Influence of synthesis conditions on mercury adsorption capacity of propylthiol functionalized SBA-15 obtained by Co-condensation

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Abstract

Thiol functionalized mesoporous silicas for aqueous mercury removal by adsorption have been synthesized by co-condensation of 3-mercaptopropyltrimetoxy silane (MPTMS) and tetraethoxysilane (TEOS) in acidic medium with the block copolymer Pluronic 123 as structure directing agent. The influence of two synthesis parameters, the time of TEOS prehydrolysis and the molar ratio \(x = \text{MPTMS} / (\text{MPTMS} + \text{TEOS})\), on both the textural properties and mercury adsorption capacities have been investigated. Materials were characterized by low-angle XRD, nitrogen adsorption-desorption, \(^{29}\text{Si}\) NMR, TGA-DTA, transmission electron microscopy and elemental chemical analysis. Adsorbents are mostly mesostructured SBA-15 type silicas with suitable textural properties for mercury adsorption and exhibit thermal stability up to at least 285ºC. The amount of propylthiol incorporated to the materials is in accordance with the MPTMS / TEOS proportion in the synthesis medium (up to 4.1 mmol of S per gram of adsorbent). We have found that it is neccessary to employ a minimal amount of TEOS in order to preserve the mesoporous structure in the resulting material when a high quantity of propylthiol groups is incorporated. Prehydrolysis of silica precursor (TEOS) for 45 minutes before MPTMS addition leads to succesful results. Longer prehydrolysis times can improve the textural and structural properties of materials but the amount of propylthiol incorporated and the mercury adsorption capacity are not superior. Experimental isotherms show that materials are efficient adsorbents of mercury at low aqueous concentration with maximum adsorption capacity as high as 4.1 mmol of Hg(II) per gram of adsorbent.

Keywords: Mesoporous silica, Functionalization, Propylthiol, Metal adsorption, Water treatment
1. Introduction

Mesostructured inorganic materials are receiving much attention owing to their noticeable applications in process such as adsorption, catalysis, fabrication of sensors and nanomaterials design [1]. Since 1990 a great variety of ordered mesostructured silica materials like FSM-16 [2], M41S [3], MSU [4], HMS [5] and SBA [6] families have been developed using different molecular templates that act as structure directing agents due to their auto-assembly properties. These materials present high superficial areas, great pore volumes and uniform pore diameters because of their mesoscopic structure. In addition, the open-framework silica structures, which are a stable support under hard working conditions, allow an easy accessibility of external molecules to the inner surface of materials and, hence, fast kinetics of chemical and physical processes are followed.

Organic functionalization of mesostructured materials has been used to modify the silica surface achieving new applications of these materials in several fields. Organic chains are incorporated onto the silica structure through C–Si covalent bonding to form a monolayer of functional groups. In this way, it is possible to control the superficial properties in order to obtain specific active sites. These hybrid organic-inorganic materials have found a great variety of applications in adsorption and catalysis [7-8]. Among them, a topical issue is the functionalization of mesostructured silica to prepare selective adsorbents for heavy metal removal from wastewater [9-10]. The ideal support for heavy metal adsorption is probably the highly ordered mesoporous silica SBA-15, obtained by using the amphiphilic triblock copolymer poly(ethylene oxide)$_{20}$-poly(propylene oxide)$_{70}$-poly(ethylene oxide)$_{20}$ as structure directing agent [6]. In
comparison with other mesostructured silica materials, SBA-15 exhibits thicker pore walls which provide high hydrothermal stability, longer pore diameter ranging from 5 to 30 nm, and higher pore volumes.

For mercury adsorption, the efforts have been mostly concerned with the incorporation of thio-groups to the mesostructured silica materials [9-16] since sulphur presents a strong affinity toward mercury according to the principle of hard and soft acids and bases of Pearson [17].

Among these possible thio-groups, propylthiol has been widely employed to functionalize SBA-15 [11, 16, 18-21] and other mesostructured materials [9-10, 12-15, 22]. The capabilities for mercury adsorption of the resulting thiol-functionalized derivatives depend on two antagonist factors, the organic groups loading and the accessibility of mercuric species to the internal adsorption sites, because functionalization process usually leads to the loss of mesoporous silica structure. Therefore, previous studies have demonstrated the importance of mesostructure preservation to obtain efficient mercury adsorbents prepared with high thiol content [10, 23].

Two common methods, grafting and co-condensation, have been used for anchoring 3-mercaptopropyltrimethoxysilane to the silica surface. In general, accessibility of approaching molecules to thiol groups is better for grafting [9-11] whereas higher quantities of organic groups are incorporated into the silica structure when co-condensation is employed [10-14]. The latter is overall preferred because of its simplicity and minor organic precursor consumption. Thus, in this work we have used the co-condensation method.
As we have reported in a previous paper, SBA-15 material allows to prepare by co-condensation efficient mercury adsorbents [16]. In order to incorporate higher amount of thiol groups into the silica material preserving the mesoscopic order, we have carried out a study of the effect of synthesis conditions on the mesostructure of propylthiol derivaties of SBA-15 materials and their mercury adsorption capacity. In this paper we present the relevant results.

2. Experimental Section

2.1 Chemicals

All chemicals were purchased from Aldrich and employed without further purification. Pluronic P123, poly-(ethylene-oxide)$_{20}$-poly-(propyleneoxide)$_{70}$-poly-(ethyleneoxide)$_{20}$, was used as structure directing agent. Tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) were used as silica and propylthiol precursors. Mercuric chloride was used for mercury adsorption experiments.

2.2 Synthesis of the thiol functionalized SBA-15 adsorbents

Mesostructured silica materials functionalized with propylthiol were obtained by co-condensation according to the general procedure previously reported [16, 18]. 4 g of Pluronic 123 were dissolved at room temperature in 125 g of HCl 1.9 M. After heating to 40°C, TEOS was added to the solution and stirred for periods ranging from 45 minutes to 8 hours before adding MPTMS. This time is referred to prehydrolysis time of TEOS precursor. Controlled quantities of silica and organosilane precursors were used to obtain molar ratios, $x = \text{MPTMS} / (\text{MPTMS} + \text{TEOS})$, ranging from 0.05 to 0.5 in the synthesis medium. The reactant mixture was stirred for 20 hours and finally aged for 24 hours at 100 ºC. Silica products were recovered by filtration and dried to air, then they
were treated with ethanol under reflux for 24 hours for template extraction, filtered and dried at 100 °C for 2 hours.

2.3 Adsorbents characterization

Textural properties of the functionalized materials were determined by measuring the N\textsubscript{2} adsorption-desorption isotherms at -196 °C (77 K) on a Micromeritics Tristar 3000 sorptometer. Surface areas were determined by using the B.E.T equation; pore size distributions were obtained from the adsorption branch of the isotherm by means of the B.J.H. model with cylindrical geometry of the pores and the pore volumes were taken at P/P\textsubscript{0} = 0.97. Low-angle X-Ray diffraction (XRD) patterns of the samples were obtained on a powder PW3040/00 X’Pert MPD/MRD diffractometer using the K\textsubscript{Cu} line. Transmission electron micrographs (TEM) were acquired on a Philips Tecnai 20 electronic microscope working at 200 kV. Covalent bonding of propylthiol to silica structure was evidenced by \textsuperscript{29}Si nuclear magnetic resonance recorded on an Infinity Plus Varian multinuclear spectrometer operating at 79.4 MHz for \textsuperscript{29}Si nuclei. NMR experiments were conducted under conditions of magic-angle spinning at 6.0 kHz and consisted of a 4.5 μs 90° pulse with a repetition delay of 15 s. Chemical shifts have been referenced to the corresponding nuclei in tetramethylsilane. Quantitative determination of the thiol functional group content was carried out by elemental microanalysis. To test the thermal stability of the samples thermal gravimetric and differential thermal analysis (TGA-DTA) were perform with a TA Instruments SDT 2960 apparatus at a heating rate of 5 °C min\textsuperscript{-1}.

2.4 Mercury adsorption experiments.

Multiple sets of batch experiments have been carried out to determine the mercury adsorption isotherms. Single runs were carried out by stirring 25 mg of
functionalized silica in 45 mL of aqueous HgCl₂ solutions at 20 °C until reaching the equilibrium time [16]. Then, mixtures were filtered with a syringe filter of 0.22 μm and the filtered solutions were collected. Mercury adsorbed amount was determined by difference between initial and final metal concentrations in the solution.

Two independent analytical techniques were used for mercury determination. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) has been used when mercury concentrations are higher than 0.1 mg L⁻¹. These measurements were performed in a Varian Vista AX spectrometer after calibration with stock solutions in the range of concentration of 0-10 mg L⁻¹. Two emission mercury lines (194 and 253 nm) were used according to the standard EPA method for mercury analysis [24]. Mercury concentrations lower than 0.1 mg L⁻¹ were determined by cold vapor atomic fluorescence spectroscopy (CVAFS). Analyses were carried out in a PSA Analytical Millennium Merlin equipment following the EN 13506 standard procedure [25].

3. Results and Discussion

3.1. Influence of the synthesis variables on the structural and textural properties of the adsorbents

In this work we have prepared thiol-functionalized SBA-15 materials by modifying two synthesis variables: (i) the time of prehydrolysis of silica precursor and (ii) the molar ratio of MPTMS related to the total molar quantity of silicon present in the synthesis medium, \( x = \frac{\text{MPTMS}}{\text{MPTMS} + \text{TEOS}} \). TEM images of synthesized materials, Figure 1, exhibit the two dimensional hexagonal porous symmetry that is characteristic of SBA-15 type silica.
**Effect of MPTMS molar ratio.** To study the influence of MPTMS molar ratio on the structural properties of adsorbents we have kept a constant prehydrolysis time of 45 minutes. The molar ratio was varied through two alternative ways. The first group of experiments has been carried out with a constant silicon molar quantity (41 mmol Si) in the synthesis medium. So, addition of increasing quantities of MPTMS involves the diminution of TEOS quantity and, therefore, the TEOS / Pluronic molar ratio. These materials have been denoted A-SBA15-SH-\(x\)-\(t\), where \(x\) indicates the molar ratio of MPTMS in the synthesis mixture expressed as percentage and \(t\) denotes the time of silica precursor prehydrolysis. The second group of materials has been prepared by fixing the TEOS molar quantity (37 mmol) and modifying MPTMS concentration in the synthesis mixture. Thus, the TEOS / Pluronic molar ratio is now constant. These adsorbents prepared from variable quantity of silicon have been denoted B-SBA15-SH-\(x\)-\(t\). Table 1 shows the initial conditions employed to synthesize the materials prepared in this work.

Composition of the synthesis gel has been modified by changing the molar percentage, \(x = \text{MPTMS} / (\text{MPTMS} + \text{TEOS})\), from 5 to 50% for both set of experiments. A and B materials are identical when \(x = 10\). Figure 2 shows the low angle XRD diffraction patterns of A-SBA15-SH-\(x\)-45 and B-SBA15-SH-\(x\)-45 samples. As observed, all of the diffractograms show the peak corresponding to the (1 0 0) reflection except for A-SBA15-SH-30-45. Samples prepared with low MPTMS molar ratios, up to 10 %, exhibit higher order diffraction peaks reflecting a good mesoscopic order. Diffraction patterns of materials obtained with larger MPTMS molar ratios only show one diffraction peak which intensity steadily decreases with \(x\).
Conversely, B-SBA15-SH-x-45 materials, prepared with a fixed quantity of silica precursor, exhibit a mesoscopic structure regardless of the amount of organic groups. These results evidence that a minimal value of the TEOS/Pluronic ratio is necessary in order to achieve thiol-functionalized materials that preserve the mesoscopic order. From this work, we recommend a value of 0.050 as seen in Table 1.

Figure 3 displays the nitrogen adsorption-desorption experimental isotherms at -196 °C (77 K) and the corresponding pore size distributions calculated by means of B.J.H. method. Both groups of materials (A and B) exhibit similar patterns with type IV isotherms according to IUPAC classification. As can be seen in the Figure, capilar condensation jump is less pronounced when more and more propylthiol groups are incorporated to the materials. Pore size distributions become broader as MPTMS content increases.

The surface areas, pore volumes and mean pore diameters are listed in Table 1. Values of these parameters decrease when MPTMS molar ratio enlarges. This diminution is observed for both groups of materials and can be attributed to the occupancy of propylthiol groups into the mesostructure. Also, Table 1 reports the unit cell parameters, $a_0$, obtained from the low angle XRD patterns and the wall thickness, $e_p$, calculated from XRD and nitrogen sorption parameters. As seen, while the unit cell parameters fluctuate between 10 and 12 nm, the wall thickness globally increases when higher MPTMS molar ratio is employed. Results obtained from nitrogen adsorption-desorption mesasurements agree well with the loss of mesostructure pointed by XRD.

$^{29}$Si NMR spectra of the samples have been carried out to verify the covalent bonding of propylthiol groups into the structure. Figure 4 shows the spectra of A-SBA15-SH-x-45 and B-SBA15-SH-x-45 samples. Two groups of resonances are
observed due to siloxane and organosiloxane groups. $Q^n$ signals at $-112, -103$ and $-94$ ppm are assigned to silicon in siloxane environments such as $Q^4 (SiO)_{3}Si$, $Q^3 (SiO)_{2}SiOH$, and $Q^2 (SiO)_{2}Si(OH)_{2}$; $T^m$ signals at $-67$ and $-58$ ppm which are attributed to silicon covalently bonded to propylthiol groups $(SiO)_{3}Si-(CH_{2})_{3}OH$, $T^3$, and $(SiO)_{2}OHSi-(CH_{2})_{3}SH$, $T^2$, respectively are also detected. Analysis of the spectra has been carried out by splitting the profiles into gaussian bands. Intensity ratios, $R_1 = I(T^m) / [I(Q^n)+I(T^m)]$, so obtained quantify the degree of organic incorporation as the ratio of silicon bonded to organic groups with respect to total silicon in the sample. As labeled in Figure 4, the measured ratios are in good agreement with the molar proportion MPTMS / (MPTMS + TEOS) employed in the initial synthesis mixture. These results confirm a high yield of organic incorporation to the silica structure by covalent bonding in all cases.

TGA/DTA analyses evidence a very similar behaviour for both series A and B of adsorbents. Thermograms of B-SBA15-SH-x-45 materials are shown in Figure 5. As observed, weight changes are more significant for materials that contain higher quantities of propylthiol. The first important weight loss begins at 250 $^\circ$C and it is attributed to the decomposition of the remaining template (6%) [18]. This weight loss overlaps with the propylthiol groups decomposition that occurs in the temperature range from 285$^\circ$C to 340$^\circ$C.

*Effect of TEOS prehydrolysis time.* Time of TEOS prehydrolysis has been previously recognized as a crucial parameter to obtain functionalized hybrid materials with good mesoscopic order [18-19, 21]. In fact, no pore order is observed in thiol-functionalized SBA-15 materials without TEOS prehydrolysis previous to MPTMS addition [19]. Also, mesoporous structure formation of the thiol functionalized material
is favoured by increasing the time of the prehydrolysis step. A minimum prehydrolysis time of at least 45 minutes has been proposed [18].

Low angle X-ray diffraction patterns for some materials A-SBA15-SH-20-t, A-SBA15-SH-30-t, A-SBA15-SH-40-t with prehydrolysis time from 45 to 300 minutes have been plotted in Figure 6. When MPTMS molar ratio is 20% and 30% a better mesoscopic order is achieved when prehydrolysis time increases from 45 to 180 minutes. However, no diffraction signals are found for materials prepared with molar ratio of 40% whatever prehydrolysis time used.

Figure 6 also shows low angle XRD diffractograms for the B-SBA15-SH-20-t, B-SBA15-SH-40-t and B-SBA15-SH-50-t with time of prehydrolysis ranging from 45 to 480 minutes. The first peak, assigned to the (1 0 0) reflection is observed in all cases. Thus, all the B-SBA15-SH-x-t are mesostructured even for MPTMS molar ratio as high as 50%. Signal intensity of the first diffraction enlarges when the time of prehydrolysis increases indicating that a more ordered structure of synthesized materials is obtained.

Nitrogen adsorption-desorption isotherms at -196 °C (77 K) and B.J.H. pore size distributions corresponding to A-SBA15-SH-x-t and B-SBA15-SH-x-t are shown in Figures 7 and 8. Textural and structural properties are summarized in Table 1. Information obtained from isotherms and low-angle XRD of A-materials is in good agreement. For MPTMS percentage of 20 and 30% it is observed in Figure 7 that the total adsorbed volume is higher as time of prehydrolysis grows from 45 minutes to 180 minutes. Surface area, pore volume and mean diameter also increase with prehydrolysis time. When MPTMS molar percentage reaches 40% the pore size distribution is very broad independently of prehydrolysis time; This fact is due to the absence of mesostructure order and then, nitrogen adsorption occurs in the interparticle region.
All of the isotherms corresponding to materials B-SBA15-SH-20-\( t \) and B-
SBA15-SH-40-\( t \) are type IV in the IUPAC classification regardless of their
prehydrolysis time. The capilar condensation jump turns more pronounced and adsorbed
volume raises when the prehydrolysis time is increased from 45 to 180 minutes. For the
molar percentage of 20 \%, further increase of TEOS prehydrolysis time leads to a
general diminution of the adsorbed volume. For materials corresponding to the 40\% of
molar percentage, the increase of prehydrolysis time beyond 180 minutes leads to no
significant changes in isotherm shape up to 300 minutes but adsorbed volume decreases
noticeably when prehydrolysis time changes from 300 to 480 minutes.

The behaviour of B-samples obtained for \( x = 50 \) is rather different. Isotherms of
materials obtained with prehydrolysis time of 240 and 300 minutes are shown in
Figure 8. Both isotherms are type IV of IUPAC clasification which indicates that
samples preserve its mesoporous nature in spite of the high MPTMS ratio. In this case,
the nitrogen adsorption capacity is lower when prehydrolysis time changes from 240 to
300 minutes. As it is explained below, this effect is due to a higher incorporation of
propylthiol groups as time of prehydrolysis is longer.

Values of superficial area, pore diameter and pore volume corresponding to B-
SBA15-SH-20-\( t \) and B-SBA15-SH-40-\( t \), rise when TEOS prehydrolysis time increases
from 45 to 180 minutes, as read in Table 1. However, the increase of prehydrolysis time
from 180 to 300 minutes yields thiol-functionalized mesostructured materials whose
textural properties decrease slightly what means that pore channels of the silica structure
are already formed for a prehydrolysis time of 180 minutes. This fact is in agreement
with the observed time of formation of the silica structure for SBA-15 materials
estimated in less than 2 hours [26]. So, further addition of the organic precursor modifies not significantly the properties of mesostructured materials.

\(^{29}\)Si NMR spectra corresponding to B-SBA15-SH-20-\(t\) y B-SBA15-SH-40-\(t\) materials are shown in Figure 9. The intensity ratios, \(R_1 = \frac{I(T^m)}{[I(Q^0)+I(T^m)]}\), calculated from the profile analyses, are in good agreement with the molar proportions MPTMS / (MPTMS + TEOS) employed in the synthesis mixture. As seen, materials prepared from the same initial MPTMS molar ratio exhibit comparable NMR profiles. These results evidence a high yield of organic incorporation to the silica structure by covalent bonding in all cases.

Figure 10 shows the DTA/TGA analyses of the B-SBA15-SH-20-\(t\) y B-SBA15-SH-40-\(t\) samples. Thermograms are similar to the previously shown in Figure 5. Decomposition of the remaining surfactant begins at 250 °C and this weight loss overlaps with the propylthiol groups breakdown that occurs at 320 °C and 340 °C for the materials obtained with 20% and 40%, respectively. As it can be seen, all materials prepared using the same MPTMS molar ratio exhibit alike thermal stability.

3.3. Determination of sulphur content of the thiol-functionalized adsorbents

Sulphur content expressed as mmol S per gram of adsorbent, obtained from elemental analysis, are summarized in Table 2. When the shortest prehydrolysis time is employed, the sulphur content steadily increases with \(x\) molar ratio values for both A and B groups of materials, up to 3.72 mmol S g\(^{-1}\) for the B-SBA15-SH-40-45 material.

In addition, materials prepared from equal MPTMS molar ratio have a rather similar content of sulphur whatever the prehydrolysis time except for \(x = 50\). In this last case, when the time of TEOS prehydrolysis increases from 240 to 300 minutes, the
amount of propylthiol incorporated into the mesostructure raises significantly from 3.7
to 4.1 mmol of S per gram of adsorbent.

3.4 Mercury adsorption capacity.

In order to test the mercury adsorption ability of the thiol-functionalized SBA-15
synthesized materials, aqueous HgCl$_2$ adsorption isotherms have been made up at 20 °C
by joining many single experimental runs with the initial mercury concentration ranging
from 30 to 1400 mg L$^{-1}$. Maximum capacities of mercury adsorption for every material
have been determined from the corresponding isotherms.

Isotherms are plotted in Figure 11 as the amount of mercury adsorbed at
equilibrium, $q_e$ (millimoles per gram of adsorbent), against the equilibrium mercury
concentration in the liquid phase, $C_e$ (milligrams per liter). As observed, all of the
mercury isotherms are type I according to IUPAC classification with a marked initial
slope indicating that materials act as adsorbents with a very high efficacy at low
mercury concentrations [16]. Maximum mercury adsorption capacities, summarized in
Table 2, have been calculated as the mean corresponding to the plateau region of the
isotherm where the mercury saturation is reached. As expected, mercury adsorption
capacity increases with the sulphur content of the adsorbents. A maximum mercury
loading of 4.0 mmol of Hg g$^{-1}$ is reached for B-SBA15-SH-50-300, the material with
the highest organic content.

Figure 12 shows the molar ratios between the amount of adsorbed mercury and
the sulphur content for each material. For the A-SBA15-SH-x-t materials the Hg/S
molar ratio is less than unity in all cases except for $x = 10$. In addition, this ratio
diminishes with increasing the organic content of the adsorbents what means that not all
of the thiol groups incorporated into the materials are accessible to mercury species.
When prehydrolysis time enlarges, no significant increments on the adsorption capacity are found.

For the second group of materials, B-SBA15-SH-x-t, and the shortest time of prehydrolysis (45 min), Hg/S molar ratios are almost the unity in all cases. Therefore, all the thiol organic groups are accessible to mercury species since they are located in either the pore surface or the particle external surface.

Figure 12 shows that when the time of prehydrolysis raises from 45 to 180 minutes, the mercury adsorption capacity decreases remarkably up to Hg / S molar ratios of 0.63, 0.82 and 0.78 for the materials corresponding to the 20, 30 and 40% of molar MPTMS percentage. This behaviour evidences that a large quantity of organic groups anchored to the silica structure are not accessible to mercury species regardless of the superior textural properties of the materials obtained with 180 minutes of prehydrolysis time. So, thiol groups should have been incorporated inside the pore walls or in the microporous channels of the silica structure. For materials synthesized with prehydrolysis time of 240, 300 and 480 minutes, Hg / S molar ratio is almost the unity. Then, in general, the use of prehydrolysis times higher than 45 minutes is inefficient except for MPTMS molar percentage of 50%. In this last case, it has been found a maximum mercury adsorption capacity of 4.0 mmol g⁻¹ for the prehydrolysis time of 300 minutes. However, we consider that the materials B-SBA15-SH-x-45 are preferable to act as efficient adsorbents because of the simplicity of synthesis, the good textural properties and high capacity for mercury loading of up to 3.7 mmol of Hg g⁻¹.

4. Conclusions

This work has verified that direct co-condensation of MPTMS and TEOS in presence of Pluronic 123 yields thiol functionalized SBA-15 type silica materials that
can incorporate high loadings of sulphur (up to 4.0 mmol S per gram of adsorbent).

Influence of MPTMS/TEOS molar ratio and TEOS prehydrolysis time on the properties of materials has been checked in order to optimize the synthesis conditions for preparing efficient mercury adsorbents. To preserve the mesoscopic order when an increasing amount of propylthiol groups incorporates to the material is necessary to make use of a minimal quantity of silica precursor that ensures the formation of the mesoporous structure. A TEOS prehydrolysis time of 45 minutes before MPTMS addition yields the best results. Longer prehydrolysis times lead to materials with better textural properties but lower mercury adsorption capacities. The Hg/S molar ratio diminishes since the active groups bounded to the mesoporous silica result inefficient. This behaviour is attributed to the fact that some thiol groups are incorporated inside the silica walls and become inaccessible to the mercury species. All materials are excellent adsorbents of mercury at very low aqueous concentration. Furthermore, it has been obtained a maximum adsorption capacity as high as 4.1 mmol of Hg(II) per gram of adsorbent.

Acknowledgements

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References


Tables

Table 1. Structural and textural properties of thiol-functionalized SBA-15 materials

Table 2. Sulphur content and maximum mercury adsorption capacity for thiol-functionalized SBA-15 materials

Figure captions

Figure 1. TEM images of some thiol functionalized SBA-15 materials prepared in this work. (a) B-SBA15-SH-20-45; (b) B-SBA15-SH-20-180; (c) B-SBA15-SH-20-240.

Figure 2. Low-angle XRD patterns of thiol-functionalized SBA-15 materials with prehydrolysis time of 45 minutes and different sulphur content: (A) A-SBA15-SH-x-45. (B) B-SBA15-SH-x-45.

Figure 3. Nitrogen adsorption-desorption isotherms at 77 K and pore size distribution of thiol-functionalized SBA-15 materials with prehydrolysis time of 45 minutes and different sulphur content. (a) A-SBA15-SH-x-45. (b) B-SBA15-SH-x-45.

Figure 4. MAS $^{29}$Si NMR spectra for the thiol-functionalized SBA-15 materials with prehydrolysis time of 45 minutes and different sulphur content. (a) A-SBA15-SH-x-45 (b) B-SBA15-SH-x-45.

Figure 5. TGA and DTA analysis of the B-SBA15-SH-x-45 thiol-functionalized SBA-15 materials with prehydrolysis time of 45 minutes and different sulphur content.

Figure 6. Low-angle RXD patterns of thiol-functionalized SBA-15 materials as a function of TEOS prehydrolysis time.
Figure 7. Nitrogen adsorption-desorption isotherms at 77 K and pore size distribution of A-SBA15SH-x-t as a function of TEOS prehydrolysis time.

Figure 8. Nitrogen adsorption-desorption isotherms at 77 K and pore size distribution of B-SBA15SH-x-t as a function of TEOS prehydrolysis time.

Figure 9. MAS $^{29}$Si NMR spectra of thiol modified B-SBA15-SH-x-t materials as a function of prehydrolysis time for MPTMS molar percentage of (a) 20 % and (b) 40 %.

Figure 10. TGA-DTA analyses of thiol modified B-SBA15-SH-x-t materials as a function of prehydrolysis time for MPTMS molar percentage of (a) 20 % and (b) 40 %.

Figure 11. Mercury adsorption isotherms obtained at 20 °C of representative materials. (a) A-SBA15-SH-x-t. (b) B-SBA15-SH-x-t.

Figure 12. Molar ratio between maximum mercury loading and sulphur content of the adsorbents as a function of prehydrolysis time for different MPTMS percentages: (a) A-SBA15-SH-x-t. (b) B-SBA15-SH-x-t.
Table 1.

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<td>B-SBA15-SH-40-45</td>
<td>37</td>
<td>24.7</td>
<td>0.050</td>
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<td>0.050</td>
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<td>24.7</td>
<td>0.050</td>
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<td>0.050</td>
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<td>0.050</td>
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</table>

Note: TEOS, MPTMS, and Pluronic are precursors used in the synthesis process. $D_p$, $S_{pm}$, and $V_p$ are the average particle diameter, BET surface area, and micropore volume, respectively. $a_0$ and $e_p$ are the average pore diameter and pore size distribution.
Table 2.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sulphur content (mmol g⁻¹)</th>
<th>Maximum mercury loading (mmol g⁻¹)</th>
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<tbody>
<tr>
<td>A-SBA15-SH-10-45</td>
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<td>4.12</td>
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</tbody>
</table>
Figure 1
Figure 2

(a) Graph showing the intensity (I) in arbitrary units (a.u.) versus 2θ in degrees for samples A-SBA15-SH-10-45, A-SBA15-SH-20-45, and A-SBA15-SH-30-45.

Figure 3

A

\[ V_{ads} / \text{cm}^3(\text{STP}) \text{ g}^{-1} \]

\[ P / P^0 \]

\[ 0.0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1.0 \]

\[ 0 \quad 100 \quad 200 \quad 300 \quad 400 \quad 500 \quad 600 \quad 700 \]

B

\[ V_{ads} / \text{cm}^3(\text{STP}) \text{ g}^{-1} \]

\[ P / P^0 \]

\[ 0.0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1.0 \]

\[ 0 \quad 100 \quad 200 \quad 300 \quad 400 \quad 500 \quad 600 \quad 700 \]

\[ d\bar{V}/d\bar{\log}(D) / \text{cm}^3 \text{ g}^{-1} \]

\[ D_p / \text{nm} \]

\[ 0 \quad 5 \quad 10 \quad 15 \quad 20 \]

a) A-SBA15-SH-10-45
b) A-SBA15-SH-20-45
c) A-SBA15-SH-30-45

d) B-SBA15-SH-5-45
e) B-SBA15-SH-10-45
f) B-SBA15-SH-15-45
g) B-SBA15-SH-20-45
h) B-SBA15-SH-30-45
Figure 4

(a) Plot showing peaks labeled $Q^3$, $Q^4$, $T^3$, $T^2$ with $R_I = 0.32$ for A-SBA15-SH-10-45 and $R_I = 0.11$ for A-SBA15-SH-30-45.

(b) Plot showing several peaks with $R_I$ values of 0.054, 0.11, 0.14, 0.22, 0.32, and 0.43 for different samples labeled B-SBA15-SH.
Figure 6

- Type A
  - \( x = 20 \):
    - \( t = 180 \) min
    - \( t = 45 \) min
  - \( x = 30 \):
    - \( t = 180 \) min
    - \( t = 45 \) min
  - \( x = 40 \):
    - \( t = 180 \) min
    - \( t = 45 \) min

- Type B
  - \( x = 20 \):
    - \( t = 480 \) min
    - \( t = 300 \) min
    - \( t = 240 \) min
    - \( t = 180 \) min
    - \( t = 45 \) min
  - \( x = 40 \):
    - \( t = 480 \) min
    - \( t = 300 \) min
    - \( t = 240 \) min
    - \( t = 180 \) min
    - \( t = 45 \) min
  - \( x = 50 \):
    - \( t = 300 \) min
    - \( t = 240 \) min

Figure 7

![Graphs showing text and data points](image-url)
Figure 8

![Graphs showing the relationship between porosity (P/P₀) and pore size (D_p) for different samples labeled B-SBA15-SH-20-45, B-SBA15-SH-20-180, B-SBA15-SH-20-240, B-SBA15-SH-20-300, and B-SBA15-SH-20-480.](image-url)
Figure 9

a

b

\( R_I = 0.22 \)

\( R_I = 0.22 \)

\( R_I = 0.21 \)

\( R_I = 0.19 \)

\( R_I = 0.42 \)

\( R_I = 0.42 \)

\( R_I = 0.41 \)

\( R_I = 0.41 \)

\( \delta / \text{ppm} \)

\( \delta / \text{ppm} \)
Figure 10

[Graphs showing DTA and weight change plots with different preheat times]

$t_{pre}_{h}= 180 \text{ min}$

$t_{pre}_{h}= 240 \text{ min}$

$t_{pre}_{h}= 300 \text{ min}$

$t_{pre}_{h}= 480 \text{ min}$

$\frac{d\text{ weight}}{dT} / \text{mg}^{-1}$

$T / ^\circ\text{C}$

$\% \text{ weight change}$
Figure 12

(a) Hg / S ratio vs. TEOS prehydrolysis time for different x values.

(b) Hg / S ratio vs. TEOS prehydrolysis time for different x values.