

Synthesis and characterization of SBA-15 materials functionalized with olefinic groups and subsequent modification through oxidation procedures

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Abstract

The synthesis of alkenyl-SBA-15 materials has been carried out through different methodologies. The direct-synthesis method used for the functionalization of SBA-15 involving the co-condensation of the alkenyl-silicon precursor together with silicon alkoxides is clearly superior than any other post-synthetic pathway, even if acid catalysts are used to drive the post-synthetic grafting of olefin groups. The direct-synthesis methodology has been deeply studied within this work, involving the influence of the silica precursor prehydrolysis time, and the loading of different olefin-silanes on the quality of the mesostructure. Small olefinic functionalities, like vinyl groups, can be incorporated in a very efficient manner up to achieve organic loadings as high as 50% mole of the olefin precursor to TEOS. The modification of these alkenyl groups through oxidation can be accomplished through post-synthetic oxidation of the olefinic group or even through an in-situ methodology where the oxidant – hydrogen peroxide – is added together with the rest of the precursor into the synthesis gel to lead complete oxidation of the double bonds towards glycolic functionalities. The resultant materials show potential as hydrophilic adsorbents and catalytic supports.

Keywords: Organic functionalization, SBA-15, olefin groups, in-situ oxidation, glycols.

1. Introduction

The synthesis of mesostructured materials [1,2] has received much attention since their discovery in early 90's because of the high potential of these solids in many fields. The high surface area and pore volume values together with the narrow pore size distribution inherent to these materials [3] make them specially attractive to be used as supports for heterogeneous catalysis [4,5], adsorbents [6], supports for chromatography stationary phases [7,8], and many others. Thus, mesostructured materials have been functionalized with both inorganic and organic species in order to provide additional physico-chemical properties to the silica parent material. Inorganic species such as salts, metals or metal oxides [9,10] are usually incorporated to the structure of mesoporous materials searching a specific catalytic activity, whereas organic species [11,12] are typically supported looking for special physical or chemical properties in the solids, such as hydrophobicity/hydrophilicity, chemical affinity and reactivity and also catalytic activity [13].

Organic functionalization of mesostructured materials can be accomplished by two main routes: post-synthetic surface transformations and direct synthesis procedures [11]. Post-synthetic surface functionalization is usually carried out through grafting procedures. Other methods, such as hydrosilylation [14] can also be employed, though these are less widespread than surface grafting. Post-synthesis functionalization usually takes advantage of the surface reactive groups, which are liable to be modified with several organic moieties to be anchored onto the silica surface. In this method both the silylation of silica and the phosphorilation of metal oxides can be included. The post-synthetic methodologies usually leads to low functionalization degrees together with a low dispersion of the functionality, since the amount of organic loading incorporation is limited by the initial density of surface silanols groups. On the other hand its

accessibility is always ensured, the materials are ordered after the process, and a great variety of functional groups can be incorporated depending on the application [15]. As alternative, the direct synthesis pathway, also named co-condensation, involves the addition of a proper functionality to the synthesis media, together with the silicon precursor and the structure directing agent. In this way, high functionalization degrees, as well as good dispersions can be achieved but the organic functionality can be blocked inside the pore walls being not accessible through the porous system [16], also affecting the ordering of the mesostructure if the functionality load is too high.

A huge variety of organic moieties have been used to functionalize mesostructured materials, looking for additional properties to be conferred onto the resultant hybrid organic-inorganic samples, from the simple methyl group to very complicated organic compounds, such as salen [17] or porphyrin ligands [18]. One of the most useful type of organic functionality to be supported onto silica framework are olefins because of the relative easiness on undergoing various modifications on the double bond, leading to a whole library of different immobilized organic functionalities. In this way, the functionalization of mesostructured materials with olefinic organic groups has been extensively studied and several works have been reported. Most of them refer to co-condensation functionalization procedures, because of the high chemical resistance of the olefinic groups under the synthesis conditions used to prepare mesostructured materials. Thus, Kruk *et al.* [19] reported the synthesis of vinyl MCM-41 materials varying the amount of vinyl loading in a wide range. This study proved the transition of the pore size from mesoporous to microporous when high loading of organic functionality was used. Nevertheless, the samples prepared with high vinyl loading evidenced damages on the structure ordering. Wang *et al.* [20] reported the synthesis of SBA-15 and SBA-16 type materials functionalized with vinyl groups also through co-

condensation routes. In this case, the amount of organosilane was kept below 20 %mole regarding the silica source. Although the ordering degree of the functionalized materials was good, it was even better for SBA-15 type samples. Later, Chong *et al.* [21] described a similar methodology for the preparation of vinyl-SBA-15 materials with higher functionality loadings. However, the samples prepared with higher loadings than 20 mole% of organosilane functionality displayed poor orderings. Wang *et al.* [22] reported a way to overcome this limit in the amount of olefinic groups without causing damages on the mesostructure through the use of $MgCl_2$ in the synthesis media. Finally, Kao *et al.* [23] have reported the synthesis of cubic SBA-1 materials containing vinyl functionalities, though the porous structure was readily blocked

Several transformations of double bonds into other organic functionalities have been applied to the modification of olefin-functionalized mesostructured materials. Thus, brominations [24,25], sulfonation [26], hydroborations [26-28] or oxidations [28,29] have been performed over olefin functionalities supported onto mesostructured materials. Thus, Asefa *et al.* [29] modified vinyl-MCM-41 type materials through a post-synthesis transformation in two stages including the epoxidation of olefin groups with mCPBA followed by the acid hydrolysis of the oxiranes to produce glycolic functionalities. Herein we report the synthesis of SBA-15 type materials functionalized with high loadings of olefinic groups and their subsequent oxidation to achieve glycolic functional groups directly attached onto mesostructured materials. For this purpose, different synthesis and oxidation pathways have been used, widely discussing the effect of using both post-synthetic functionalization pathways and co-condensation single-step synthesis routes. Besides, the oxidation of olefin pendant groups was also investigated using two different strategies, post-synthetic oxidation and in-situ oxidation – in which hydrogen peroxide is added as oxidant agent into the synthesis gel –.

2. Experimental

2.1 Materials and methods. Pluronic P123 (PEO₂₀-PPO₇₀-PEO₂₀; Aldrich) was used as structure directing agent for the preparation of SBA-15 type mesostructured materials. Tetraethyl orthosilicate (TEOS, Aldrich), vinyltrimethoxysilane (VTES, Aldrich) and butenyltriethoxysilane (BTES, Aldrich) were used as silicon precursors for the pure siliceous and organically modified mesoporous materials respectively and were used as received. Toluene (Scharlab) was distilled from sodium prior to be used as solvent for the grafting functionalization. Hydrogen peroxide 30 %wt. in water was used as oxidation agent, both in the post-synthetic and in-situ oxidations. When used, organic loading refers to the molar ratio organosilicon precursor to silica or silica precursor in the synthesis of olefin functionalized materials through post-synthetic grafting or co-condensation procedures respectively.

2.2 Synthesis of SBA-15 pure silica. The synthesis of pure siliceous SBA-15 materials was accomplished through the method reported by Zhao *et al* [2]. In a typical synthesis 4 g of pluronic P123 were dissolved in 125 mL of aqueous 1.9N hydrochloric acid in a round bottom flask at room temperature. After complete dissolution, the mixture was warmed up to 40°C and 8.6 g of TEOS were added in a single step. The solution was then vigorously stirred for 20 hour at 40°C and hydrothermally aged at 100°C for another 24 hours. The product was then recovered by filtration and air dried. Finally, surfactant was removed from inside the porous structure by calcination in static air at 550°C for 5 hours to give the product as a white powder.

2.3 Synthesis of vinyl- and butenyl-SBA-15 materials. SBA-15 type materials were functionalized with vinyl and butenyl functionalites using alkenyltrialkoxo silanes as olefinic starting precursors. The functionalization of SBA-15 materials was carried out by two different ways. The first route involves the co-condensation of the olefinic

starting material with tetraethyl orthosilicate. The second strategy was the post-synthetic modification of a pure siliceous material through a grafting step.

2.3.1 Co-condensation. This synthesis method is a modified version of the procedure above described for the preparation of pure siliceous material. Thus, after the addition of the TEOS to the warm solution containing the structure directing agent, the alkenyl functionality starting precursor was added to the synthesis media. At this point two different synthesis variables were evaluated: the prehydrolysis time for TEOS and the molar ratio alkenyl precursor / orthosilicate. Thus, TEOS was prehydrolyzed, because the strong effect this parameter shows both in the incorporation of organic functionalities in SBA-15 materials and mainly in the ordering degree of final materials [30,31]. Thus, this parameter was varied in the range from 0 – simultaneous addition of TEOS and alkenyl functionality – up to 90 min, whereas the molar ratio alkenyl starting precursor to TEOS was varied from 0.2 to 1.0. The resultant suspensions thus obtained were stirred for a period of 20 h at 40°C, and hydrothermally aged at 100°C in an autoclave under autogenous pressure. The solid was then recovered by filtration and air dried. The surfactant removal was performed by extraction with ethanol in a similar way to that reported by Zhao *et al.* [2]. Typically, 1 g of as-made material was treated with 100 mL of ethanol under reflux overnight. The solids were then recovered by filtration while still warm and thoroughly washed with fresh ethanol before air dried.

2.3.2 Grafting. The post-synthetic functionalization of pure silica SBA-15 materials was accomplished by means of thermal and catalytic grafting. Thus, a suitable amount of SBA-15 material – typically 2 g – previously outgassed at 160°C under high vacuum overnight, was suspended in dry toluene. The alkenyltrialkoxo silane precursor was then added to the resultant suspension and stirred for 1 hour to allow the diffusion of the organic functionality in the porous structure of the material followed by refluxing

during 24 hours. If catalytic, the grafting procedure was carried out in presence of p-toluene sulfonic acid (PTSA) in the refluxing medium – molar ratio alkenyl precursor to PTSA of 40 –, accordingly to the procedure reported by Garcia *et al.* [15]. The solids were then recovered by filtration and washed with toluene in a Soxhlet apparatus overnight. After filtration under vacuum the resultant materials were then dried at 120°C overnight.

2.4 Oxidation of olefinic groups. The oxidation of the olefin functionalities to glycolic groups was carried out in two different ways, after the synthesis of the olefin-functionalized materials and simultaneously during the preparation of the material, called in-situ oxidation. In both cases hydrogen peroxide was used as oxidizing agent. Thus, for the post-synthesis oxidation, 1 g of olefin functionalized SBA-15 material was suspended in 200 mL of acetone and hydrogen peroxide was added in a molar ratio $\text{H}_2\text{O}_2 / \text{double bonds} = 5:1$. The suspension was then warmed up to 55°C and stirred for 24 hours before recovering the material by filtration. Then, the material was washed with fresh acetone and dried. On the other hand, in-situ oxidation was carried out through the addition of hydrogen peroxide to the synthesis medium during the preparation of the functionalized material through the co-condensation pathway. In this case, a similar procedure to that described by Margolese *et al.* [32] for the preparation of sulfonic acid functionalized mesoporous SBA-15 materials was used. This method is the same as above described unless in this case an aqueous solution of hydrogen peroxide (30 %wt.) is added together with the alkenyl precursor in a molar ratio $\text{H}_2\text{O}_2 / \text{olefin} = 5:1$. The rest of the synthesis procedure comprises the same steps already described.

2.5 Characterization techniques. Olefin and glycol functionalized SBA-15 type materials have been characterized by means of different analytic techniques. Thus,

nitrogen adsorption-desorption recorded at 77K were acquired on a TriStar 3000 unit (Micromeritics). The samples were previously outgassed under nitrogen flow for 12 hours at 125°C. Surface area values were calculated through the B.E.T. method. Pore size diameter was determined by the B.J.H. method using the K.J.S. correction. Total pore volume was recorded at $p/p_0=0.985$. X-ray diffraction patterns were collected on a Philips X'pert diffractometer using the Cu K α line in the range $2\theta = 0.5^\circ$ to 5.0° with a step size of 0.2° . FTIR analyses were collected, using the KBr buffer technique, on a Mattson Infinity series apparatus in the wavelength range from 4000 to 400 cm^{-1} with a step size of 2 cm^{-1} and collecting 64 scans for each analysis. Solid-state ^{13}C and ^{29}Si MAS NMR experiments were performed on a Varian Infinity 400 MHz spectrometer fitted with a 9.4 T magnetic field. These nuclei resonate at 100.53 and 79.41 MHz, respectively. An H/X 7.5 mm MAS probe and ZrO_2 rotors spinning at 6 kHz were used. On CP experiments, the cross-polarization time was determined to guarantee the total proton polarization verifying the Hartmann–Hann condition. In addition, to allow an accurate quantification of silanol groups, ^{29}Si NMR spectra using one-pulse sequence were also obtained. For ^{13}C acquisition, $\pi/2$ pulse, number of scans, repetition delay and contact time were 4.25 μs , 2000 scans, 3 s and 1 ms respectively. The ^{29}Si experiments accumulated 3000 scans with a $\pi/2$ pulse of 3.5 μs and 15 s of repetition time.

3. Results and discussion

3.1 Synthesis of olefin-functionalized SBA-15 materials

The functionalization of SBA-15 materials with olefinic substrates has been accomplished using two different olefin groups – vinyl and butenyl functionalities – in order to determine the effect of the size of the organic group on the final properties of the mesostructured materials. Attempts of functionalization with allylic groups were

unsuccessful because the stabilization of negative charges by silicon atoms at beta position destabilizes the olefin group which is removed during the surfactant extraction step with ethanol. Different synthesis variables were studied to achieve high organic functionalization degrees, always preserving well ordered mesostructures. Table 1 lists the functionalization procedures and synthesis conditions assayed in the preparation of vinyl- and butenyl-SBA-15 materials as well as their physicochemical properties.

3.1.1 Vinyl-SBA-15 materials

The synthesis of olefin-functionalized SBA-15 type materials was firstly accomplished by treating a pure silica sample with vinyl triethoxysilane through different grafting methods. Thus, SBA-15 material was treated with the vinyl precursor both in presence and absence of PTSA as grafting catalyst. Both treatments led to remarkable changes on the original textural properties measured for the parent pure siliceous material (see Table 1, samples S0 to S2 - figure 1). Thus, the surface area and pore volume greatly decreased when grafting vinyl functionalities, whereas the observed reduction on the pore size was much lower. Additionally, the differences between the silica support and the treated materials are greater for the sample prepared through catalytic grafting (Table 1, sample S2). Several conclusions can be derived from these differences: Firstly, the loss of surface area and pore volume without the consequent proportional reduction in the pore size indicates partial blocking of the porous structure so that, the functionalization through grafting leads to non-homogeneous distribution of the silylating agent on the particle. Secondly, higher extension on the functionalization degree can be achieved when using catalyzed grafting route, as it could be stated from the observed increase in the pore wall thickness. Besides, the incorporation efficiency of vinyl functionalities through these grafting methods has been evaluated by means of

solid state ^{29}Si MAS NMR experiments. Figure 2 depicts the silicon spectrum showing different species present in both the functionalized samples and the pure silica parent material. The area below the curves calculated from deconvolution of ^{29}Si NMR spectra represents the number of silicon atoms of each species. Two different groups can be distinguished in the ^{29}Si NMR spectra, located in the regions around -66 ppm and -100 ppm chemical shift. The first one is attributed to the presence of T silicon atoms, which are silicon species directly bonded to carbon atoms coming from the olefin precursor. Q signals, the second type of silicon atoms, resulted from the hydrolysis and condensation of the TEOS silicon precursor, show three different kinds of silicon environments. The first class corresponds to silicon atoms directly bonded to other silicon atoms by oxygen bridges. The number of these bonds can be 4 (Q^4 species, $\delta = 110$ ppm), 3 (Q^3 species, $\delta = 100$ ppm) or 2 (Q^2 species, $\delta = 90$ ppm), the coordination sphere being completed with hydroxyl groups. Thus, being the amount of T groups directly related to the presence of vinyl functionalities, the functionalization degree can be calculated as the ratio between the area calculated for T groups referred to the area below Q plus T groups. In this way, the incorporation efficiency can be calculated as the functionalization degree referred to the initial amount of organic loading added into the synthesis gel. However, the vinyl incorporation degree reached when using PTSA as grafting catalyst is much higher than that obtained through the thermal grafting, according to the higher area below the curves corresponding to T groups in the former (see table 1, samples S1 and S2).

The synthesis of SBA-15 materials functionalized with vinyl groups was also performed through a co-condensation pathway. This synthesis was optimized by means of studying different variables, like the prehydrolysis time for TEOS before the addition of the vinyl source. The influence of this parameter was assessed on the textural parameters, the

ordering degree achieved on the final mesostructured materials as well as on the incorporation efficiency of the vinyl group. Figure 3 displays the influence of prehydrolysis time for TEOS on the nitrogen adsorption-desorption isotherms (Figure 3A) and X-ray diffraction patterns of the final samples (Figure 3B). All the materials display the classical type IV isotherms, accordingly to the I.U.P.A.C. classification, featuring a pronounced steep region due to capillary condensation at relative pressure $P/P_0=0.6-0.7$, characteristic of mesostructured materials. With regards to the effect of the TEOS prehydrolysis time on the textural properties of the vinyl functionalized SBA-15 materials, increasing this parameter results in lower values for total pore volume and surface area, whereas the pore size slightly increases (See table 1). Besides, unlike sample S3 – prepared without prehydrolyzing the TEOS source – the samples display steep H1 hysteresis loops in the isotherms typical from large pores in mesostructured samples with narrow pore size distributions (Figure 3A inside). In contrast sample S3 shows less pronounced slope on the hysteresis loops which leads to a wide pore size distribution suggesting the material probably does not possess a considerable extent of pore ordering.

This behaviour can be explained considering the interaction between the precursor of the vinyl group and the surfactant micelles. Since vinyl precursor is a hydrophobic functionality, its interaction with the micelles is most likely, bearing in mind its organic nature. This interaction could distort micelles because of the strong affinity and the possible penetration of vinyl groups inside the surfactant micelles. This distortion is avoided when prehydrolyzing the TEOS precursor, since the hydrolysis of the alkoxide groups of TEOS occurs simultaneously to the condensation of silicon species, though at different rates. This previous step to the addition of the olefinic substrate creates a film of silica around the micelles providing some additional stability against the strong

interaction with the vinyl group. Although the silica is readily formed once TEOS has been added to the synthesis medium, the coverage of micelles is not complete in early stages, and thus vinyl functionalities can migrate through the forming silica layer to interact with the surfactant, though the longer prehydrolysis time, the more difficult access of vinyl groups to the micelles. In this way, larger prehydrolysis times lead to somewhat lower incorporation efficiency of vinyl groups, as it can be stated from data collected from ^{29}Si MAS NMR analyses (See table 1). Sample S6, prepared with a TEOS prehydrolysis time of 90 minutes, display lower concentration of vinyl groups than the other materials (Table 1, samples S3-S5), probably because hindered access of the vinyl silane precursor to the micelles.

The above mentioned conclusions are supported by XRD analyses. X-ray diffraction patterns recorded for samples S3 to S6 have been depicted in figure 3B. All the samples, unless sample S3 because of the above mentioned reasons, display the typical diffraction pattern of a mesostructured material with a hexagonal $p6mmc$ array of pores. The ratio between the intensities obtained for 110 and 100 diffractions can provide an approximation to the ordering degree of the sample, being higher when higher ratio is achieved. Thus, sample S3 display a much poorer ordering degree than the other materials since the 110 diffraction is completely missed. When increasing the TEOS prehydrolysis time, the ratio between intensities grows, which means a better ordering degree (Figure 3B insets). This fact supports the conclusions about the interaction of the organic groups and the surfactant micelles.

When comparing the post-synthesis functionalization procedure with the co-condensation method (See table 1), it is noteworthy that unlike the direct synthesis [24], the grafting procedure do not lead to complete immobilization of the starting vinyl precursor. Thus, the incorporation efficiency is not 100%, though the catalyzed grafting

leads much higher incorporation of olefin species than thermal grafting, more than twice, as already described. Besides, it should be considered the anchoring points for the immobilization of the alkenyl functionalities are limited when using the grafting procedure since those are completely dependent on the amount of accessible silanol groups. On the contrary, the immobilization of the organic groups through direct-synthesis is not limited in this matter and in this way, this method show a higher potential to achieve large functionalization degrees on the final materials – almost 100% incorporation (See table 1, samples S3-S5). Thus, the rest of the research was carried out using the co-condensation method as functionalization technique. Besides, since increasing the TEOS prehydrolysis time leads to better ordered materials but lower incorporation of vinyl functionality, the synthesis conditions used in the rest of the investigation here reported were selected by compromising both facts. Thus, 60 minutes were selected as the proper time for prehydrolyzing TEOS because almost total incorporation of vinyl groups is achieved (99%), while keeping highly ordered mesostructured materials.

Another important parameter studied in the preparation of vinyl-functionalized SBA-15 materials, once the optimal TEOS prehydrolysis time was fixed, was the maximum organic loading that the SBA-15 structure can accommodate keeping a high ordering degree. For this purpose, several loadings of vinyltrimethoxysilane were used, ranging from 10% to 50% of organosilane to TEOS on a molar basis (Table 1, samples S5, S7-S9). Nitrogen adsorption-desorption tests revealed the dramatic influence of the organosilicon amount on the final textural properties of the vinyl-functionalized materials. Thus, increasing the organic loading promotes a great decrease on the surface area, pore size and pore volume. Those reductions are more intense insofar as the organic content increases, probably as consequence of destructuration of the material for

large organic loadings. This fact is easily assessed through nitrogen adsorption-desorption experiments (see figure 4(A)). Whereas low organic loading leads to well structured materials, increasing the amount of vinyltrimethoxysilane causes not only a great decrease on all the textural properties, but the shape of the isotherm is also shifted. Thus, from sample S5, containing 10% mole of vinyl functionalities, to sample S9 – 50% loading of vinyl silane – the hysteresis loops become wider, indicating the partial destruction of order in the material. With regards to the pore size distributions, not only the maximum of the distributions are displaced towards lower pore size but also the area below the curves decrease when higher loading of vinyl functionalities are used. These facts suggest the incorporation of the organic functionalities takes place inside the mesopores. The increase of the organic loading shows some consequences on the quality of the structure ordering. XRD patterns (see figure 4(B)) recorded for the samples with increasing quantities of vinyl functionalities reveals that the mesostructure of the materials is partially affected. Thus, for the sample with the lowest amount of vinyl silane groups the diffraction pattern is that typical from hexagonal mesostructured silicas, but the diffractions corresponding to larger interplanar spaces are partially missed for samples with higher organic loading. This result could be a consequence of the loss of long range ordering, probably because, as stated above, an excessive amount of vinyl functionality causes some distortion in the structure directing agent micelles and thus, the ordering of the mesophase is not as high as that achieved for a non-functionalized pure silica SBA-15 material. Nevertheless, the main diffraction peak is clearly visible for all the samples – though quite less intense in sample S9 showing the largest amount of vinyl silane among the tested materials –, shifted towards lower angle values insofar as the amount of organic functionality becomes higher. This means larger interplanar d_{100} spacings that combined with smaller pore sizes results in wider pore

wall thickness. This result supports the above mentioned conclusions about the incorporation of the organic functionality onto the surface of mesopores, and increasing therefore the size of the pore walls.

With regards to the incorporation efficiency of the organic functionality onto the final materials, figure 5 depicts the ^{29}Si NMR experiments carried out on samples S7-S9, as well as ^{13}C NMR spectrum recorded for sample S9. As in the case of the vinyl-SBA-15 materials prepared through the grafting procedures, the samples prepared with different organic loadings also display both Q and T silicon groups. The area below T groups increase when higher loadings are used. The deconvolution of the ^{29}Si NMR curves gives surprising results since, regardless to the amount of vinyltrimethoxysilane used in the synthesis of the materials, almost 100% of the organic functionality precursor is finally incorporated to the mesostructured materials. This is a quite interesting result if compared with similar reported studies in which the incorporation of the organosilane precursor to the final materials is not complete for such high loadings as those used in the present study [20,21]. Besides, some authors have reported the complete destructuration of the final materials when using very high vinyl silane functionalization degrees, but in our case the samples present rather good structure ordering, bearing in mind the high concentration of loaded vinyl silane groups, even for sample S9 – 50% vinyl silane / TEOS molar ratio –. Regarding the ^{13}C NMR spectrum, tertiary carbons located at vinyl double bonds are clearly visible, demonstrating the initial olefinic functionality structure is well preserved during the synthesis of these materials. Secondary signals, such as those corresponding to remaining surfactant after extraction with ethanol, are also visible – 15 and 60 ppm chemical shift – but, in this case, their low intensity suggests that the structure directing agent is present in low quantities.

As result of this study about the influence of the organic loading on the final properties of vinyl-SBA-15 materials, it can be concluded that the incorporation of vinylsilane functionalities can be achieved in 100% efficiency, regardless the initial amount of the olefinic group in the synthesis media. These materials show rather good structure ordering, even for such high amounts of vinyl loading as those used for the preparation of sample S9 – which display good mesostructure as showed in TEM images depicted in figure 6. With regards to the textural and structural properties, the functionalized materials showed high surface areas, pore volume and pore sizes, though shifted to lower values when high loadings were used. Increasing the amount of olefinic functionalities also led to increasing values for the pore wall thickness – up to 9 nm for the material prepared from 50:50 vinyltrimethoxysilane:TEOS mixture (sample S9) –.

3.1.2 Butenyl-SBA-15 materials

Once the study about the incorporation of vinylsilane functionalities into the structure of SBA-15 materials revealed the possibility to incorporate high loadings of this functionality, the same study was carried out for larger olefinic groups. In this case, butenyl(trimethoxy)silane was used as larger olefinic substrate. The amount of butenyl(trimethoxy)silane was varied in the range 20 to 50% mole with regards to TEOS. Table 1 lists the textural and structural properties of butenyl-SBA-15 materials (Samples S10-S12). It seems there is no correlation between the amount of starting organosilane compound and the textural and structural properties of the final materials, except that the total pore volume diminishes when increasing the loading of the olefinic substrate indicating the porosity of final samples becomes lower. However, the nitrogen adsorption-desorption isotherms (figure 7(A)) clearly lay in the type IV group accordingly to the I.U.P.A.C. classification, showing H1 hysteresis loops, characteristic

from mesostructured materials. No great differences can be observed in the nitrogen adsorption isotherms corresponding to the different butenyl-functionalized SBA-15 materials, though the decreasing on the maximum adsorbed volume are clearly evident insofar as the amount of olefinic substrate is increased. Regarding the pore size (figure 7(A) inside), all the materials display quite narrow pore size distributions, though wider than those achieved for the vinyl functionalized materials. This fact is indicative of a lower ordering degree in the mesostructures probably as consequence of the bigger size of the butenyl functionality which partially distorts the surfactant micelles during the synthesis stage. These conclusions are supported by the XRD diffraction patterns (figure 7B) which shows only the main diffraction signal corresponding to the 100 planar spacing. With regards the 110 and 200 diffractions, usually present in diffraction patterns from hexagonal ordered mesostructures, both are missed, suggesting the ordering range of the mesoscopic array of pores is quite low. In this sense, TEM images (not shown) reveal samples showing the highest amount of butenyl functionalities (table 1, samples S11 and S12) show a rather good hexagonal ordering typical from SBA-15 materials. This could explain why the main diffraction peak is present in XRD patterns whereas those signals corresponding to longer spacings are missed. With regards to the incorporation degree of the olefinic species onto the samples, ^{29}Si NMR experiments (figure 7(C)) indicate a much different behaviour of this organosilicon precursor compared to vinyl functionalities. Thus, the incorporation efficiency of butenyl species is low if compared with vinyl-SBA-15 materials. This behaviour could be explained attending to the size of butenyl fragments, which are larger than vinyl functionalities and thus, lower amount of these organic compounds can be accommodated inside the micelles during the synthesis of the olefin-functionalized mesostructured materials. Thus, sample S12, showing the highest butenyl(trimethoxy)silane loading among the

tested materials, and being the sample with the highest incorporation degree, only shows slightly more than 50% incorporation efficiency which is almost half of that incorporated on the same materials when using vinyl functionalities. Figure 7(D) displays the ^{13}C NMR spectrum recorded for sample S12. As in the case of vinyl-functionalized materials, the olefin double bonds are clearly visible (^{13}C $\delta \approx 120$ ppm), together with the signals corresponding to the rest of the carbons at the butenyl moiety. Besides, signals located at 15 and 65 ppm, attributed to the presence of surfactant, are also visible, indicating the efficiency of the surfactant extraction step is not complete. This could be related to the strong affinity between the hydrophobic olefinic functionality and the organic structure directing agent, which difficulties the removal of the template as observed in other hybrid organic-inorganic SBA-15 type materials [33,34]. Nevertheless, butenyl-functionalized mesostructured SBA-15 materials, as in the case of vinyl functionalization, display good mesoscopic ordering, as it can be easily observed in HRTEM microphotographs (figure 8), where the typical honeycomb structure of SBA-15 material is clearly visible for sample S12, containing the highest amount of butenyl groups loading among the tested materials.

As conclusion from this study it can be noticed that butenyl SBA-15 materials can be prepared with high loadings of olefinic groups, though the incorporation of these functionalities to the final mesostructured materials is lower than functionalization degrees achieved with smaller olefins such as vinyl groups. Although XRD patterns reveal a much lower ordering degree in these materials than in vinyl-SBA-15 samples, TEM images confirm the good mesoscopic structure of final sample.

3.2 Oxidation of olefinic groups incorporated to SBA-15 materials

Once the optimal conditions for the preparation of olefin-functionalized SBA-15 materials have been determined for both the vinyl and butenyl groups, the study on the oxidation of these olefins towards glycolic functionalities was tackled. Nevertheless, this investigation was carried out for samples prepared with ‘moderate’ olefinic groups loadings (33% by mole) in order to ensure a high oxidation extent over the immobilized double bond functionalities. Thus, different oxidation strategies were tested for oxidizing olefin substrates. First, a post-synthetic strategy, based on a eventually oxidation once the vinyl and butenyl SBA-15 materials have been prepared, such as that reported by Ozin *et al.* [29], using m-chloro perbenzoic acid (mCPBA) as oxidant. Secondly, a direct synthesis method was also tested, consisting on the preparation of olefin-functionalized SBA-15 materials in presence of hydrogen peroxide as oxidant. In this way, the double bonds at the organic functionalities are oxidized in-situ during the synthesis step and thus, no post-synthetic modifications are required. This strategy has been previously reported for the preparation in single step sulfonic-acid functionalized SBA-15 materials [35] prepared from thiol-containing silane precursors which are oxidized during the synthesis step.

Table 2 lists the physico-chemical properties of vinyl and butenyl samples prepared by a co-condensation starting from a molar ratio TEOS to olefin precursor of 2:1 in mole. Both samples have been treated by oxidation both through the post-synthetic method using mCPBA and through the in-situ oxidation method involving the use of H₂O₂. No great differences can be observed with regards to the textural and structural properties, unless certain reduction of the surface area for oxidized samples. In reference to the incorporation of the organic groups, ²⁹Si NMR experiments reveal that for both olefins, vinyl and butenyl functionalities, there is not any significant loss of the organic moiety

comparing the unmodified material and the subsequent post-synthesis oxidized sample. On the other hand, samples prepared in presence of hydrogen peroxide (S14 and S16 samples) by the in-situ oxidation pathway display roughly half of the organosilicon loading present on their parent non-oxidized samples (S8 and S11). This fact could be ascribed to a negative effect of the oxidant in the incorporation efficiency of the vinyl and butenyl groups during the synthesis of the material.

Figure 8-9 displays the FTIR spectra recorded for the samples functionalized with vinyl groups. Both samples S8 and S13, which is that functionalized with vinyl groups followed by oxidation with mCPBA, display characteristic FTIR bands corresponding to vinyl groups: 1413 cm^{-1} and 3066 cm^{-1} attributed to C-H vibrational modes and 1605 cm^{-1} which is assigned to C=C stretching [23]. These results evidence the presence of a large amount of vinyl functionalities in sample S13, suggesting a low efficiency for mCPBA as oxidant in this reaction. On the contrary, the same signals are completely missed in the spectrum corresponding to sample S14, prepared through the in-situ oxidation. This result could be a consequence of the absence of organosilane functionalities attached onto the final material, but the presence of signals located at 1380 cm^{-1} , 1450 cm^{-1} and 2974 cm^{-1} evidence the presence of $\text{CH}_n\text{-O}$ bonds, which could be attributed to the presence of either epoxide or glycolic groups. Nevertheless, this means the vinyl group has been completely oxidized during the synthesis step involving the presence of hydrogen peroxide in the preparation medium. On the other hand, the absence of an absorption band in the region of $810\text{-}950\text{ cm}^{-1}$ indicates there are not epoxide groups attached onto the sample, so that, the most feasible result is the oxidation of vinyl functionalities has been followed by a hydrolysis of the oxirane group to lead glycolic groups. This conclusion is logical, bearing in mind the strong acid aqueous media used for the synthesis of these materials, which easily hydrolyses

epoxide groups leading to the ring aperture towards glycols. In this sense, it can be concluded the extension of the oxidation reaction is quite high – almost complete – when using the in-situ oxidation procedure, unlike the oxidation with mCPBA which is not efficient in this sense.

| Figure [9-10](#) supports the conclusion about the presence of organosilicon species in oxidized materials, since the detection of T groups through ^{29}Si NMR experiments evidences the presence of $\text{SiO}\equiv\text{Si-R}$ species, where R could be vinyl or oxidized vinyl groups. Nevertheless, the observed reduction in the incorporation efficiency of organosilicon precursors, both in vinyl and butenyl functionalities, is clearly visible in the lower area values achieved for T groups in ^{29}Si NMR spectra recorded for samples prepared through in-situ oxidation. This reduction could be a consequence of different factors though a negative effect of hydrogen peroxide in the incorporation of olefin groups most likely. This negative effect could be caused by the rapid oxidation of vinyl functionalities which is followed by the oxirane group opening by hydrolysis to form the glycolic functionalities. In this way, the organosilicon species loss their hydrophobic nature and the interaction with the surfactant micelles seems not so easy, causing the reduction in the incorporation degree of olefinic functionalities.

| Figure [10-11](#) displays the spectra recorded for both the vinyl- (A) and butenyl- (B) functionalized materials and the oxidized samples prepared from. Samples treated with mCPBA by post-synthetic oxidation (samples S13 and S15) display highly intense resonances for secondary carbons, located at 130 and 135 ppm, which correspond to the presence of double bonds. In this way, this oxidation strategy seems to be inefficient, considering the similarities between the spectra corresponding to un-oxidized samples and those achieved from mCPBA-treated materials. On the other hand, no double bond-signals are detected for samples prepared by in-situ oxidation. Moreover, two strong

resonances in the range 60-70 ppm are clearly intense on the spectra recorded for sample S14 and in the range 50-65 ppm for sample S16. These facts indicate the presence of glycolic functionalities, more than oxirane groups, which usually display lower carbon chemical shifts. Thus, these results support the above mentioned conclusions about the opening of the oxirane groups because acid hydrolysis of the same. Besides, this result confirms the good performance of the in-situ oxidation method in comparison to other post-synthetic oxidation methodologies, such as the epoxidation of double bonds with meta-chloro perbenzoic acid, to lead homogeneous mesostructured materials showing high content of glycolic groups. The so prepared materials display high potential for the heterogenization of different metal species as well as adsorbents for the selective retention of polar substances.

Conclusions

The syntheses of alkenyl-functionalized SBA-15 have been carried out both by post-synthetic grafting and co-condensation methodologies. Whereas the former leads to partial incorporation of the olefinic substrate, even if acid catalyst as PTSA is used, the direct synthesis method ensures almost total incorporation as well as achieving high functionalization degrees. Vinyl pendant groups can be incorporated in a very efficient manner onto the surface of SBA-15 material, though partial prehydrolysis of the TEOS starting material has to be performed in order to preserve the good mesoscopic ordering of the material. However, using the direct-synthesis procedure allows incorporating vinyl-silane loading, as high as 50% of the alkenyl group referred to TEOS. On the contrary, larger alkenyl functionalities, such as butenyl organic groups, are more difficult to be incorporated, and lower functionalization degrees are achieved. Finally, the oxidation of these double bonds towards glycolic groups is easily achieved through

the in-situ oxidation of the alkenyl groups, involving the use of hydrogen peroxide in the synthesis media of the alkenyl-SBA-15 materials. This new synthesis procedure, in which the functionalization and modification of the organic groups attached to SBA-15 material is clearly more efficient than other previously reported methodologies such as the post-synthetic oxidation with mCPBA as oxidant.

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Figure Captions

Figure 1. N₂ adsorption desorption isotherms (inset) and pore sizes distributions calculated for samples functionalized with vinyl groups through grafting procedures.

Figure 2. ²⁹Si NMR spectra recorded for vinyl-functionalized samples prepared through grafting procedures and parent silica material.

Figure 3. (A) N₂ adsorption desorption isotherms and pore sizes distributions (inset) and (B) XRD patterns collected for vinyl-functionalized samples synthesized with different TEOS prehydrolysis times.

Figure 4. (A) N₂ adsorption desorption isotherms and pore sizes distributions (inset) and (B) XRD patterns collected for vinyl-functionalized samples synthesized with different olefin loadings.

Figure 5. ²⁹Si NMR spectra recorded for vinyl-functionalized SBA-15 materials prepared with different olefin loadings. Inset: ¹³C MAS-CP NMR spectra recorded for sample S9.

Figure 6. TEM images collected for vinyl-functionalized sample S9.

Figure 7. (A) N₂ adsorption desorption isotherms and pore sizes distributions (inset), (B) XRD patterns (C) ²⁹Si NMR spectra and (D) ¹³C MAS-CP NMR spectra collected for butenyl-functionalized SBA-15 materials showing different olefin loadings.

Figure 8. TEM images collected for butenyl-functionalized sample S12.

Figure 9. FTIR spectra recorded for vinyl-functionalized SBA-15 materials, parent material, after oxidation with mCPBA and prepared in presence of H₂O₂.

Figure 10. ²⁹Si NMR spectra recorded for (A) vinyl- and (B) butenyl-functionalized SBA-15 materials. From bottom to top: parent materials, postsynthesis oxidation with mCPBA and prepared in presence of H₂O₂.

Figure 11. ¹³C MAS-CP NMR spectra recorded for (A) vinyl- and (B) butenyl-functionalized SBA-15 materials. From bottom to top: parent materials, postsynthesis oxidation with mCPBA and prepared in presence of H₂O₂.

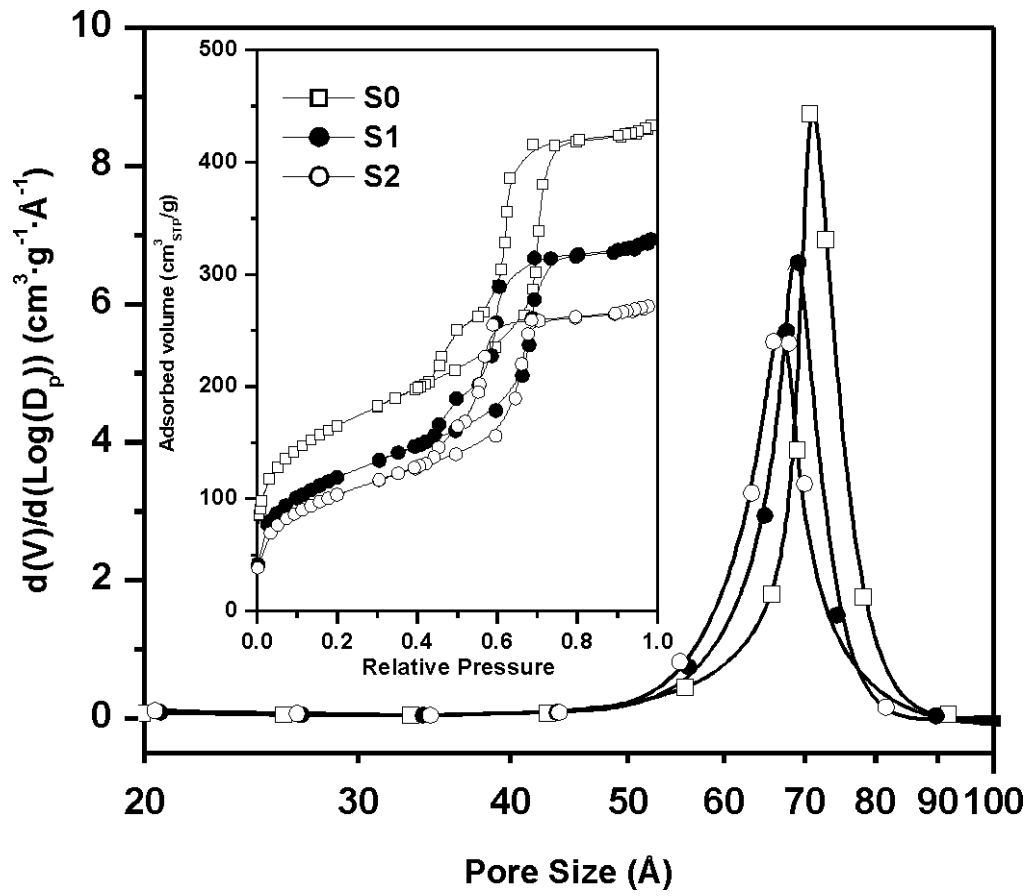


Figure 1

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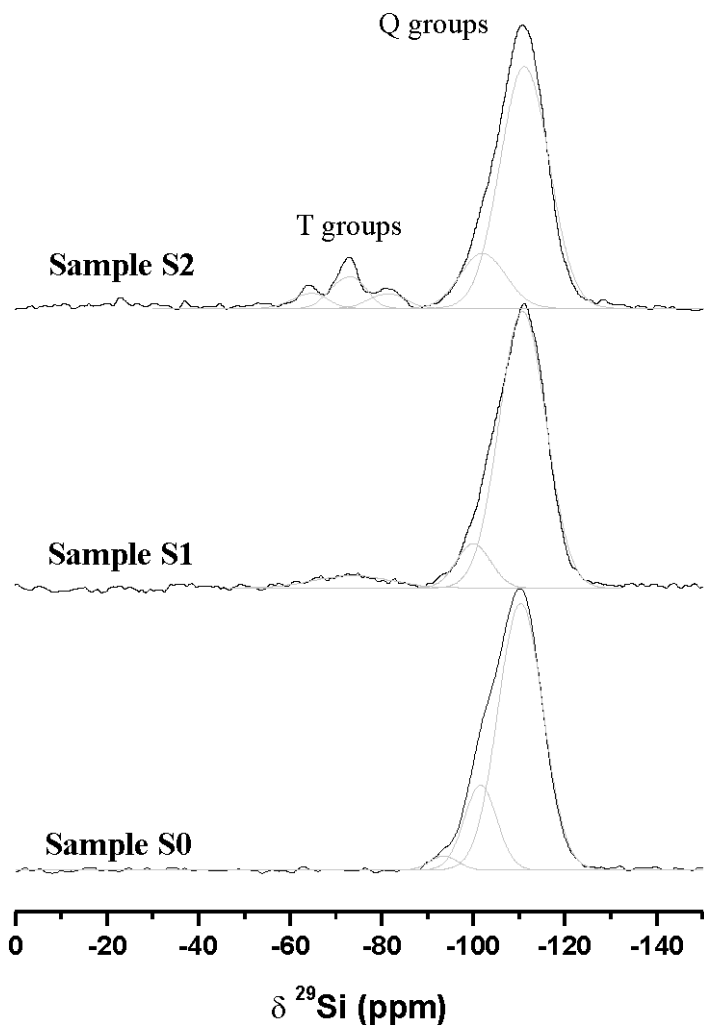


Figure 2

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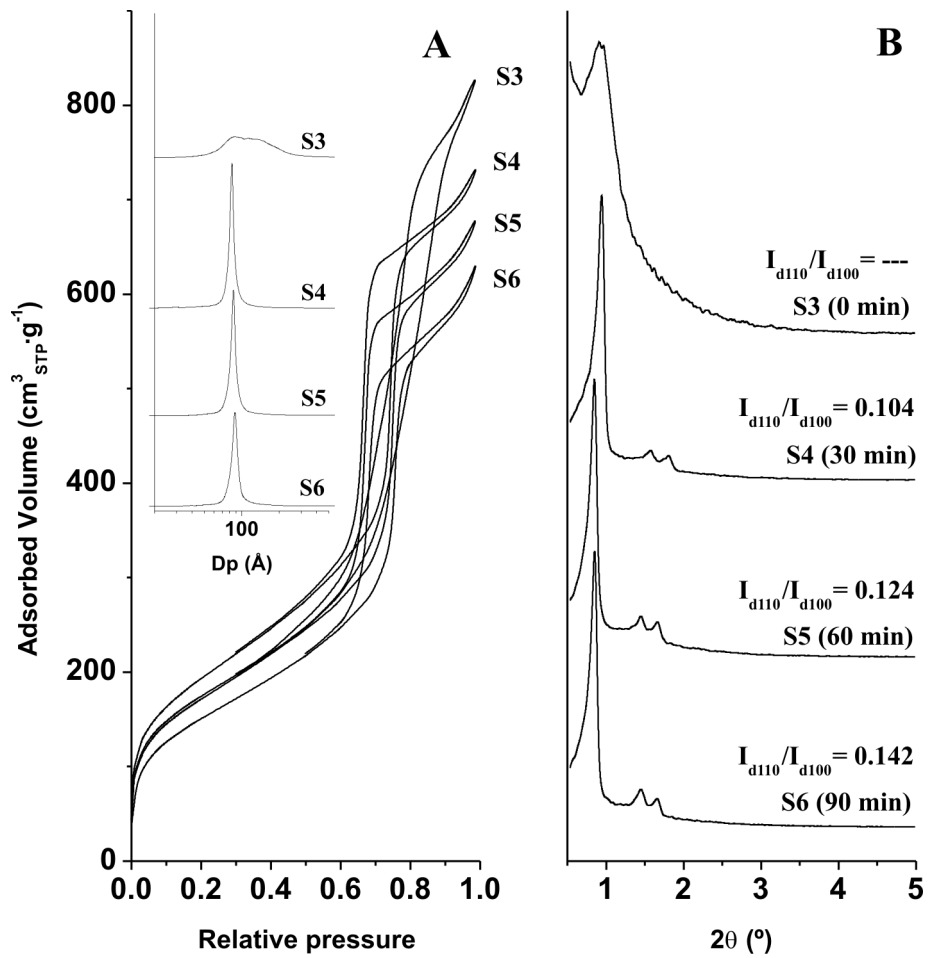


Figure 3

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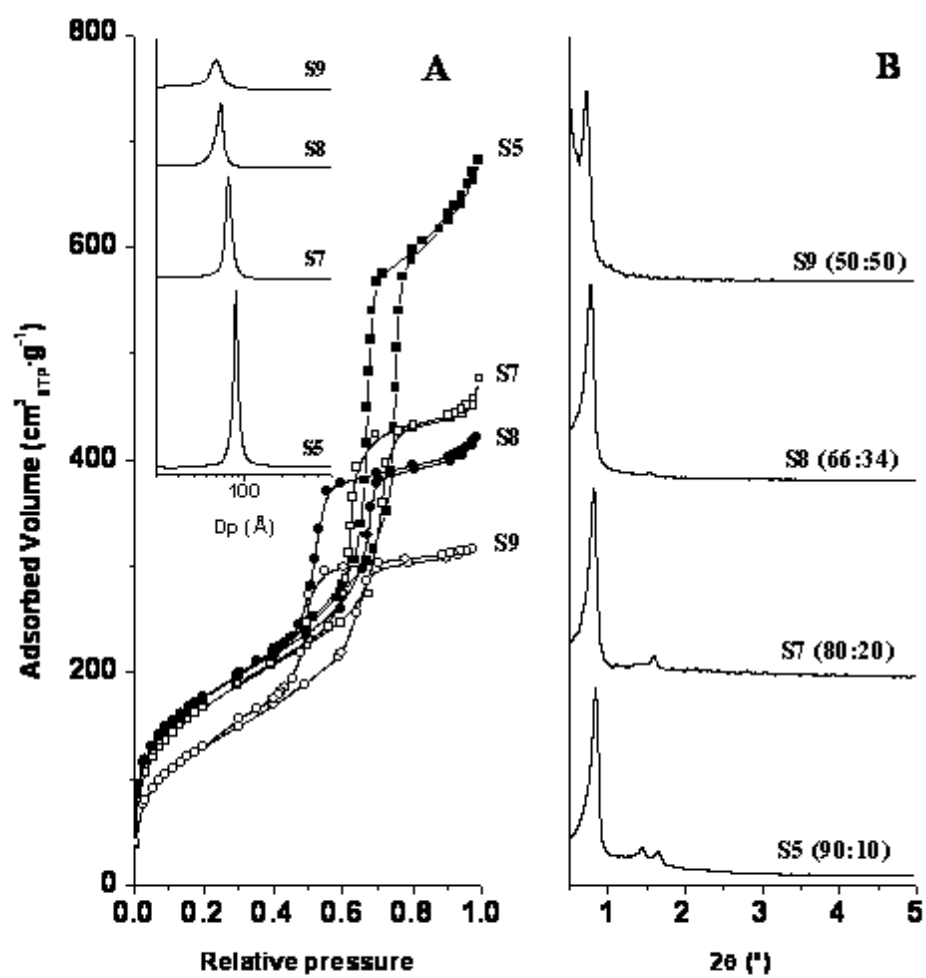


Figure 4

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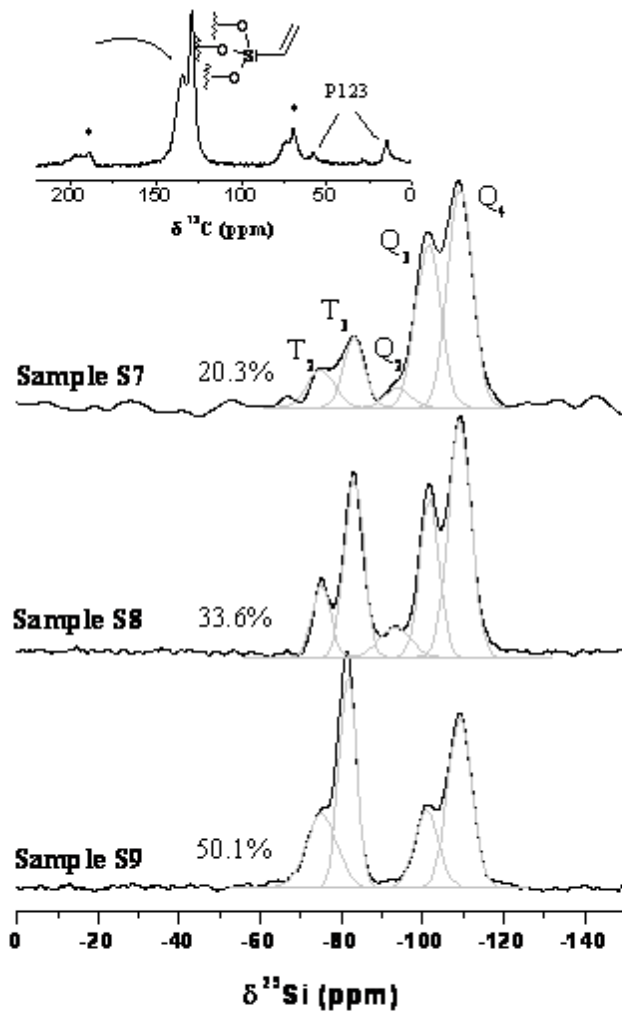


Figure 5

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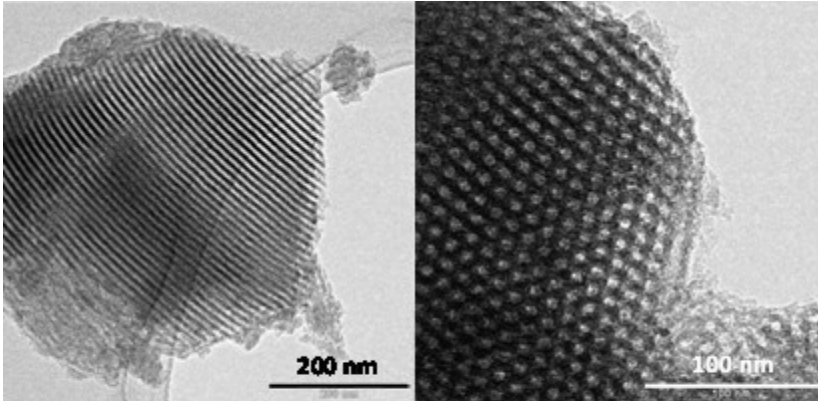


Figure 6

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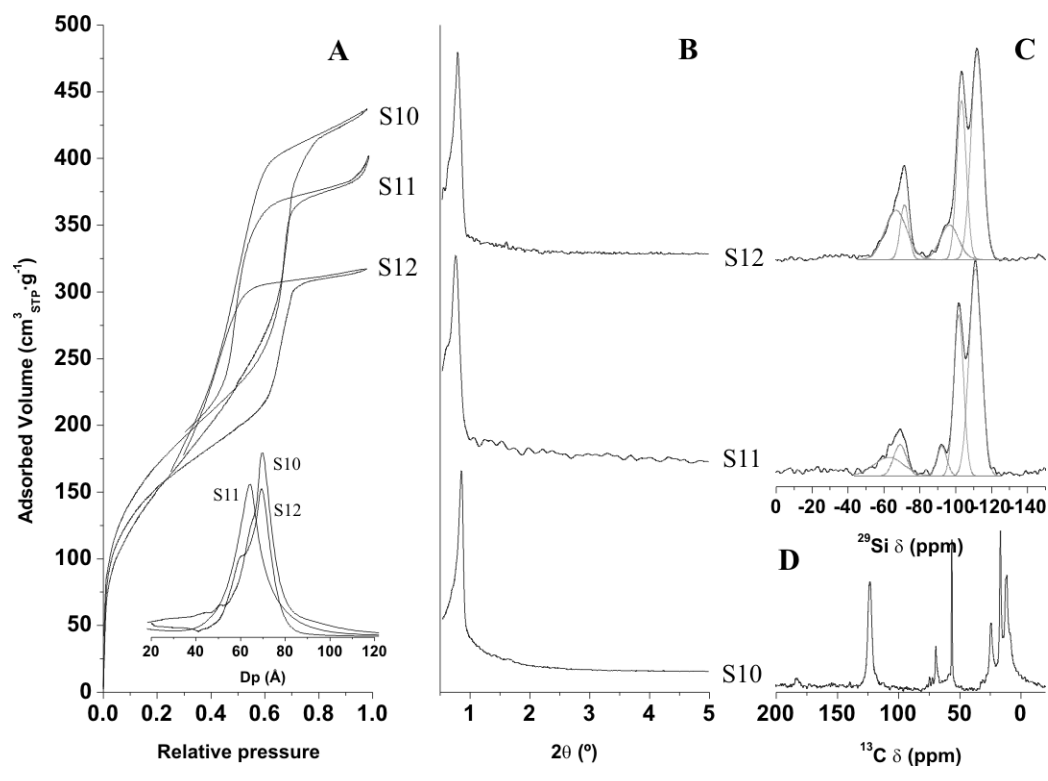


Figure 7

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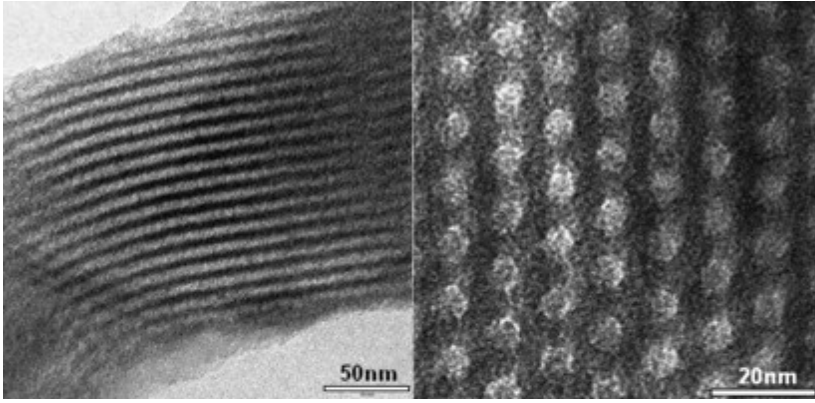


Figure 8

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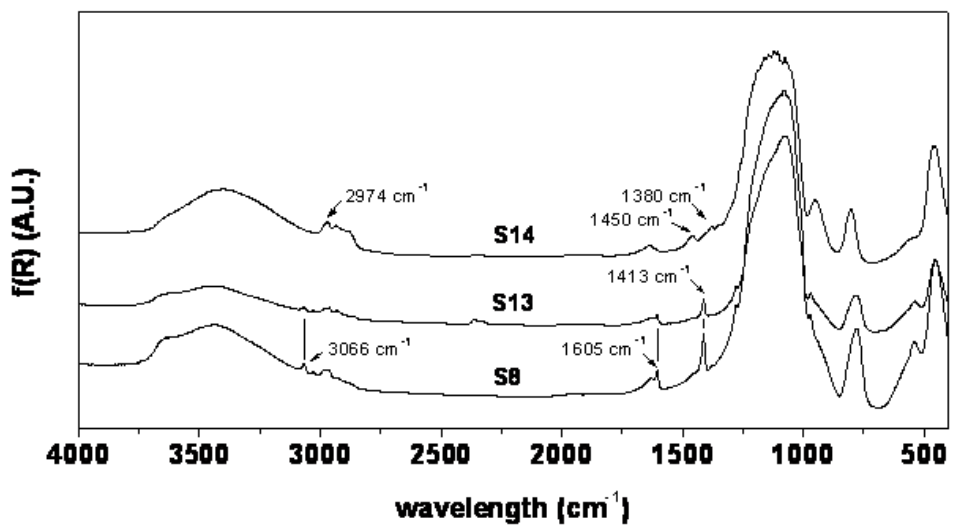


Figure 9

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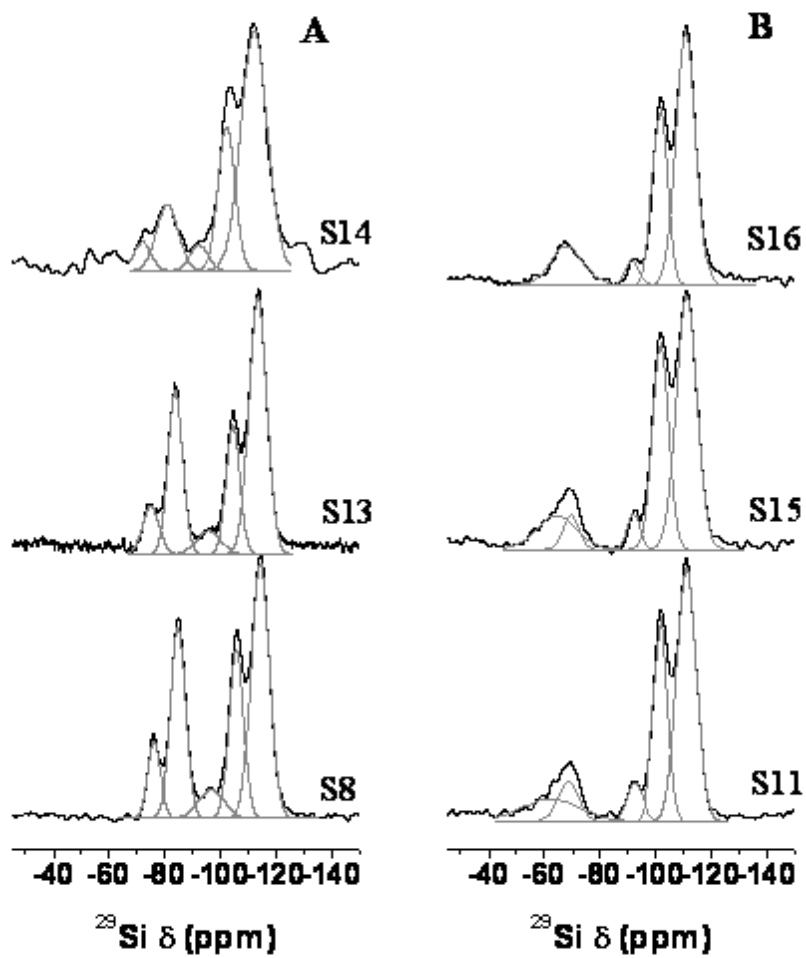


Figure 10

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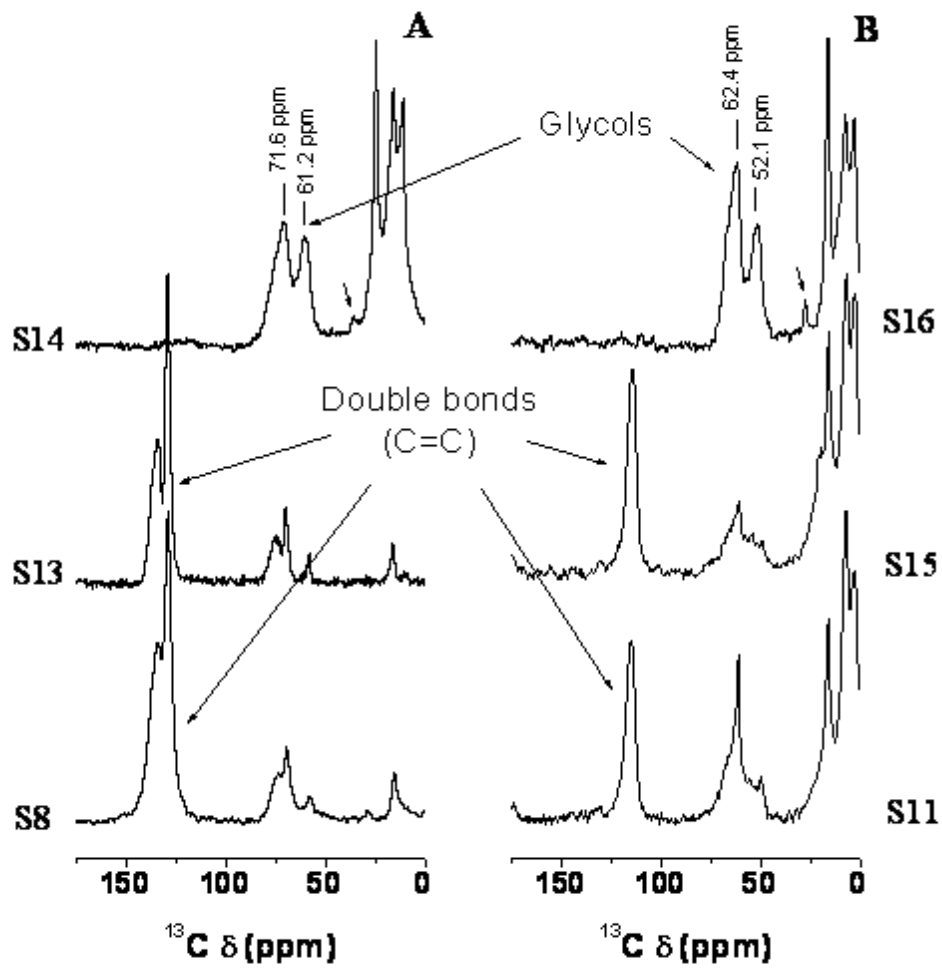


Figure 11

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