DSC) using Labsys TG/DSC SETARAM. Transmission electron microscopy (TEM) micrographs used JEOLE-3432 operating at 80 keV. Infrared spectra (IR) were recorded on a FT-IR spectrometer using IR-Prestige-21(SHIMADZU) in KBr matrix in the range 4000–400 cm^{-1}. Elemental analysis of S and Si was conducted by Energy-dispersive X-ray spectroscopy (EDX/SEM) using JED-2300, JEOL.

3 Results and discussion

Fig. 1 presents X-ray diffraction patterns of the as-synthesized thiol functionalized SBA-15 with different molar ratios of TEOS/TSPT. All the samples have a single intensive reflection at 2θ angle around 0.8^0 as in the case for typical SBA-15 materials and the reflection is generally related to a regular pore size and an ordered pore arrangement [7]. The (110) and (200) reflections decrease gradually in intensity as the relative amount of TSPT in the initial mixture increases, which indicates a decrease of the ordering hexagonal. The broad peak of (100) and low intensity indicate the very poor hexagonal mesostructure as the molar ratio of TEOS/TSPT changed up to 5.75.

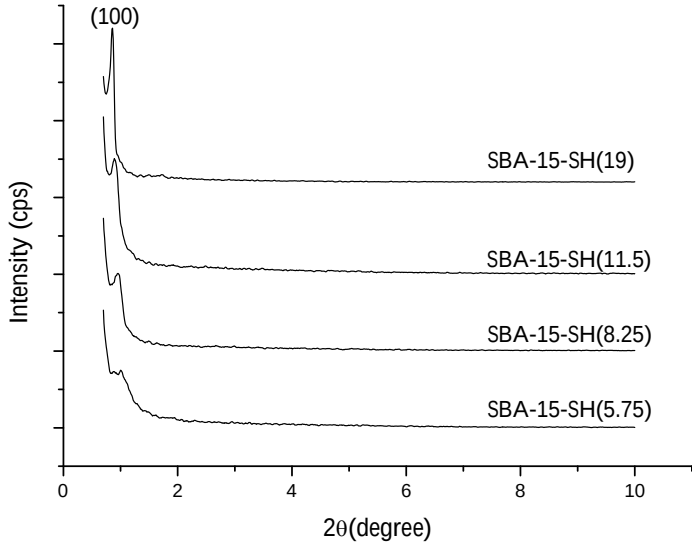


Fig. 1. *XRD patterns of as-synthesized thiol functionalized SBA-15 with different molar ratio of TEOS/TSPT.*

It is clear that the simultaneous addition of TSPT and TEOS to synthesized gel results in a decrease in hexagonal mesostructure. The question rises is that if the TEOS is allowed to prehydrolyze a suitable time and TSPT is added latter, then quality of thiol functionalized SBA-15 including thiol content and hexagonal ordering may be improved.

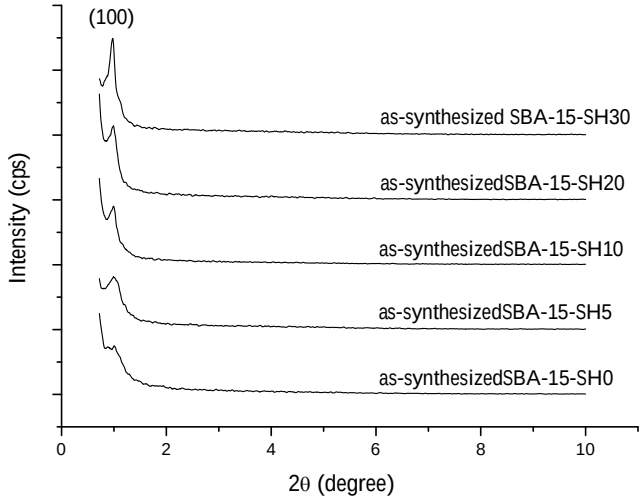


Fig. 2. *XRD patterns of as-synthesized thiol funtionalized SBA-15 with different times of addition of TSPT to synthesized gel.*

Fig. 2 shows XRD patterns of as-synthesized thiol functionalized SBA-15 with different time spans of adding TSPT to synthesized gels. As can be seen, the intensity of peak (100) characteristic for mesostructure increases with the time of TEOS prehydrolyzation. The reason why needs further study. After 30 minutes of TEOS prehydrolization, the addition of TSPT to synthesized gel was favorable for the formation of highly ordered hexagonal mesostructure. The sample with initial molar ratio of TESO/TSPT=5.75 which was synthesized under condition of TEOS prehydrolyzation for 30 minutes was used for the study of the template removal.

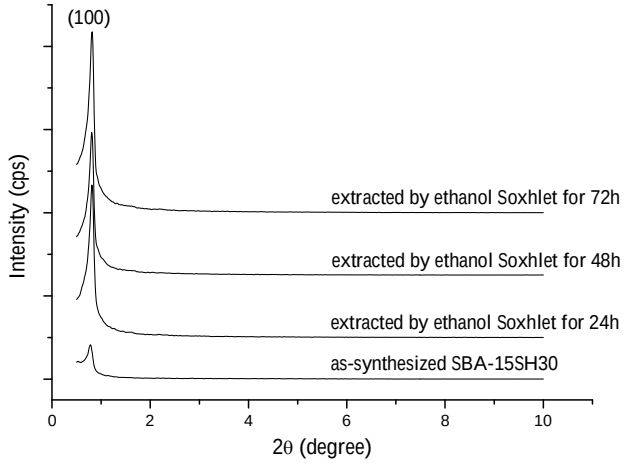


Fig. 3. *XRD patterns of as-synthesized thiol functionalized SBA-15 and thiol functionalized SBA-15 extracted by ethanol Soxhlet.*

Fig. 3 shows XRD patterns of thiol functionalized SBA-15 from which the template was removed by the extraction of ethanol soxhlet. It can be seen that the d_{100} value of 10.8 nm for extracted SBA-15SH30 decreases in comparison with that of 11.3 nm for as-synthesized SBA-15SH30 indicating that the removal of template may cause the shrinkage of hexagonal cell. The prolonged extraction time led to increase remarkably the intensity of peak (100) which is characterized for mesoporous hexagonal structure, both d_{100} of sample extracted for 48 and 72 hours are the same, suggesting that the extraction progress could end at 48 h.

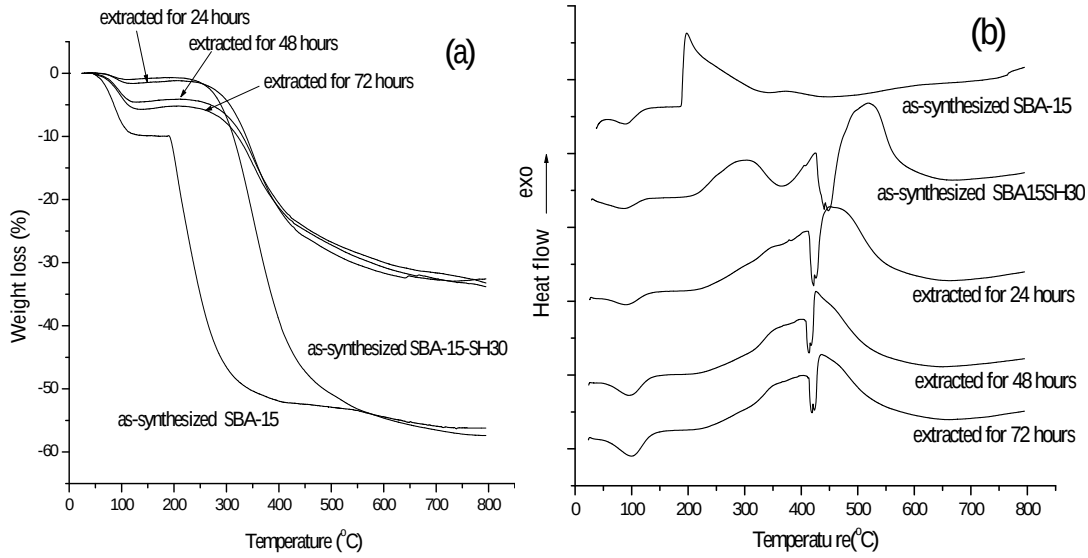


Fig. 4. *(a). TG curves and (b) DSC curves of as-synthesized SBA-15, as-synthesized thiol functionalized SBA-15 and thiol functionalized SBA-15 extracted by ethanol Soxhlet.*

The introduction of thin groups into SBA-15 is confirmed by the results of TG-DSC. As seen from Fig. 4, for the as-synthesized pure SBA-15 materials, a weight loss of about 2.3 wt.% is observed at a temperature lower than 120^{o}C, which is due to the evaporation of adsorbed water (or ethanol), and the further weight loss (about 43.7 wt.%) at temperatures higher than 180^{o}C and less than 300^{o}C corresponding to large exothermic peak around 210^{o}C is attributed to the surfactant decomposition. For the as-synthesized thinly functionalized SBA-15, the broad exothermic peak should be attributed to surfactant decomposition while endothermic peak at 450^{o}C and exthothermic peak at 500^{o}C is attributed to decomposition of silanol grounds to form siloxan and thiol groups. Total weight loss is around 56.4 %. Besides the weight loss due to adsorbed water at 100^{o}C, the extracted functionalized samples lost weights in one step at 350^{o}C (approximately 30%), which corresponds to the loss of thiol groups. The fact that the shapes of TG-DSC for samples extracted for 48 and 72 hours are similar further confirms the extraction progress ending after 48 hours. The result of elemental analysis by EDX indicates the existence of thiol groups in the functionalized materials, and the ratio of TEOS/TSPT estimated by elemental analysis is 8.07 higher than that of 5.75 in the initial mixture which might result from the effect of the surfactants left after

the Soxhlet treatment. The content of TSPT incorporated to silica framework SBA-15 in the present work is rather high in comparison with other works [8].

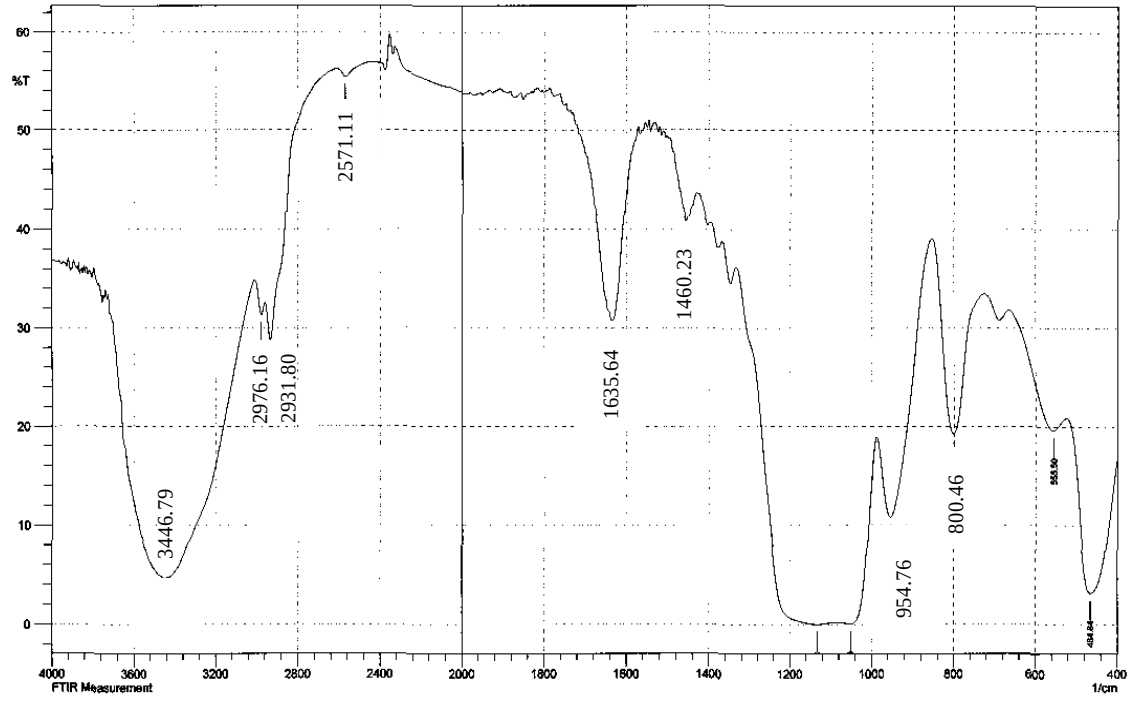


Fig. 5. *IR spectrum of SBA-15-SH30 sample*

The existence of thiol group is further confirmed by IR spectrum. The FT-IR spectrum of SBA-15-SH30 sample is shown in Fig. 5. A weak vibration band observed at 2571 cm^{-1} is assigned to the S–H stretching vibration. The sharp absorption band at 3446 cm^{-1} is attributed to stretching of O–H on the surface silanol groups with hydrogen bond and the remaining adsorbed water molecules. The absorption bands at 2976 and 2931 cm^{-1} are ascribed to the asymmetric stretching and symmetric stretching of (–CH_2–), respectively, while the absorption 1460 cm^{-1} to the bending of (–CH_2–) group. The absorption bands at 1051 and 800 cm^{-1} are due to Si–O–Si and Si–O stretching vibrations, respectively. The band at 954 cm^{-1} is assigned to Si-OH stretching [5]. The adsorption band at 1635 cm^{-1} is due to deformation vibrations of adsorbed water molecules ($\delta_{H–O–H}$).

The mesoporous ordered hexagonal structure is further confirmed by isotherms of adsorption/desorption for nitrogen. The isotherms of the functionalized SBA-15, extracted SBA-15SH(5.75) and extracted SBA-15SH(8.25) are shown in Fig. 6. It can be seen from Fig. 6 that all the samples exhibit type IV isotherms with apparent hysteresis loop, indicative of the existence of defined mesopores in the frameworks. The adsorbed amount at the saturated pressure decreases as the concentration of TSPT increases, indicating that the more content of TSPT is incorporated, the lower porosity may be obtained. The capillary nitrogen condensation step shifts gradually to lower vapor pressure with the higher TSPT content, which is related to the decrease of the

mesopore diameter. The textural properties of samples were presented in Table 1. The pore diameter ranging from 5.0 nm to 6.4 nm and dependent on the relative content of TSPT, which is consistent with what is implied in the isotherms. As shown in Table 1, the surface area decreases dramatically from 587 to 543 m^2 g^{-1} and pore volume from 0.65 to 0.57 cm^3 g^{-1} as the molar ratio of TEOS/TSPT decrease from ∞ to 5.75. The decrease of pore structure with the addition of thiol groups can be described as follows. The methoxy terminal of TSPT may co-condense with TEOS to form inorganic framework and the mercaptopropyl branch may react with the hydrophilic groups of P123 template via H-bonding to form an organized structure. Upon removal of P123 template, the mercaptopropyl chains may rearrange to act as linked organic functionalities protruding from the inorganic walls into the pore channels [9], thus resulting in the occupation of space inside the pore and the gradual increase of pore wall thickness. The more TSPT content is introduced, the more pore space may be packed and the smaller pore diameter can be obtained. The evolution of pore structure might also result from the co-surfactant effect of TSPT, which interacts with the templates and reduces the diameter of the micelles [10].

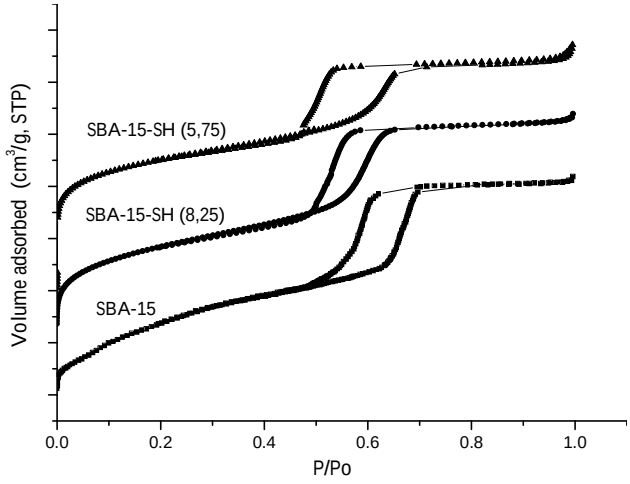


Fig. 6. *Isotherms of SBA-15 and the thiol-functionalized SBA-15 with different molar ratios of TEOS/TSPT.*

Table 1. *Textural properties of SBA-15 and the thiol-functionalized SBA-15 with different molar ratios of TEOS/TSPT*

Sample	S_{BET} (m^2/g)	d_p (nm)	t_w (nm)	V_t (cm^3/g)
SBA-15	587.8	6.4	5.8	0.66
SBA-15-SH (8.25)	568.7	5.6	7.0	0.62
SBA-15-SH (5.75)	543.7	5.0	7.5	0.57

4 Conclusion

The functional thiol groups were introduced into the surface of SBA-15 silicas by the co-condensation of 3-mercaptopropyltrimethoxysilane and tetraethyl orthosilicate. The functionalized SBA-15 materials with a highly ordered hexagonal can be obtained even for as high as 5.75 molar ratio of TEOS/TSPT in the reaction mixture when the time of adding TSPT to synthesized gel is 30 minutes. The Soxhlet ethanol extraction for 48 hours is favorable for the complete removal of template from thiol-functionalized SBA-15. The addition of thiol groups also results in a decrease both in surface area and pore size, as well as pore volume, of the functionalized SBA-15 silicas. The porosity decreases dramatically when the ratio of TEOS/MPTES is around 5.75, with a loss of ~ 20 % for both the surface area and pore volume.

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