Direct synthesis and post-oxidation of SBA-15 and MCM-41 functionalized with butenyl groups.

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2

Olefins and derivatives are interesting compounds to anchor onto the surface of silica supports since their reactivity allow to form a large variety of organic functionalities. In this work, the synthesis of mesostructured silicas (MCM-41 and SBA-15 type materials) functionalized with butenyl groups is studied through the use of post-synthetic grafting or direct-synthesis procedures. Results confirm the higher functionalization degree achieved in the final mesostructured materials when using direct synthesis procedures. Unlike MCM-41 materials, which become microporous when high organic content are attached on, SBA-15 type butenyl functionalized silicas keep the features of a mesoporous solid. Post-synthetic and in-situ oxidations of butenyl groups during the preparation of the mesostructured silicas have been carried out using H_2O_2 as oxidant, leading to materials functionalized with glycol species attached to inorganic mesoporous materials, which are attractive to be used as supports for anchoring different catalytic species.

1. INTRODUCTION

One way to modify the physical and chemical properties of mesoporous materials, like MCM-41 [1] and SBA-15 [2], for improving the attachment of different compounds lies on the incorporation of organic functionalities onto their surface. These organically functionalized materials have a great interest in the development of new catalysts and adsorbents with a wide range of applications, since the surface properties such as hydrophobicity [4], or catalytic behaviour can be easily controlled [3]. For this purpose, many different reagents have been used employing different synthetic procedures [5] like post-synthetic grafting of organosilanes [6] or direct-synthesis methods like co-condensation of organotrialkoxysilanes with tetraalkoxysilanes [7].

The most used procedure for modifying mesostructured supports with organic functionalities is based on the reactivity of the surface hydroxyl groups, used as anchoring points for the organic functionalities [8]. The most important advantage of this grafting method is the formation of the mesoscopic structure before functionalization, although the control over the degree of incorporation of the organic group and the homogeneity of the final materials is difficult to reach [9,10].

On the other hand, direct synthesis procedures based on the incorporation of the organic moieties during the synthesis of the mesostructured solids offer a more uniform surface coverage with functional groups, *better* stability of the attached organic chains and a higher control over the surface properties of the resultant materials [10,11].

Olefins are useful organic groups, not only because the double bond is quite stable under the synthesis conditions but it can be turned into a large variety of compounds through many kind of reactions [12]. As it has been previously reported by Kruk et al. [13] vinyl groups attached onto the surface of MCM-41 type materials, can be easily transformed into alkylboranes, alcohols, epoxides and diol groups, leading to materials useful as catalyst supports. However the M41s materials thus obtained show a strong decrease of the mesoporosity, specially for large functionalization degrees, which affects their use in many applications. In this work we describe the synthesis of mesostructured silicas, functionalized with butenyl chains through grafting and direct-synthesis methods as well as their oxidation to glycol species, which are useful functionalities to be used as anchoring sites for many different applications.

2. EXPERIMENTAL

2.1. Synthesis

Grafting procedures to obtain SBA-15 (S-1,S-2) or MCM-41 (S-6,S-7) type materials consist of dispersing 2 g of the mesoporous support , previously calcined *at 550 ºC*, in 300 ml of toluene under reflux with the desired amount of organosilane (butenyltriethoxysilane, BTES, Gelest). The resultant solution is then kept under reflux for 24 h. Finally, the solid is recovered by filtration and intensively washed with toluene.

Direct-synthesis Butenyl-SBA-15 type materials (S-3, S-4, S-5) were synthesized using a method derived from that reported by Zhao et al. [2]. First 3.20 g of Pluronic P-123 (Aldrich) were dissolved, under stirring, in 100 ml of a 1.9M HCl aqueous solution at room temperature. The homogeneous solution obtained was then heated up to 40 ºC before adding 7.11 g of tetraethylorthosilicate (TEOS, Aldrich). After one hour of TEOS prehydrolisis, the butenyl functionality (BTES) was added into the aqueous suspension, using a molar ratio BTES/TEOS = 1:1, 1:2 or 1:5. The resultant mixture was then stirred at 40ºC for 20h and hydrothermally aged at 110ºC for 24 hours. Finally, the solid was filtered off and the template was removed by an extraction treatment with ethanol under reflux and *subsequently air-dried*.

Direct synthesis Butenyl-MCM-41 type materials (S-8,S-9,S-10) were synthesized following a procedure similar to the method reported by Lin et al [10]**.** Thereby, 2.12 g of cetyltrimethylammoniumbromide (CTABr, Aldrich) were mixed with 80 g of distilled water and 6.57 g of dimethylamine (DMA, Scharlab), used as basic agent, at room temperature. When mixture was completely homogeneised, 8.26 g of TEOS were added dropwise to the suspension. Additionally, after 1 hour TEOS prehydrolisis, a certain amount of the butenyl precursor (BTES) was added, using molar ratios BTES/TEOS = 1:1, 1:2 or 1:5, and then the mixture was stirred for 4 hours at room temperature. All the samples were aged in an autoclave at 110ºC for 48 h. The products obtained were filtered off, washed with distilled water before removing the template by solvent extraction with an acidic solution of hydrochloric acid in ethanol and *finally air-dried*.

Double bond oxidations have been carried out through two methods: in situ (S-12) and post-synthetic (S-11) procedures. The in-situ oxidation procedure consists of adding the hydrogen peroxide by dropping into the synthetic media, following a similar procedure to that reported by Margolese et al. for oxydizing thiol groups [7] in the synthesis of sulphonic-containing SBA-15. The oxidant molar ratio in the synthesis media was H_2O_2:BTES = 5:1. On the other hand, oxidation reactions have been carried out through a post-synthetic procedure by dropping H_2O_2 on a suspension of the functionalized material in acetone under stirring. Typically, 0.5 g of butenyl functionalized-material was suspended in 300 ml of acetone. Then an aqueous solution of 30 wt % H_2O_2 was added in a molar ratio H_2O_2:BTES = 5:1. The suspension was stirred at 55 ºC for 24 h before filtering off the solid. Finally, the oxidized material is washed with acetone and air-dried.

2.2. Experimental techniques

X-Ray powder Diffraction (XRD) data were acquired on a PHILIPS X´Pert diffractometer using Cu Kα radiation. Fourier transform-IR (FT-IR) spectra were recorded in a MATTSON spectrophotometer using the KBr buffer technique. Nitrogen adsorption-desorption isotherms at 77K were determined using an adsorption porosimeter (Micromeritics, TRISTAR 3000). The surface area measurements were obtained according to the BET method. Pore size distribution was obtained applying the BJH model.

Solid-state ^{29}Si NMR and ^{13}C CP MAS NMR experiments were performed on a VARIAN-Infinity 400 spectrometer. Chemical shifts were referenced to tetramethylsilane (TMS).

Transmision Electron Microscopy (TEM) images were taken using a PHILIPS Tecnai 20 electron microscope operating at 200 kV.

Thermogravimetric analysis were carried out in a DSC-TGA apparatus (SDT simultaneous 2960 from TA instrument) under air atmosphere from ambient temperature up to 700°C using a 5°C/min rate.

3. RESULTS AND DISCUSSION

3.1. Butenyl-functionalized mesostructured silicas

Table 1 summarizes the synthesis conditions, textural properties and organic content for the butenyl-functionalized mesostructured materials. Comparing pure silica SBA-15 and MCM-41 with the organic modified ones, table 1 shows a clear tendency related to selected method for incorporating the organic moiety. In this sense, the grafting procedures hardly modify the textural properties of raw materials, while the direct synthesis methods supply remarkable changes, stressed as the organic loading is increased.

Table 1.
Synthesis conditions, textural properties and organic content for the butenyl-functionalized materials

Material	Sample	Synthesis Procedure	BTES/TEOS molar ratio	S_{BET} $(m^2 g^{-1})$	D_p (Å)	V_t $(cm^3 g^{-1})$	T/(Q+T) ^{29}Si NMR
Pure silica SBA-15			---	652	89.2	0.960	0.0%
SBA-15	S-1	Grafting	1:2	617	88.8	0.966	0.0%
	S-2		1:1	570	89.6	0.855	2.3%
	S-3	Direct synthesis	1:5	572	69.7	0.663	5.4%
	S-4		1:2	629	66.8	0.606	15.0%
	S-5		1:1	560	69.7	0.484	23.8%
Pure silica MCM-41			---	1010	27.2	0.750	0.0%
MCM-41	S-6	Grafting	1:2	941	28.5	0.832	1.4%
	S-7		1:1	934	26.2	0.706	8.8%
	S-8	Direct synthesis	1:5	896	27.3	0.737	6.3%
	S-9		1:2	982	24.5	0.669	17.5%
	S-10		1:1	563	22.3	0.283	28.4%

The extent of BTES incorporation into the mesostructured materials was monitored by means of solid state ^{29}Si NMR. Different resonance lines can be observed for the siloxane [Q^n = Si-(OSi)$_n$-(OH)$_{4-n}$, n = 2-4; Q^4 at -110 ppm, Q^3 at -100 ppm and Q^2 at -90 ppm] and organosiloxane [T^n = RSi(OSi)$_n$-(OH)$_{3-n}$, n = 1-3; T^3 at -65 ppm and T^2 at -57 ppm] species. Regarding the organic content anchored onto the final materials [T/(T+Q)], it seems clear that the direct synthesis procedures lead to materials with higher contents on organic functionalities compared to that achieved through grafting methods. For both synthetic routes, the final organic content attached onto the silicas is higher as the BTES/TEOS ratio increases, although higher incorporation efficiencies are achieved for MCM-41 type materials. This different behaviour is found for both synthetic paths, grafting and direct synthesis, but its explanation is different depending on the synthesis route. MCM materials are able to incorporate higher organic contents through grafting procedures since the surface silanol

density is higher than that present on SBA-15 materials [14]. On the other hand, the differences found for the materials obtained through the co-condensation pathway may be explained by a different behaviour of the butenyl-silane in the formation of the solid depending on the pH of the synthesis media, basic for MCM-41 or acidic for SBA-15.

The conclusions drawn from the ^{29}Si NMR spectra about butenyl incorporation in the mesostructured materials are supported by the results of the thermogravimetric analysis (TGA) in air. Analysis of the samples show a peak centered at 220 °C corresponding to the loss of BTES and the remaining surfactant species after extraction with ethanol. Assuming a similar surfactant content for all the samples (measured for the pure silica material), BTES content in direct synthesis SBA-15 have been determined as 3, 17 and 26 molar %, for samples S-3, S-4 and S-5 respectively

Fig. 1 displays the XRD spectra recorded for the samples obtained through direct synthesis procedures for both structures, MCM-41 and SBA-15. All of samples show the typical diffraction pattern of a mesostructured solid, being the main diffraction signal (d_{100}) located at lower angles for SBA materials, since the distance between pore rows is greater for these materials. Regarding to other XRD signals characteristics for a bidimensional hexagonal ordered structure, like those related to d_{110} or d_{200} spacings, there is no evidence of their presence and therefore, these materials show a lower ordering degree than unfunctionalized samples (not shown).
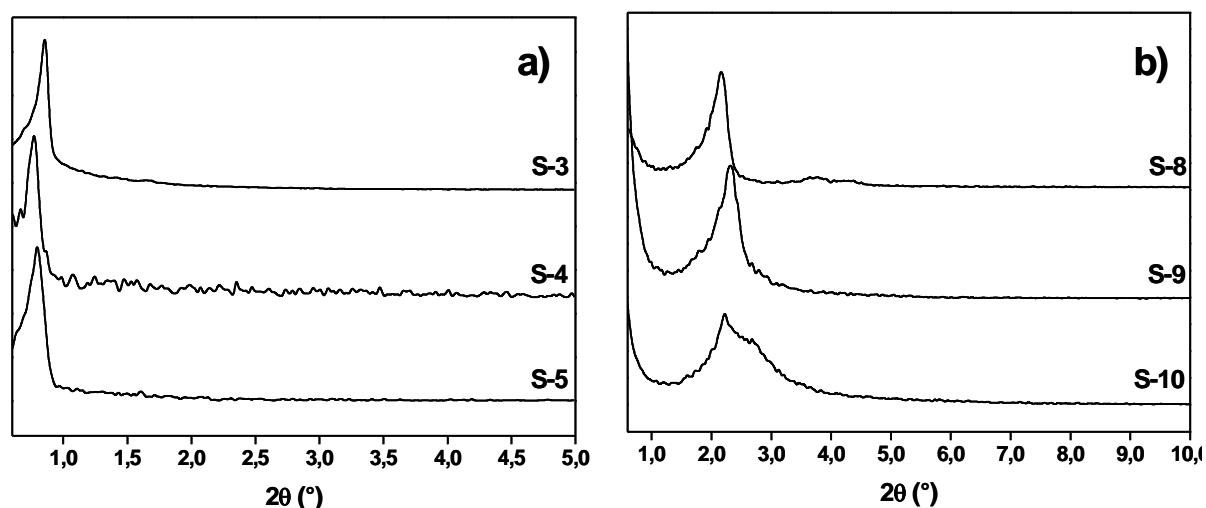

Fig.1. XRD spectra of the direct synthesis materials. a) SBA-15 materials and b) MCM-41 materials.

These results suggest that the co-condensation of butenyl species determines the ordering degree of functionalized materials. An increase of BTES loading leads to a lower order, as it is shown for the MCM-41 type materials, where the d_{100} signal intensity is largely decreased as well as its width is increased. On the other hand, all of the SBA-15 materials show a similar diffraction pattern suggesting a different interaction during synthesis for between the surfactants used for the synthesis of SBA-15 and MCM-41 materials and the butenyl groups. Thus, the ordering of MCM-41 seems to be more dependant on the butenyl loading than SBA-15 samples are.

Fig. 2 shows TEM micrographs from samples S-4 and S-9. Although these samples have been synthesized with the same content of butenyl groups, the quantity is enough to cause great differences between both materials. While SBA-15 material (sample S-4) show a highly ordered honeycomb structure, typical of an hexagonal array with highly regular parallel

layers, MCM-41 material (sample S-9) shows a wormlike porous structure, very different from the one corresponding to non-functionalized MCM-41 material.
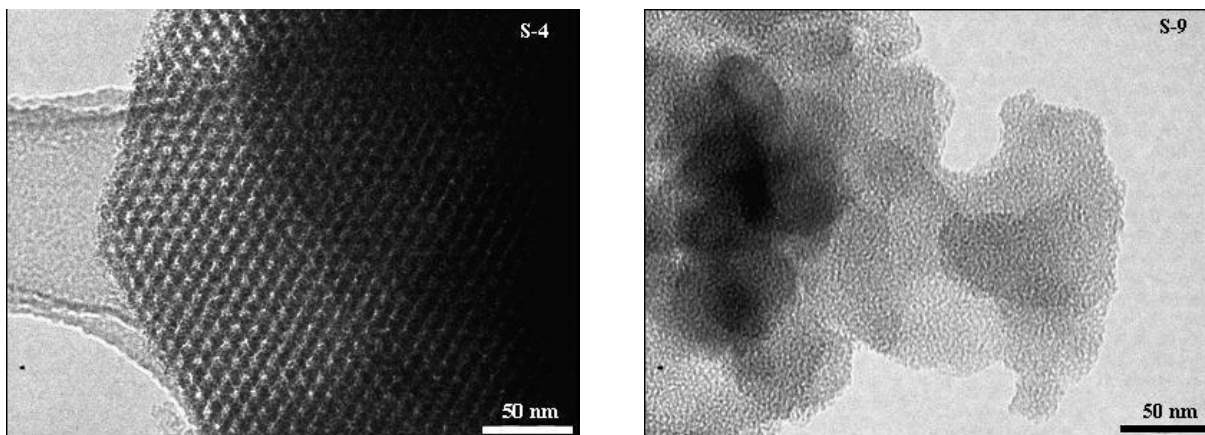

Fig.2. TEM micrographs for samples S-4 and S-9.

This different behaviour is also observed in the analysis of the textural properties determined by the adsorption-desorption of nitrogen at 77K. Fig. 3 displays the adsorption-desorption isotherms (a and b) obtained for SBA-15 and MCM-41 materials as well as their pore size distribution (c and d) calculated by BJH method. SBA-15 samples present type IV isotherms, typical of mesoporous solids. The organic content promotes a drastic change on the textural properties, since the pore volume and surface area decrease when increasing the organic phase. On the other hand, the step in the adsorption branch of the isotherms remains almost in the same position, independently of the functionalization degree and therefore, the maximum of the pore size distribution is similar for all these samples (fig. 3, c). MCM-41 type materials show a different trend when increasing the organic loading, mainly for high butenyl incorporation. Thus, the isotherms of MCM-41 samples depicted in fig. 3, b) shows an striking inflection, becoming from a mesoporous solid with a type IV isotherm (S-8) for the lower butenyl loading to a microporous material showing a type I isotherm (S-10) for the highest organic content.
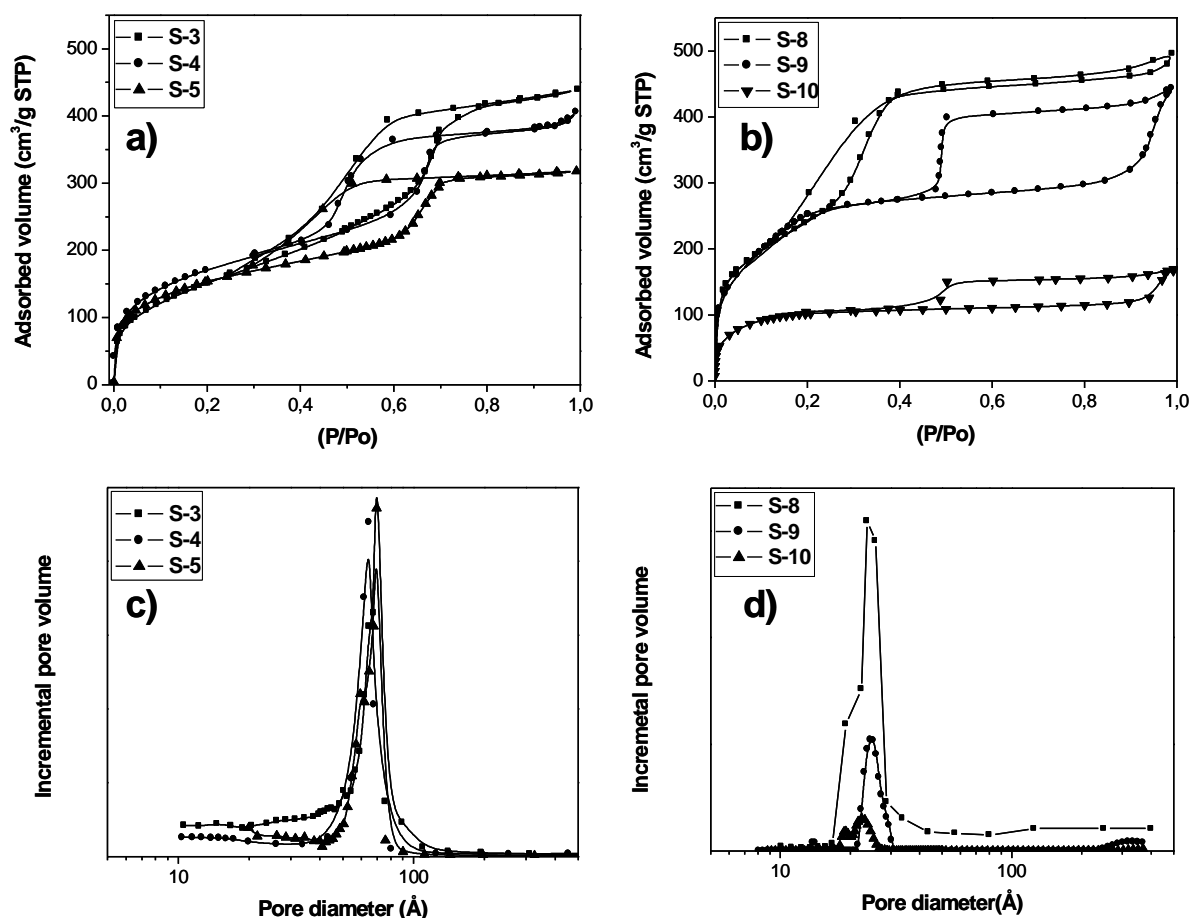
Fig.3. N$_2$ adsorption-desorption analysis for direct synthesis materials. a) SBA-15 isotherms b) MCM-41 isotherms, c) SBA-15 pore size distribution, d) MCM-41 pore size distribution

Nitrogen adsorption-desorption analysis also indicates a different interaction between butenyl groups and the structure directing agents used in the synthesis of MCM-41 and SBA-15. The high organic loading achieved for SBA-15 suggests that butenyl groups do not affect the ordering of the triblock copolymer template micelles in solution, allowing the generation of a structure with narrow pore size distribution. On the other hand, the less ordered MCM-41 type materials and its microporous nature prove the strong interaction between butenyl functionalities and the CTABr template during the synthesis of the material.

3.2. Oxidation of butenyl groups

In the second part of this work, the oxidation of butenyl functionalized materials previously synthesized has been studied with the purpose of transforming the end-chain double bound into glycolic groups. Thus, those mesoporous silica materials functionalized with diol groups are suitable to be used as anchoring support for different active phases in the preparation of heterogeneous catalysts.

Two oxidation procedures have been studied as detailed in experimental section: in situ during synthesis and post-synthetic methods, selecting SBA-15 as support. Table 2 summarizes the textural properties obtained by nitrogen isotherms and final organic content measured by solid state ^{29}Si NMR of the materials.

Table 2
Synthesis conditions and organic content for the synthesized oxidized materials

Sample	Oxidation Procedure	BTES/TEOS molar ratio	S_{BET} $(m^2 g^{-1})$	D_p (Å)	V_t $(cm^3 g^{-1})$	T/(Q+T) ^{29}Si NMR
S-4	Non-oxidized	1:2	629	66.8	0.606	15.0%
S-11	Post-synthesis	1:2	574	70.0	0.547	13.5%
S-12	In-situ	1:2	603	66.7	0.668	11.0%

As it is shown from the table, BET-surface, pore diameter and total pore volume of the oxidized materials (samples S-11 and S-12, respectively) are quite similar to that obtained for the non-oxidized sample (S-4). On the other hand, regarding final organic content, the in situ oxidation path leads to materials with lower functionalization degree .

Fig. 4 shows the solid state ^{29}Si (a) and ^{13}C (b) NMR spectra of the S-4 and S-12 samples. From ^{13}C NMR, it is possible to determine the different carbon assignments. Thus, in sample S-4 (non-oxidized) the peaks labelled with asterisks correspond to the carbon species of surfactant P123, while the peak at 120 ppm is attributed to the double bond carbon from butenyl groups. Sample S-11 hardly presents modifications with regards to S-4, indicating a low degree of double bond oxidation.
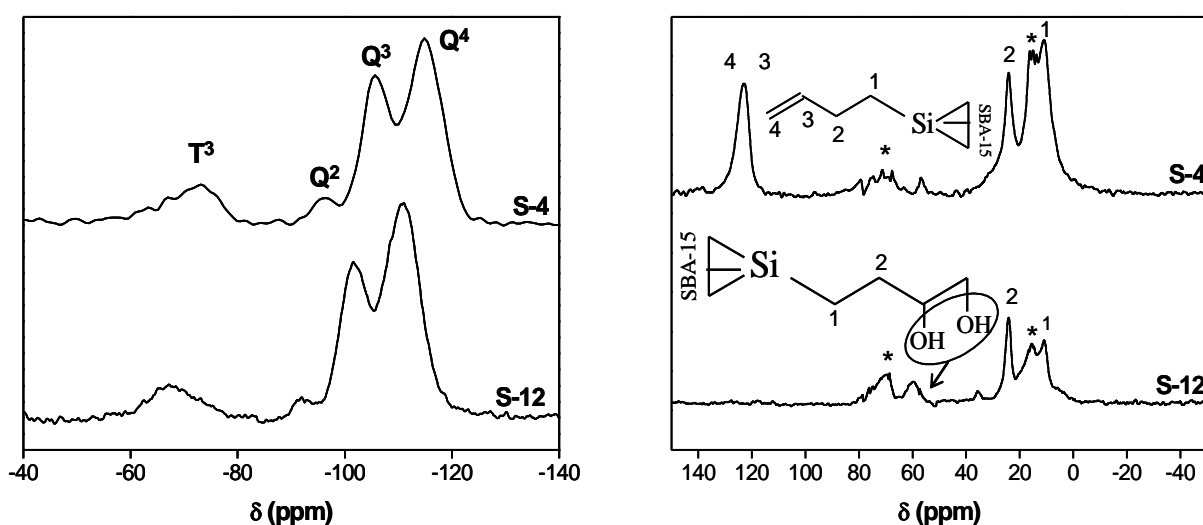

Fig.4. NMR spectra of oxidized samples. a) ^{29}Si MAS NMR, b) ^{13}C CP MAS NMR. Asterisks denote surfactant compound.

On the contrary, in-situ oxidation, sample S-12 shows the overwhelming extinction of signal at 120 ppm, attributed to double bound, which accounts for the total conversion to a glycol group, corroborated by the ^{29}Si NMR spectrum, where the presence of T groups evidences the Si-C bonds existence.

4. CONCLUSIONS

Direct synthesis procedures leads to SBA-15 and MCM-41 materials with higher contents on organic functionalities compared to that achieved through grafting methods. While SBA-15 material shows a highly ordered honeycomb structure, typical of an hexagonal array, MCM-41 type material presents a wormhole porous structure, even if the lowest BTES percentage is used. While the butenyl groups do not seem to affect the micelle organization with triblock copolymer template used in SBA-15 synthesis, the transformation of MCM-41 materials into microporous samples prove the hard interaction between butenyl functionalities and the CTABr template. The conversion of butenyl species into glycol groups can be achieved by in-situ oxidation method with greater oxidation efficiency, being these modified materials suitable to be used as anchoring sites for different active phases in the preparation of heterogeneous catalysts.

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