

Synthesis of sulfonic SBA-15 by co-condensation and Soxhlet extraction: optimization by shortening the preparation time

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Abstract

Propyl sulfonic SBA-15 catalysts are of great interest in several fields of chemistry and have exhibited high activity towards numerous reactions. Nonetheless, the incorporation of these functional groups on SBA-15 silica poses several challenges. Grafting techniques may conduct to a non-uniform dispersion of the functional groups on the surface. Co-condensation of the functional precursor during the synthesis of the silica overcomes this drawback, but requires longer syntheses and it has the disadvantage that removal of surfactant cannot be done by calcination because of the thermal stability of the functional groups present on the surface. Thus, the detemplation is limited in this case to extraction by standard procedures which generally involve large amounts of solvent per gram of catalyst, long contact time and limited yield of the template removal.

The aims of this work were, on the one hand, to study the reduction of the ripening time for catalysts prepared by co-condensation with sulfonic groups and, on the other hand, to develop a standard procedure which allows achieving a high yield of detemplation and optimizes the amount of solvent needed and the time required, as well as employ a commercially available solvent.

Different characterization techniques allowed to conclude that the obtained materials exhibited high surface area and a good degree of mesoscopic order, comparable with materials obtained by traditional procedures. Also, a high degree of template removal was achieved and the sulfonic groups were preserved in functionalized materials. These results are relevant for a further scale-up of the catalysts production.

1. Introduction

Solid acid catalysts are of great interest in several industrial reactions, being among them the zeolites the most widespread ones. Their main advantages are their crystalline structures with small, regular pore size and high stability, and their strong and uniform acidity. However, their small pore size is a major disadvantage for reactions involving bulky molecules as reagents or products, leading to diffusion limitations or even impeding the reaction. Thus, ordered mesoporous materials gain attention as a solution to these drawbacks. They are amorphous solids which are synthesized with large, uniform pores in their structure due to the addition of a template together with the precursors, which is later removed.

SBA-15 is one of the best candidates for catalytic applications [1]. It was reported for the first time by Zhao in 1998 [2]. It is an amorphous silica with thick walls, uniform cylindrical pores arranged in a 2-D hexagonal structure and some random pore interconnections. The synthesis procedure requires high acidic media and the presence of the non-ionic surfactant P123 © as a template. The removal of the latter (detemplation) could be performed via calcination [2], extraction [3], irradiation [4, 5] or oxidation [6].

SBA-15 synthesis comprises two primary steps. The first one is carried out at atmospheric pressure, under stirring and at relatively low temperatures, and is usually called ripening. This is usually followed by a

second stage consisting of the treatment of the gel in an autoclave, at higher temperature and self-generated pressure, without agitation, which is usually called ageing.

The first stage (ripening) results in the appearance of the mesostructure, through the formation of surfactant micelles and the condensation of silica around them in a cooperative self-assembly process [7]. The second stage (ageing) improves the crosslinking of the silica and is crucial for the consolidation of the structure, and entails minor transformations (enlarged pores, development of interconnections).

Since the silica has no intrinsic acidity, acidic functional groups must be added in order to obtain a catalytic active material. The attachment of organic functional groups could tune the hydrophilic-hydrophobic character of the silica surface to give sorbent chemical selectivity for specific molecules or ions [8]. In the case of propyl-sulfonic functional groups, their incorporation can be done via post-synthesis grafting techniques or co-condensation in the first synthesis step (direct synthesis) [9].

Grafting techniques have several drawbacks, such as that they involve extra steps, require high amounts of solvent per gram of catalyst, and in addition there are concerns about the uniform anchoring of the groups along the pores. The main disadvantages of this method includes: (i) the reductions of pore size and pore volume caused by the attachment of functional group on pore surface [10]; (ii) density limitation of reactive silanol group that would limit the loading of functional group on the pore surface, being possible that cross-linking between functional groups and silanol groups on surface occurs [11]; (iii) difficulty in achieving uniformity of the functional group and tedious process which involves more than one step of preparation [12].

The co-condensation of the functional precursor seems to be more convenient to obtain standard catalysts for industrial applications. There is evidence that the direct synthesis leads to a uniform dispersion of the functional groups on the surface of the material while its structure is preserved [2]. A disadvantage of this procedure is that the functional groups are already present in the material when the surfactant is going to be removed, thus limiting the demtemplation to extraction methods which are not harmful to them. Standard procedures involve large amounts of solvent per gram of catalyst, long contact time and limited yield of the template removal.

It has been shown that co-condensation procedure yields better results when, instead of mixing all the precursors at the beginning of the ripening step, a pre-hydrolysis of the silica precursor is allowed (0.5 to 3 h) and the functional precursor, along with the oxidant agent is added later, and then 24 h ripening is completed [9].

However, several authors have reported that the formation of the mesostructure is relatively fast in SBA-15 [13] and within an interval from 30 minutes to a few hours a material with similar properties to that obtained after 24 h of ripening can be obtained [14, 15].

Therefore, a reduction in the synthesis time is studied in this work, keeping the pre-hydrolysis step, after which the functional precursor is added and ripening takes place for only 4 h. The ageing and extraction

steps are not altered. The materials obtained in this way exhibit very similar properties to those prepared complying with a standard ripening of 24 h.

Regarding the extraction, typical procedures involve stirring and reflux for 24 h in ethanol (approximately 250 ml solvent per gram of as-synthesized material) [16]. The use of Soxhlet apparatus can reduce significantly the time and the amount of solvent needed, since the material is always contacted by fresh solvent being refluxed and the extracted polymer concentrates in the bottom flask (Scheme 1, Supplementary data) [17]. Zhang et al. studied the template removal by extraction with absolute ethanol in a Soxhlet apparatus [18], considering different extraction times and ageing temperatures. They found that the template content decreased rapidly during the first three hours of extraction and then remained almost constant. Complete removal of the surfactant was not achieved and the remaining content was lower as the pore size was larger. The amount of ethanol employed was still high (approximately 250–1000 ml per gram of sample). Ávila et al. [19] studied the extraction with a Soxhlet apparatus using different solvents. Water, acetonitrile, dichloromethane, acetone, methanol and ethanol were assessed as solvents (approximately 42 ml per gram of sample). Water was not effective and methanol, acetonitrile and ethanol proved to be the best solvents amongst the studied. Remaining surfactant was almost constant for 6, 24 and 48 h extractions, in agreement with the findings already mentioned.

Hydrochloric acid solutions in ethanol and diethyl ether were also employed for the removal of organic templates in mesoporous materials [20]. Extracted materials showed a higher degree of cross-linkage in comparison with the as-synthesized samples. A small contraction of the lattice was also observed.

Since extraction is an energy-intensive operation and an important source of waste, it is the objective of this work to develop a standard procedure which allows achieving a high yield of detemplation and optimizes the amount of solvent needed and the time required, as well as use a cheap, commercially available solvent. Therefore, the protocol, together with a synthesis time reduction, would be feasible to be industrially applied for large-scale catalyst synthesis.

Obtained materials exhibited high surface area and a good degree of mesoscopic order, comparable with materials obtained by the above-mentioned procedures. A high degree of template removal was achieved and the sulfonic groups were preserved in functionalized materials.

2. Experimental

2.1 Synthesis of *mesoporous silica SBA-15*

Mesoporous materials were synthesized according to standard procedures [9]. The SBA-15 material was prepared as follows: 4.5 g of Pluronic © P123 (Sigma-Aldrich) were dissolved in 140 ml of 1.9 N hydrochloric acid and kept under stirring overnight. Then the solution was heated to 40 °C and 0.046 mol (10.2 ml) of tetraethoxy-silane (TEOS, Sigma-Aldrich) were added. After 24 h of ripening (or after 4 h in reduced-time preparations), the mixture was transferred to a Teflon-lined autoclave and aged at 130 °C for another 24 h. Finally, the material was vacuum-filtered, washed with distilled water and dried.

The efficiency of commercial ethanol (96 wt.%) for the surfactant removal from the solids, and the influence of hydrochloric acid addition were studied in a Soxhlet device. The first step of the optimization of the preparation procedure was carried out in order to find the more efficient composition of the extraction solution. To do this, 1 g portions of non-functionalized silica from the same batch were contacted with different alcoholic solutions during 18 h and then dried. Samples after 6 and 12 h were also taken in some cases. Solutions employed were:

- a. 200 ml commercial ethanol (96 wt.% ethanol, 4 wt.% water).
- b. 200 ml commercial ethanol plus 2 ml commercial hydrochloric acid (resulting composition: 94.6 wt.% ethanol, 4.9 wt.% water, 0.5 wt.% HCl).
- c. 200 ml commercial ethanol plus 20 ml commercial hydrochloric acid (resulting composition: 83.6 wt.% ethanol, 11.6 wt.% water, 4.8 wt.% HCl).

For comparative purposes, other solids SBA-15 were prepared as reference using the classical procedure to remove the surfactant, by calcination under air flow, heating at 1.5 °C/min up to 550 °C and keeping the temperature during 2 or 6 h.

2.2 Direct synthesis of sulfonic-functionalized mesoporous silica

The extraction method was also tested for sulfonic-functionalized materials, which were prepared following the one-step synthesis procedure [1, 21], where a certain mol% of TEOS employed as silica-source in the preparation was replaced with 3-mercaptopropyl-trimethoxy-silane (MPTMS, Sigma-Aldrich), and hydrogen peroxide (H_2O_2) was used as oxidant. In every procedure, 0.046 mol of total silanes were employed and the corresponding proportion of TEOS and MPTMS was varied. 4.5 g of P123 were dissolved in 140 ml 1.9 N HCl overnight. Then TEOS was added and a 1 h prehydrolysis was carried out. After that, MPTMS and H_2O_2 were added. After 24 h of ripening, the mixture was transferred to a Teflon-lined autoclave and aged at 130 °C for another 24 h. Finally, the material was vacuum-filtered, washed with distilled water and dried. The surfactant was then removed by Soxhlet extraction with acidic ethanol, following the same procedure described in section 2.1, but contacting every whole batch (about 5 g) with 200 ml of solution. Materials were labeled with the code 24/S(N), where N is the mol% of MPTMS referred to the overall quantity of MPTMS and TEOS added, and ranged between 5 and 15. It is important to highlight that in this preparation procedure 40 ml of solvent per g of catalyst were used, which is significantly smaller than the value traditionally used.

Along with the novel detemplation procedure, a reduction in the standard ripening time from 24 h to 4 h was implemented and both series were then compared. The reduced time preparations involved the same steps, conditions and reactive amounts, with the only change of the ripening time (prehydrolysis and ageing durations were kept the same). These materials were labeled 4/S(N), with N representing the MPTMS quantity as already stated.

2.3. Characterization

Nitrogen adsorption–desorption isotherms were recorded at liquid-nitrogen temperature (-196°C) and relative pressure (P/P_0) interval between 1×10^{-3} and 0.975 in a Micrometrics ASAP 2020 equipment. Before the adsorption, samples were evacuated at 150°C during 3 h under vacuum of 1×10^{-5} Pa. Total pore volume was measured at the $P/P_0 = 0.975$ single point. The BET model in the relative pressure range $P/P_0 = 0.05\text{--}0.3$ [22] was used to calculate the total surface area, while the micropores volume and external surface area were derived from the t-plot, according to Lippens and de Boer [23]. The pore-size distribution was calculated employing the Broekhoff and de Boer (BdB) method [24] implemented via the code developed by Lukens [25], applied to both branches of the isotherm, having good agreement between both distributions.

The structure formation was corroborated by small-angle X-ray scattering (SAXS) in a SAXS/WAXS system Xenocs Xeuss 1.0, with a voltage of 50 kV and a current of 0.6 mA, equipped with an X-ray detector PILATUS 100 K (Dectris, Switzerland) and a Cu K α X-ray source with a wavelength of 1.54178 Å. The solids were loaded into an aluminum sample-holder and spectra were recorded in transmission mode at room temperature. Distance between sample and detector was kept constant during experiment, being 1360 mm.

Transmission electron microscopy (TEM) imagery was obtained with a JEOL 2100 Plus microscope equipped with a LaB $_6$ gun. Samples were suspended in ethanol and then two drops were deposited over a copper-grid. Bright field images were obtained under a voltage of 200 kV.

S and Si contents in the solids were measured by Energy-dispersive X-ray fluorescence (ED-XRF), using a Shimadzu equipment, model EDX-720, and working in the energy dispersion mode.

The amount of remaining surfactant in non-functionalized materials was characterized by temperature-programmed oxidation (TPO), which was carried out using a modified technique. CO_2 produced during surfactant burning was converted to CH_4 in a methanation reactor containing a nickel/kieselguhr catalyst and operating at 400°C . A H_2 stream (35 ml/min) was fed to this reactor, in order to quantitatively convert CO_2 into CH_4 . This compound was then continuously monitored by an FID detector. Typically, 10 mg of solid were placed in a quartz cell, and heated at $12^{\circ}\text{C}/\text{min}$, using 5% O_2/N_2 as carrier gas flowing at 30 ml/min. Additional details of the technique can be found elsewhere [26]. The calibration of the system was carried out with pulses of 1.26% CO_2/N_2 .

The remaining surfactant in functionalized materials and the oxidation-state of the groups was characterized by temperature-programmed stripping (TPS), employing a similar technique as TPO. Typically, 10 mg of solid were placed in a quartz cell, and heated at $12^{\circ}\text{C}/\text{min}$, using N_2 as carrier gas flowing at 30 ml/min. The pyrolysis products were monitored by an FID detector.

Thermogravimetric analyses (TGA) were performed in a Mettler-Toledo TGA/SDTA851^e module. Approximately 10 mg of sample were loaded into an alumina crucible and heated at 12 °C/min, from 20 °C to 750 °C, with a N₂ flow rate of 50 ml/min. The differential thermal gravimetric profiles (DTG) were obtained from the TGA profiles.

The amount of acid sites in the catalysts was determined by potentiometric titration. Potential was measured with an electrode of LiCl saturated in ethanol connected to a Metrohm 913 pH meter. Typically, 30 mg of solid were suspended with 40 ml acetonitrile in a 50 ml Erlenmeyer flask under vigorous stirring and kept until potential stabilization. Then, a solution of 0.01 M butylamine in acetonitrile was pumped at a rate of 0.10 ml/min into the flask while potential was recorded until values reached a clear plateau. The equivalency point was determined by a modified Gran linearization method [27].

3. Results And Discussion

3.1. Structure and Sulphur incorporation

The functionalized SBA-15 materials presented the same hexagonal 2-D mesostructure as non-functionalized SBA-15, as it was corroborated by SAXS (Fig. 1). The cell parameter remained almost constant, but the diffraction peaks were less sharp as sulfur content increased, indicating a progressive loss in ordering. For the material 4/S15 (curve g) and 24/S15 (curve f), it can be observed a very wide (100)-peak with a shoulder, indicating a poor ordering in the material. Moreover, nitrogen-sorption experiments showed an elongated hysteresis (Fig. 2) and a wider pore-size distribution (Fig. 3), as well as considerably lower pore volume than those of the other SBA-15 materials (Table 1).

Table 1
Morphological properties and acidity of the different materials

Material	S _{BET} (m ² /g)	V _P (cm ³ /g)	D _p (nm)	a ^a (nm)	S/Si ^b (mol%)	Acidity ^c (mmol/g)
4/S0	660	1.10	8.8	12.1	–	–
24/S0	601	1.27	8.9	–	–	–
4/S5	549	1.10	10.5	12.3	3.9%	0.37
24/S5	498	1.07	10.0	11.8	3.8%	0.34
4/S10	623	1.13	9.5	12.6	7.9%	0.81
24/S10	644	1.15	10.1	12.7	8.5%	0.88
4/S15	627	0.70	7.9	12.5	15.5%	1.55
24/S15	659	0.78	8.9	12.9	12.1%	1.24
^a hexagonal cell characteristic distance						
^b atomic proportion of Sulphur over Silicon, in percentage						
^c amount of titrated acid sites						

A reduction in synthesis time was tested, consisting in keeping the suspension only 4 h under stirring between the MPTMS addition and the transfer to the autoclave (4 h since TEOS addition in the case of non-functionalized materials). SAXS and nitrogen sorption confirm that the materials obtained have almost the same structural and textural properties (Figs. 1 to 3). Figure 4 compares the most relevant textural properties for every preparation.

From the results of ED-XRF (Table 1) can be seen that the incorporation of sulfur-containing functional groups is about 80% of the theoretical values. As will be shown below, the results of TGA and stripping analyses (Figs. 7 and 8) showed the full oxidation of the mercaptans, being sulfonic groups the only present species. The amount of acid sites measured by acetonitrile titration exhibited a good correlation with the Sulphur content, indicating that the sulfonic groups are accessible and thus catalytically relevant. These quantities resulted comparable with those obtained by a co-condensation method followed by a standard extraction [9]. Moreover, the amounts of acid sites in the materials were higher than those of sulfonic SBA-15 produced by grafting methods and post-oxidation protocols with much higher Sulphur content [28].

3.2. Template extraction and functional groups oxidation

The detemplation of SBA-15 in a Soxhlet device was studied. Figure 5 shows the carbon content measured by TPO, after different detemplation times using the different solutions mentioned previously. For comparison, the carbon content detected after calcination is also included. It can be seen that all the extraction methods remove almost 90% of the surfactant, remaining an amount which is only removable by calcination. Hydrochloric acid addition improves the kinetics of extraction, allowing a reduction in the detemplation time, however there is no practical difference between the addition of 1% and 10% of hydrochloric acid.

In order to have further insight in this phenomenon, the temperature-programmed oxidation (TPO) for the non-functionalized SBA-15 sample was conducted before (non-extracted) and after the different detemplation procedures. The resulting profile for the non-extracted sample (Fig. 6) clearly shows two regions: a main peak below 650 K and a smaller, broad peak above 650 K. Surfactant Pluronic® 123 consists in hydrophobic and hydrophilic sections, and the latter could be partially embedded in the silica wall after condensation [29], thus being more difficult to be extracted and therefore needing higher temperatures to be burnt. This portion of the surfactant would be then the fraction corresponding to the second half of the profile. The TPO result obtained after ethanol extraction shows that this solvent removes mainly the surfactant that burns below 650 K, but it only partially dissolves the polymer strongly attached to the silica walls. Hydrochloric acid addition leads to a faster extraction, removing a greater amount of surfactant. Nonetheless, the fraction of remaining polymer with higher burning temperatures is only slightly reduced with the increase of hydrochloric acid concentration (see the insert in Fig. 6).

It is important to study the stability of the functional groups, so the extraction procedure was then applied to a functionalized sulfonic SBA-15 catalyst. Figure 7 exhibits the first derivative of the weight loss curves (DTG) obtained from TGA analyses of a 4/S10 material, before (A) and after (B) extraction only with ethanol in this case, during 18 h. The peak centered around 350 K corresponds with adsorbed water and residual ethanol. The peak located between 750 and 800 K represents the decomposition of propyl-sulfonic functional groups [9]. The surfactant loss, as was discussed above, was associated with a sharp peak centered at 425 K, which is absent for the extracted material. Weight loss of the 750 K peak was 19.6% (non-extracted sample) and 17.8% (extracted with ethanol), both percentages referred to the final weight of the experiment, in order to avoid the effect of surfactant and water content. In agreement with this fact, Sulphur content of the samples measured by ED-XRF dropped from 10.2% (non-extracted sample) to 7.9% (extracted sample), representing a 20% decrease. Taking into account that the sample was treated in the autoclave with 1.9 N hydrochloric acid, up to 130°C, it seems difficult that the groups be hydrolyzed during the extraction procedure, which is much less severe than the previous step in the autoclave. The most probable cause of the decrement is a poor linkage of the groups with the surface or even condensation in small clusters not linked with the main structure which are washed by the extraction.

Figure 8 shows the nitrogen stripping profiles for sulfonic-functionalized SBA-15 materials (with different Sulphur-loads) after extraction with ethanol and 1% hydrochloric acid and also for a non-extracted sample. Peaks below 400 K are consistent with the presence of ethanol, probably due to insufficient

drying. The absence of a peak around 450 K in extracted samples is associated with the extraction of most of the surfactant, in agreement with the results obtained with non-functionalized materials. The main peak, centered around 800 K, corresponds with the decomposition of propyl-sulfonic groups, while the small peak around 600 K is related with the propyl-mercaptan groups [9]. Therefore, the oxidation performed during the synthesis was nearly complete. Moreover, there is good agreement between the stripping and the DTG curves for the first sample. The nitrogen stripping with a FID detector features more sensitivity and makes it possible to detect very small contributions of non-oxidized mercaptans, even though it is not quantitative.

4. Conclusions

Sulfonic-functionalized SBA-15 materials with high amount of acid sites, uniform pore-size-distribution and high surface area can be prepared according to a straightforward procedure requiring less time and reducing significantly the amount of waste produced. The key factor is the use of a Soxhlet extractor to reduce the amount of solvent required. This improvement also enables the handling of bigger batches of solid, which, along with the usage of commercial solvents, is crucial for a scale-up of the catalysts production.

Declarations

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Competing interests

The authors declare that they have no conflict of interest.

Author contributions statement

L.G. Tonutti performed most of the experiments and wrote the manuscript. M.A. Maquirrian contributed to the experimental part and preparation of figures. C.A. Querini reviewed and discussed the results, and contributed to the improvement of the manuscript contextualizing the information. B.O. Dalla Costa reviewed and discussed the results, and contributed to the improvement of the manuscript contextualizing the information.

All authors reviewed the final manuscript.

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Figures

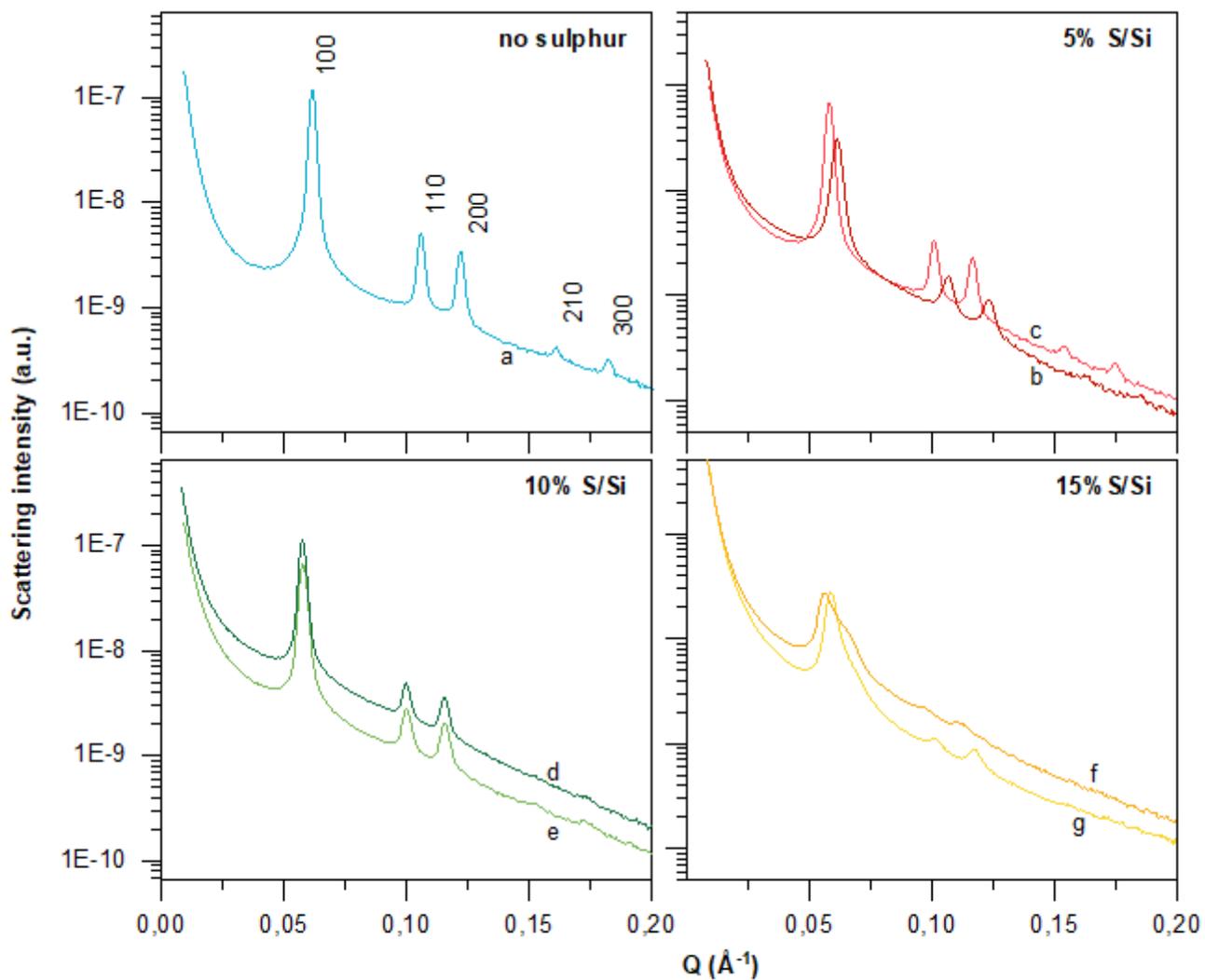


Figure 1

Figure 1

SAXS of SBA-15 synthesized with different sulfur loads and under different synthesis times. (a) 4/S0; (b) 24/S5; (c) 4/S5; (d) 24/S10; (e) 4/S10; (f) 24/S15; (g) 4/S15. In curve **a**, the structure planes are indexed

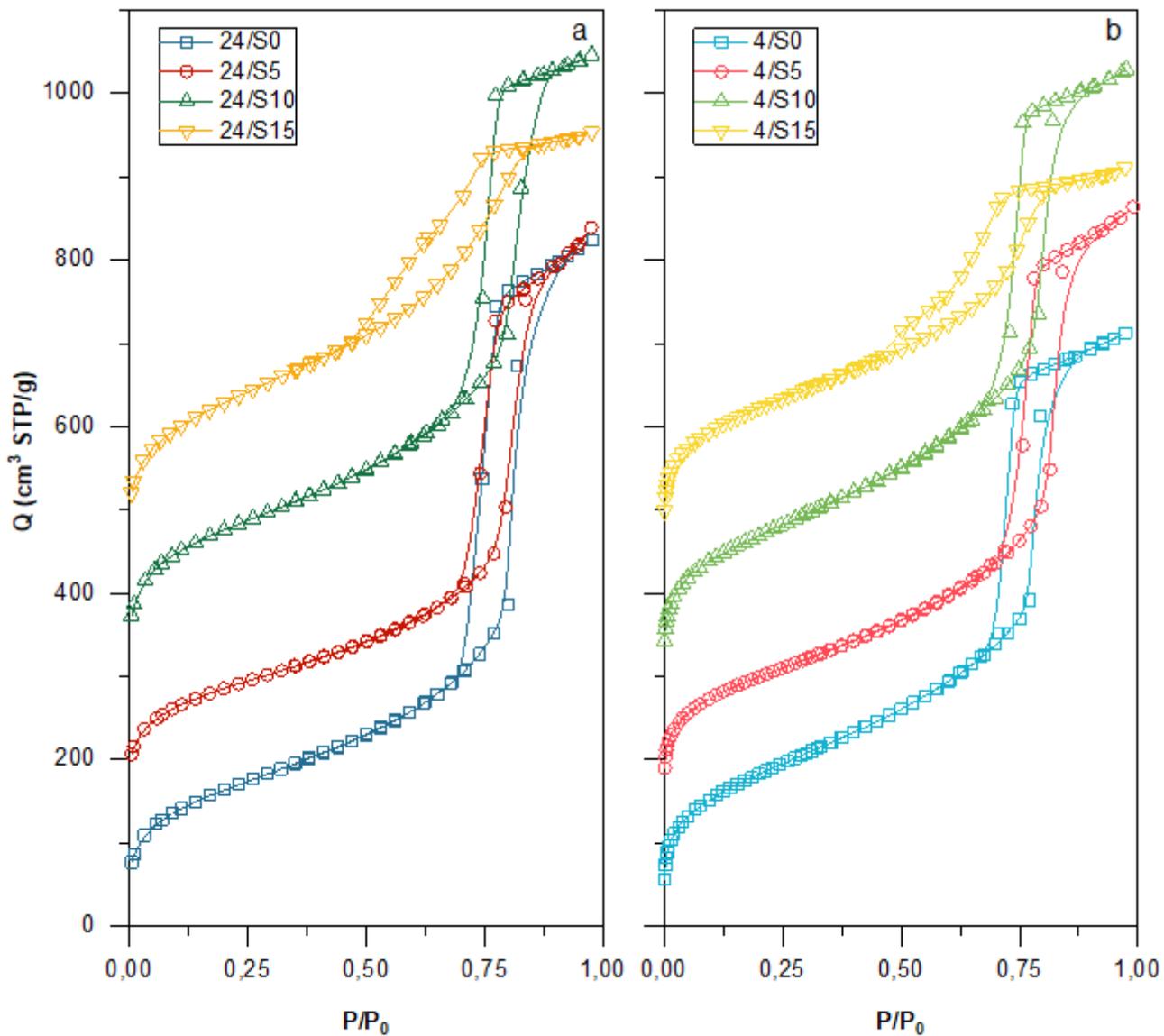


Figure 2

Figure 2

Nitrogen adsorption-desorption isotherms of SBA-15 synthesized with different sulfur loads and under different synthesis time. Every curve is offset 150 cm³/g of the one immediately below

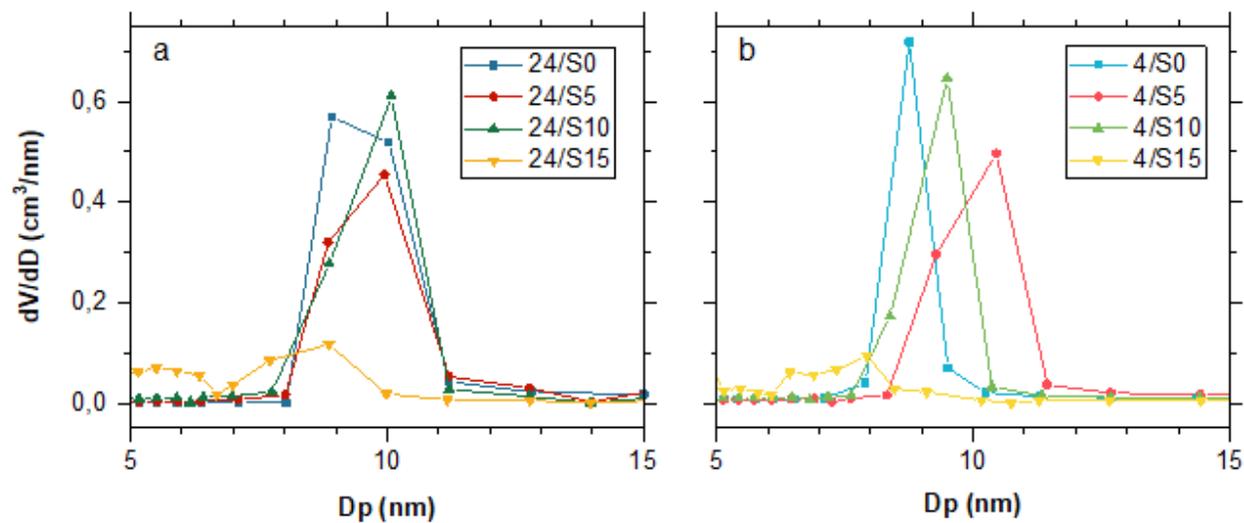


Figure 3

Figure 3

Pore-size distributions of SBA-15 synthesized with different sulfur loads and under different synthesis time. Values obtained from the desorption branch

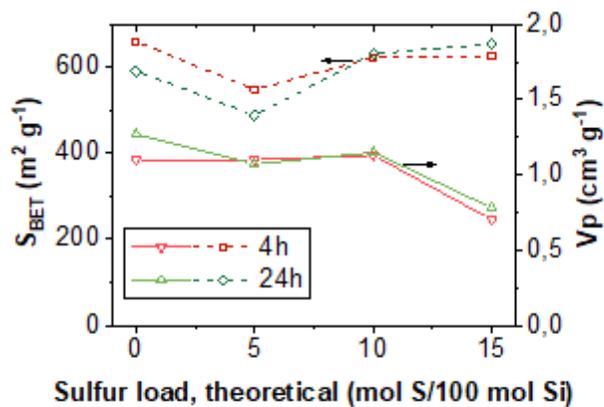


Figure 4

Figure 4

Influence of the sulfur load and the synthesis time on textural properties in SBA-15.

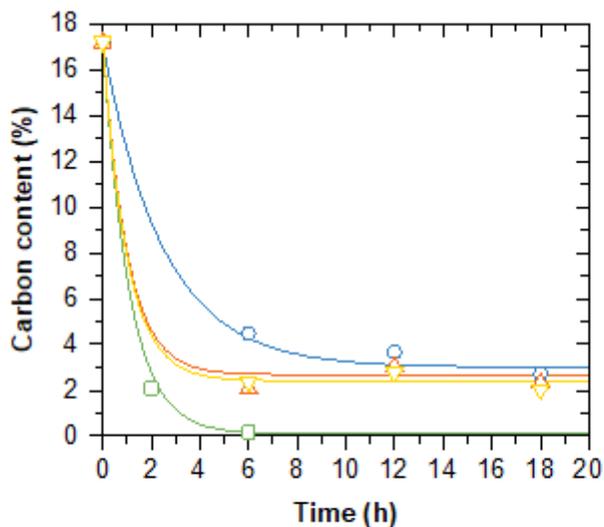


Figure 5

Figure 5

Carbon content determined by TPO over SBA-15 samples subjected to different detemplation procedures: (■) calcined, (●) extracted with ethanol, (▲) extracted with ethanol and 1% HCl; (▼) extracted with ethanol and 10% HCl

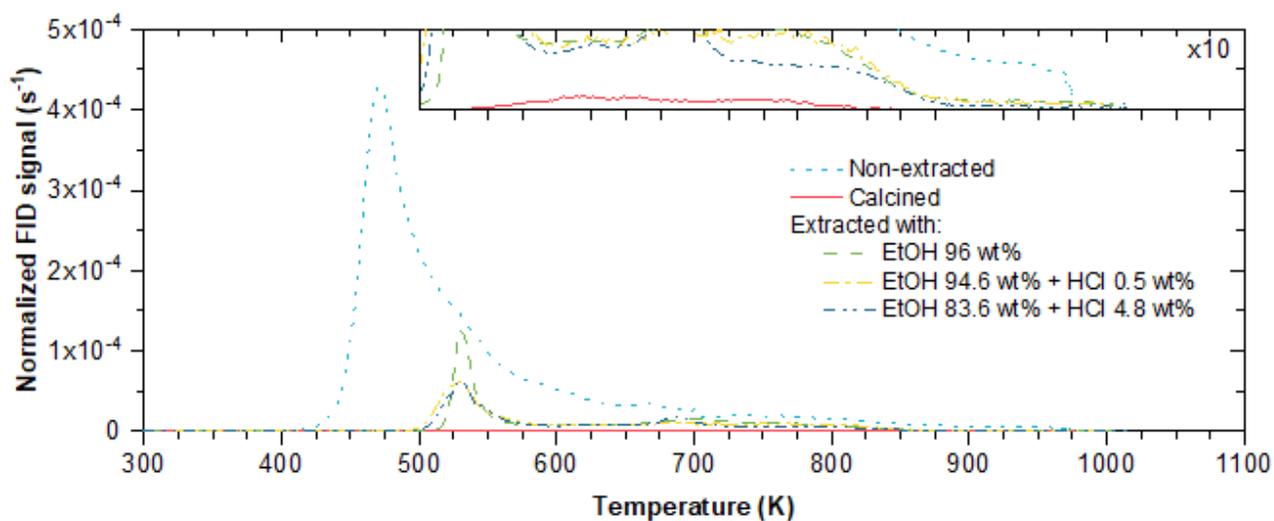


Figure 6

Figure 6

TPO profiles of SBA-15 sample before (non-extracted) and after different detemplation procedures

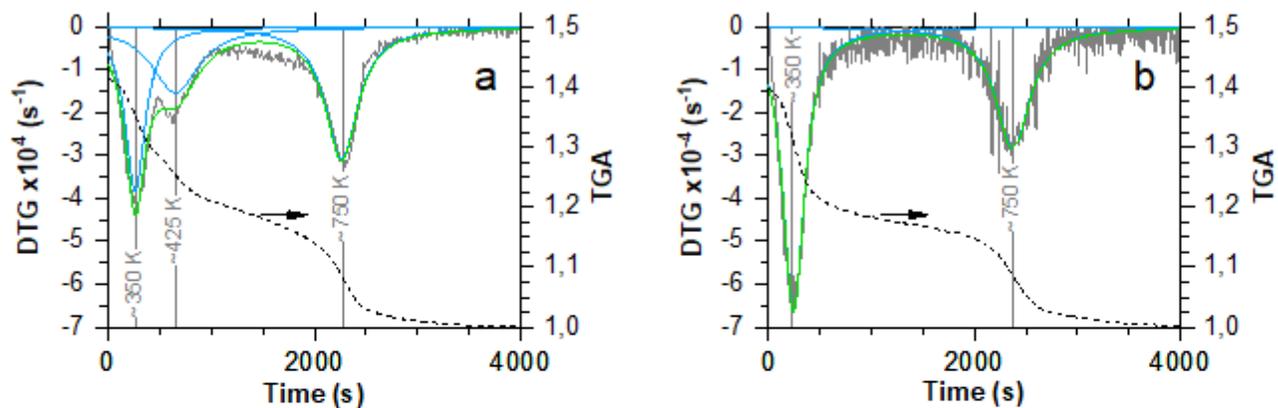


Figure 7

Figure 7

DTG profiles of a Sulfonic functionalized SBA-15 before (A) and after (B) ethanol extraction

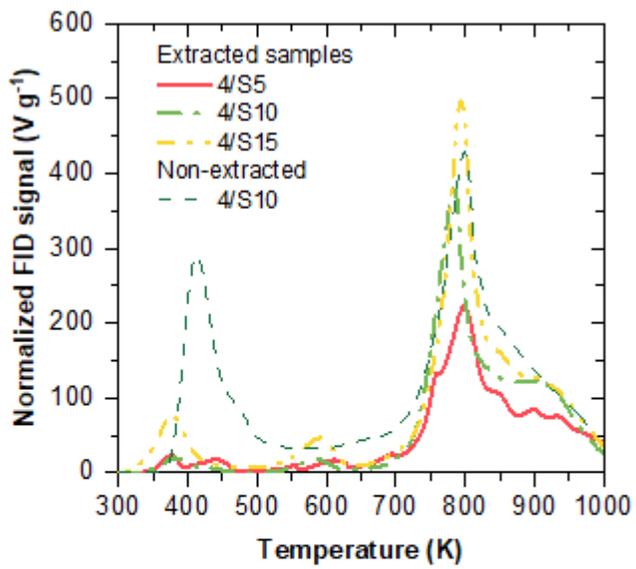


Figure 8

Figure 8

Nitrogen stripping profiles of different sulfonic-functionalized mesoporous materials