

Direct synthesis of organically modified Ti-SBA-15 materials

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Abstract

Organically-modified Ti-SBA-15 materials have been prepared through a direct synthesis procedure based on the co-condensation of tetraethyl orthosilicate (TEOS), alkyltriethoxysilanes (R-TES) and titanocene dichloride as silicon, organic species and titanium sources respectively. The prehydrolysis time for the TEOS and the amount and type of alkyl functionality were studied in order to achieve mesostructured organic-modified Ti-SBA-15 materials. The synthesized samples were assayed in the catalytic epoxidation of 1-octene with TBHP as oxidant. The catalytic results reveal a direct correlation between the activity of the catalyst per titanium site and the length of the alkyl chain. Higher lengths of the alkyl chain induce a significant increase of the activity of the titanium sites due to the enhancement of their hydrophobic microenvironment. Likewise, improved efficiency in the use of the oxidant has also been observed when using organic modified Ti-SBA-15 materials, being correlated this effect with the reduction of the non-oxidative decomposition of TBHP. Finally, the reutilisation tests indicate very high stability of the prepared catalysts in epoxidation reactions with TBHP.

Keywords

Ti-SBA-15; Mesoporous; Organic functionalization; Direct synthesis; Epoxidation

1. Introduction

Titanium-containing silica-based catalysts have been a subject of interest for researchers since the development of the Shell catalyst [1] and the TS-1 [2] zeolitic material. Isolated titanium species, like those present in the mentioned materials, display a very high catalytic activity in oxidation reactions like olefin epoxidation. Nevertheless, these materials display some disadvantages, like the high sensitivity of titanium species against water molecules in the Shell catalyst or the small pore size of the zeolite, that reduce their application range. Several authors have focused their research on producing new titanium-functionalized silica-based materials in order to overcome the above mentioned drawbacks. One of the most interesting choices is the use of the silica-based mesostructured materials as catalytic supports [3]-[4]. These materials, featured by an open structure and ordered array of mesopores, have been a matter of intensive research during the last years [5] and many investigations have been carried out on the functionalization of these silica-based materials to provide them additional characteristics. More specifically, the synthesis of titanium-containing mesostructured materials has been widely studied since the development of Ti-MCM-41 material by Corma and co-workers [6]. These materials have revealed to be catalytically active in the epoxidation of olefins with alkyl hydroperoxides, and thus this research has promoted new investigations in the preparation of new titanium containing mesoporous materials [7]-[9]. Among these options, the titanium-functionalized SBA-15 material has recently received much attention because of its superior mechanical and chemical resistance compared with other mesostructured materials [10]-[13]. For this purpose different synthetic pathways can be employed, being the post-synthetic methodologies [7],[11],[14] and the direct synthesis protocols [10] the most widespread alternatives,

though the latter option display several advantages like the higher dispersion degree and stability of the final metallic sites.

On the other hand, unlike the highly crystalline titanium-containing zeolitic materials, titanium functionalized mesostructured catalysts trend to display low efficiency in the use of the oxidant [15], an essential parameter for the economic proficiency of this kind of processes [16]. This behavior has been attributed to the large quantity of silanol groups [17] present in amorphous silica, which catalyze the non-oxidative consumption of hydroperoxides [18],[19]. These silanol functionalities are located onto the surface of the mesostructured materials, and they are much less plentiful on highly crystalline zeolites. One of the most extended solutions for this disadvantage is the surface hydrophobization of titanium-containing silica-based materials, in order to reduce the interaction of silanol groups with oxidants and thus, decreasing the non-oxidative reactions. For this purpose different strategies, all of them based on the use of organosilicon species as hydrophobization agents, have been employed, from the simplest post-synthetic silylation [20] to the preparation of hybrid organic-inorganic mesoporous organosilicas [21],[22]. Organic functionalization of mesostructured materials can be accomplished, like in the case of the immobilization of titanium species, by using different synthetic methodologies [23]: post-synthetic treatments and direct synthesis procedures. In a similar way to that previously mentioned, direct synthesis procedures, also called co-condensation methods, lead to more homogeneous distribution, higher dispersion and functionalization degrees than post-synthetic treatments. Regarding the effect of these methods on the behaviour of the materials with regards the decomposition of oxidants, the former one involves the reduction of the amount of silanol functionalities by reaction with organosilanes, whereas the second one simply reduces the interaction between the surface silanol groups and the

hydroperoxides, because of changes produced on the adsorption / desorption processes of reactants on the surface of these materials. In both cases, the result is a more efficient use of the oxidants in olefin epoxidation reactions using alkyl hydroperoxides [21].

Herein, we present a direct synthesis procedure for both the incorporation of titanium species and organic functionalities in a single step to yield organically modified Ti-SBA-15 mesostructured materials. This facile and simple one-pot synthesis procedure allows to directly prepare in a single step Ti-SBA-15 materials able to catalyze in good extension the oxidation of 1-octene and, thanks to the hydrophobisation occurring on the surface of the materials because of organic functionalization, using in a very efficient manner the alkyl hydroperoxides employed as oxidants.

2. Experimental

2.1 Synthesis of organically-modified titanium-containing SBA-15 materials

SBA-15-type materials have been prepared using a similar procedure to that previously described in literature [10]. Ti-SBA-15 materials were synthesized using tetraethyl orthosilicate (TEOS, Aldrich), titanocene dichloride (Cp_2TiCl_2 , Aldrich) and different alkyltrialkoxysilanes (methyltriethoxysilane, Met-TES; ethyltriethoxysilane, Et-TES; propyltriethoxysilane, Pr-TES; and butyltriethoxysilane, But-TES; Aldrich) as silicon and titanium precursors and organic functionality sources respectively. Both types of silicon precursors, TEOS and alkyltrialkoxysilanes, were co-condensated using a similar method to that reported by Corma *et al.* [24]. Triblock copolymer Pluronic 123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, Aldrich) was used as structure directing agent and concentrated HCl aqueous solution was used as the acid source. In a typical synthesis 4 g of the surfactant were dissolved in 125 ml of 0.5N hydrochloric acid. The solution was then heated up to 40°C before adding an appropriate amount of the titanium precursor. Prior to the

addition of the silicon precursors the titanium source was prehydrolyzed for 180 minutes in order to increase its incorporation efficiency [10]. Different samples were obtained with the purpose of studying the effect of the order of addition used for the different silicon sources. Afterwards, the resultant mixture was stirred at 40°C for 20 hours and hydrothermally aged at 100°C under static conditions for 24 additional hours. The solid product was recovered by filtration and air-dried overnight. Surfactant was removed by solvent extraction, in order to preserve the integrity of organic species, using the method reported by Zhao and co-workers [4].

2.2 Characterization techniques.

Nitrogen adsorption-desorption isotherms were recorded in a manometric adsorption porosimeter (Micromeritics, TRISTAR 3000) at 77K. The surface area values were calculated by the B.E.T. method. Pore size distributions were obtained applying the B.J.H. method using the K.J.S. correction to the adsorption branch of the isotherm. The total pore volume was assumed that recorded at $P/P_0 = 0.985$. X-ray powder diffraction patterns were acquired on a Philips X'pert diffractometer using the Cu $K\alpha$ radiation line in the 2θ range from 0.5° to 5.0° with a step size of 0.02° . Diffuse Reflectance UV-VIS Spectrometry (DR UV-VIS) assays were recorded under ambient conditions on a Varian Cary-500 spectrophotometer equipped with a diffuse reflectance accessory in the wavelength range from 200 nm to 600 nm. Titanium content was determined by ICP-atomic emission spectroscopy. The samples (100 mg) were dissolved in water using aqueous hydrofluoric acid and the resultant solution transferred into 1 L calibrated flask and diluted with water. An absorption standard solution of Ti ($1000 \mu\text{g ml}^{-1}$ in water) was used for the calibration of the equipment. Solid-state ^{29}Si NMR experiments were performed on a VARIAN-Infinity 400 spectrometer operating at a frequency of 79.4 MHz under the following conditions: magic-angle spinning at 6 kHz; $\pi/2$ pulse, 4.5 μs ;

a repetition delay of 15 s; and 3,000 scans. Chemical shifts were referred to tetramethylsilane.

2.3 Catalytic tests

The catalytic activity of the titanium-functionalized materials was assessed in the epoxidation of 1-octene with anhydrous tert-Butyl Hydroperoxide (TBHP, 5.5N in decane, Fluka) (TBHP:1-octene molar ratio of 1.2). The catalytic tests were carried out in a two-necked round bottom flask magnetically stirred and immersed in a temperature controlled bath under nitrogen atmosphere. All reactions were performed for 6 h at 100°C. In a typical assay both, the catalyst and 1-octene (1-octene: catalyst mass ratio of 12:1; mass of catalyst 0.8 g) were loaded in the flask and the system was then warmed up to the reaction temperature. After heating, the oxidant was added in a single step by means of a syringe. Under the reaction conditions, epoxide was the unique reaction product. The oxidant conversion was calculated by iodometric titration whereas the content of the rest of the products were quantified by gas chromatography analysis. Besides the conversion of the reactants, several other reaction parameters have been used for the comparison of the activity obtained using different catalysts. The definitions of the reaction parameters are as follows: the oxidant efficiency is the proportion of converted oxidant used in the formation of the oxirane and the turnover frequency has been defined as the number of moles of produced epoxide divided by the number of moles of titanium added within the catalyst and by the reaction time, expressed in hours. The titanium leaching extension during the epoxidation tests was assessed by direct measuring the metal content in the reaction media after the filtration of the catalyst. Reutilisation tests were carried out, washing the catalyst in ethanol between tests, in order to eliminate the possible adsorbed reactants and products from the surface of the catalysts which could interfere in the following test.

3. Results and Discussion

The combined functionalization of SBA-15 materials with titanium species as well as organic functionalities through direct synthesis procedures has involved several partial investigations. In this sense, starting from the synthesis method previously described in literature [10], this was modified for the incorporation of the organic functionalities. Thus, the influence of the addition order of the silicon precursors to the synthesis gel, the prehydrolysis of the TEOS starting compound, the organic functionality loading and finally the type of organic functionality were studied. Table 1 summarizes the synthesis conditions followed for the preparation of the materials obtained during this research as well as their physicochemical properties, including the initial and final metal content, the organic functionality content and the textural and structural parameters.

3.1 Order of addition of the silicon precursors

In order to determine whether the addition of the TEOS precursor before adding the alkyltriethoxysilane starting compound is better or not, three different samples were prepared (Table 1, samples S1-S3). For this study methyltriethoxysilane was used as the organic functionality source and the order of addition was varied as follows: sample S1 was prepared by the addition in first place of the TEOS precursor, followed by a prehydrolysis step of 45 min, and finally the addition of the alkyltriethoxysilane. Sample S2 was prepared by the joint addition of both silicon precursors and finally S3 sample was prepared using a reversed order to that used for sample S1. All of these materials were prepared using a 4% of titanium in the synthesis gel, referred in weight to the total amount of silicon species expressed as silica.

All the materials prepared during this study show lower titanium content than that achieved for the inorganic Ti-SBA-15 material (Sample SBA (4%)), used as reference.

This fact could be partially due to the incorporation of the methyl functionalities onto the surface of the hydrophobized materials which dilutes the titanium content in the final materials, but such a pronounced reduction in the incorporation of the metal species is very large to be caused only by the dilution of the sample. Thus, difficulties in the incorporation of metallic sites because of competition between alkyltrialkoxysilanes and titanocene species for attaching sites to the forming silica can also play an important role. In contrast, the incorporation of the methyl functionality is almost complete for all the hydrophobized materials. Nevertheless, no great differences, regarding the titanium loading as well as the methyl functionalization degree, are observed when comparing the samples prepared with different orders of addition of the silicon starting materials. Thus, in this sense, the final chemical composition of the methyl-Ti-SBA-15 materials is not influenced by the order of addition of the silicon precursors, but incorporation of metallic species could be disfavoured when using organic functionality silicon precursors.

The environment of the immobilized titanium species has been assessed by means of DR UV-Vis spectroscopy. Figure 1(A) depicts the UV spectra recorded for the samples prepared with different orders of addition of the silicon precursors. All the samples display two contributions to the overall spectrum, formed by the absorption of UV radiation at 215 and 320 nm. The first one is usually ascribed to the electronic transitions occurring in isolated tetrahedrally coordinated titanium species bonded to oxygen atoms [25]. On the other hand, the signal centred at 320 nm is conventionally attributed to the presence of titanium species with octahedral coordination, like those present in bulk titanium dioxide. Nevertheless, the calcination of these samples leads to the complete removal of this latter absorption band, indicating its origin is not the presence of titanium oxide domains but probably cyclopentadienyl groups remaining

attached to some titanium sites, even after surfactant removal using ethanol under reflux. In previous works we have reported the treatment of titanium-functionalized materials, prepared both by post-synthesis grafting or by direct synthesis procedures, with ethanol under reflux. This treatment causes the modification of the DR-UV spectra of the Ti-SBA-15 materials because of the removal of cyclopentadienyl groups, probably because of displacement of Cp functionalities by ethanol to form ethoxide groups directly attached to titanium sites [10],[26]. This behaviour is also found for the sample SBA (4%) prepared without organic functionalization. One possible explanation for this fact is the surfactant extraction during the washing step is not completely efficient and thus, some part of the porous structure remains filled with the remaining surfactant. This fraction of the porosity mainly corresponds to the microporous system connecting the mesoporous channels [27]. Thus, the titanium sites located at those micropores will preserve their original coordination to Cp rings because of protection by the surfactant, and only those accessible by ethanol could be attacked by the solvent. Additionally, it has to be considered that the expected hydrophobic behaviour of the surface of the methyl-functionalized Ti-SBA-15 sample repels polar molecules like ethanol used for the surfactant extraction. In this manner, the titanium sites located next to methyl groups do not react with ethanol because of repulsion between the alkyl chain of the functionalization agent and the polar solvent. Accordingly, the more organic nature, the higher intensity for the cyclopentadienyl UV signal, but not clear differences are evident between the methylated samples. Besides, all of the samples seems to present equally isolated titanium sites, as it can be inferred from the DR UV-Vis spectra recorded for the calcined samples, all of them showing potential activity in oxidation reactions.

Regarding the textural properties, all of the materials display type IV isotherms, accordingly to the I.U.P.A.C. classification, featured with H1 hysteresis loops, indicating a homogeneous pore size distribution of mesopores (see supplementary data). The very narrow pore size distributions, calculated by the BJH method, supports this fact. On the other hand, functionalized materials display lower surface area, pore volume and pore size values than pure siliceous Ti-SBA-15 material (Table 1, sample SBA (4%)). In this case, the observed differences can be ascribed to the incorporation of the methyl functionality onto the surface of the mesopores, reducing the void volume inside the mesoscopic channels which finally leads to the observed reduction of the textural properties. This fact is supported by the results achieved by XRD analyses. Thus, when comparing the organically modified materials with the reference sample, thicker pore walls are achieved indicating the alkyl functionality is attached to the silica framework. Nevertheless, here again, no differences are observed for the materials prepared using different orders of addition of the silicon precursors.

Figure 1(B) shows the X-ray diffraction patterns achieved for the methyl-functionalized Ti-SBA-15 samples as well as the reference Ti-SBA-15 material. Although all the samples display diffraction patterns typical from a mesoscopic p6mm structure formed by the hexagonal array of mesopores, some differences can be distinguished between samples. Thus, the ratio between the intensities of the d_{110} and d_{100} signals is usually employed as an index for the evaluation of the ordering degree of a mesoporous material [27]. Taking this into account, the reference sample showing the highest ratio d_{110}/d_{100} , is the most ordered sample among the tested materials. In contrast, incorporating methyl groups leads to much lower d_{110}/d_{100} ratios, meaning the insertion of the organic functionality distorts the mesoscopic structure. Besides, some differences are detected when using different orders of addition of the silicon precursors. Thus,

sample S1 shows a higher ordering index than samples S2 and S3, in fact for the latter it has been impossible to calculate this parameter since d_{110} diffraction is completely missed. This result indicates the addition in first order of the TEOS precursor leads to higher ordering degrees than the other tested addition orders. The explanation for this behaviour can be found in the hydrophobic nature of the methyltriethoxysilane starting compound which drives the interaction between this silicon precursor and the surfactant micelles. The addition of this chemical in first place, or even together with the TEOS, can favour a deep interaction between micelles and the organosilicon precursor, causing the distortion of the micelles and leading to less ordered mesoporous structures. In contrast, the addition of the TEOS starting material in first order leads to a rapid hydrolysis of this precursor and subsequent condensation of silica species around the micelles. Thus, a thin film of silica is formed surrounding the micelles and acting as an scaffold which avoids their deformation. Nevertheless, in the early stages of this process, the condensation degree of the silica is not so high to avoid the access of methyl functionalities to the micelles, occupying locations at the interphase micelle-silica, but prevents their deformation [28]. In conclusion, the addition of the TEOS precursor in first place leads to more ordered materials than the rest of the conditions employed in this study. Regarding the rest of the properties no great differences can be detected among the functionalized samples so that, prehydrolysis of the TEOS precursor followed by the addition of the hydrophobization agent has been chosen as the synthesis conditions for the rest of the research.

3.2 Loading of organic functionality

The loading of the methyltriethoxysilane precursor in the initial synthesis gel was varied in order to explore the possibility of increasing the organic incorporation in the prepared materials. The influence of this synthesis variable on the final properties of the

mesostructured samples has been studied, varying the organic loading from 5% to 10% and 20% on a molar basis (Table 1, Samples S1, S4 and S5). Regarding the chemical composition of the final materials and in a similar way to that previously described, the increasing of the organic functionality in the synthesis gel leads to a reduction in the metal loading, because of the dilution of the metal species, but competition between the organosilicon and titanium precursors can play an important role. In fact, the observed reduction in titanium incorporation is higher than that expected by the simple dilution of the sample because of incorporation of organic functionalities.

The incorporation of the alkyl functionality has been evaluated by ^{29}Si solid state MAS-NMR spectroscopy, which results have been depicted in figure 2. The signal located at -66 ppm chemical shift is attributed to the presence of T silicon atoms, which are silicon species directly bonded to carbon atoms coming from the methyltriethoxysilane starting material. Q signals, 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. Since the ^{29}Si NMR analyses have been carried out using single pulse the results are quantitative and thus, the areas below the gaussian curves obtained from the deconvolutions of the spectra are proportional to the abundance of each species. Thus, the ratio of the peak area achieved for T groups referred to the total area below the overall spectrum indicates almost a total incorporation of the methyl functionalities onto the surface of the final materials, even for the 20% methylsilane loaded S5 sample. Likewise, the lower ratio of Q^3 and Q^2 species to Q^4 and T silicon environments indicates a lower hydrophilicity degree of the tested material because of the decrease of

the hydroxyl population. This is particularly evident for samples S4 and S5, compared with S1, where a great lowering in the intensity of the Q² and Q³ signals is achieved, whereas the intensity of the signal related to the organosilicon species (T groups) is enhanced. This result indicates a reduction of the surface hydroxyl population on the samples and thus, the increasing of the hydrophobic nature of the final materials when high loadings of Met-TES are used, because of two contributions: the reduction of hydroxyl population and the presence of the organic functionalities. Since the methyl silane starting precursor shows affinity both for the forming silica, because of the presence of the silicon atom, and the surfactant, because of the methyl group, we consider the most probable location for this moiety during the synthesis step is the interphase silica-micelle. The separation of the micelle from the pure inorganic silica by the methyl functionalities avoids the direct contact between the silanol groups, if present, and the surfactant micelles. Bearing in mind the aggressive hydrothermal conditions used for the synthesis of these materials, if the formed silanol groups are not stabilized because of interaction with micelles, they can be removed during the ageing step. Thus, if the amount of methyltriethoxysilane is increased, this effect is much more pronounced, which is in accordance with the observed reduction in the silanol population when higher loading of organic functionality are used.

Regarding the environment of the titanium sites, the coordination of the metallic atoms was evaluated by means of DR UV-Vis spectroscopy (see supplementary data). The spectra recorded for the methylated Ti-SBA-15 materials, display, as previously described for the study before, two contributions to the total UV absorption, being attributed to the electronic transitions at tetrahedral titanium species and cyclopentadienyl ligands coordinated to titanium sites. This latter signal becomes more and more intense insofar the methyl functionality loading increases. This behaviour can

be explained attending to the promoted organic nature of the materials. When increasing the organic content attached to the mesostructured material, the nature of the samples becomes more and more hydrophobic and thus the affinity between the sample and polar chemicals is reduced. Accordingly, the access of the ethanol molecules to the surface of the silica, the most probable location for the titanium sites [10], is hindered because of the repulsion between the washing solvent and the hydrophobic methyl functionalities. In this sense, the previously mentioned substitution of the cyclopentadienyl ligand by ethoxide groups is restricted and the UV signal attributed to the former is more intense for the higher organic loading.

Nitrogen adsorption-desorption isotherms recorded for samples with different methylsilane loadings have been included in figure 3(A). Some differences between the analyzed samples, regarding the shape of the isotherms, are evident. Thus, although all the materials display type IV isotherms, the shape of the hysteresis loops evolves from type H1 for sample S1 to type H2 for sample S5. Thus, unlike the presence of H1 hysteresis loops which is related to well defined narrow pore size distribution, H2 hysteresis loops are often found for disordered materials. In this sense the evolution of the shape of the hysteresis loop means a decrease in the ordering degree of the materials insofar the functionalization degree increases. This conclusion is in fairly good agreement with the calculated pore size distributions, included in figure 3(B). Sample S1 display a very narrow pore size distribution which becomes wider when increasing the loading of the organosilicon precursors. Thus, the full width at half maximum (noted as σ) of the calculated distributions increases from sample S1 to S4 and even more for sample S5, a fact which is related to the reduction in the ordering degree as previously concluded. Additionally, a displacement of the maximum of the pore size distributions, usually taken as the mean pore size, to lower values has been

detected. This reduction in the effective size of the pores is accompanied by an increasing of the surface area and total pore volume (Table 1). The explanation for this opposite trend is found in the reduction of the unit cell parameter (a_0) when increasing the loading of the methylsilane functionality (Table 1). This reduction means the number of pores per unit of volume increases when higher methylsilane loadings are employed. In other words, the width of the micelles of the structure directing agent becomes lower when increasing the amount of organosilane in the synthesis media. Nevertheless, the reduction observed in the unit cell parameter is not so high as that achieved for the pore sizes and thus, the resultant wall thickness increases with the organic loading. All these changes can be related to a deep interaction occurring between the methylsilane functionalities and the surfactant micelles, expanding the corona region in a similar way to that detected for PMO materials with SBA-15 topology [21]. This increased interaction could allow an interpenetration between the micelle and the pore wall caused by covering of the surfactant with methyl functionalities. In this way, the interplanar spacing is not largely modified but this phenomenon causes a reduction of the pore size when high loadings of organic functionality are used.

Figure 3(C) displays the X-ray diffraction patterns achieved for the materials prepared with different loadings of methylsilane. Although all the samples display low angle diffractions, meaning the presence of a structure at the mesoscale, the increasing of the organic loading decreases, as above noticed from other results, the ordering degree of the materials. Thus, the samples functionalized with a high organic loading exhibit low intense diffractions. Moreover the low angle halo almost overlaps the diffractions for samples prepared with high organic loadings, indicating poor signals. Besides, sample S4 (10% organosilicon loading) show very low intense d_{110} and d_{200} diffractions indicating a poor order, signals which are completely missed for sample S5 (20%

loading). Thus, in order to properly achieve well-structured mesoporous organically-modified Ti-SBA-15 materials, the organic loading added to the synthesis media should not be increased above 5%.

Since the increasing of the organosilicon loading greatly decreases the ordering of the resultant material, low organic charges have to be considered. On the other hand, using low alkyltrialkoxysilane to TEOS molar ratios yields less organically functionalized materials. For this reason further experiments based on the use of organosilicon precursors with larger organic groups have been developed, in order to obtain hybrid materials with a more pronounced organic nature. Thus, the lack of organic loading has been compensated by increasing the size of alkyl chain.

3.3 Length of the alkyl chain at the organosilicon precursor

The organic nature of the materials has been increased by using longer alkyl chains at the alkyltriethoxysilane precursor whereas low functionalization degrees were employed in order to preserve the mesostructure. Thus, besides the methyl group, ethyl, propyl and butyl functionalities have been employed. In order to increase the amount of titanium species supported onto the final materials, the synthesis gel was formed including a 6% of titanium, referred in weight to the total silicon species expressed as silica. Table 1 shows the physicochemical properties achieved for the samples prepared for this study as well as for a pure inorganic Ti-SBA-15 material, used as reference, with increased titanium loading too (Table 1, sample SBA(6%) and samples S6 – S9). As in previous assays, the use of larger organic functionalities in the organosilicon precursors leads to a decrease in the final titanium content supported onto the final materials, because of dilution of the metal species and competition effects, nevertheless the metal content is much higher than in previously described materials, because of the

higher loading of the metal precursor used for the synthesis of the materials under study. This fact, the increasing in the titanium incorporation efficiency with regards the materials prepared from 4% titanium, could mean that the impediments caused by the presence of alkyl functionalities are overcome because higher metal loading. In other words, the negative effect of the presence of organosilanes for the incorporation of titanium species is saturated. On the other hand, the incorporation of the organic species becomes less effective when increasing the size of the alkyl chain. Thus, the incorporation efficiency of the organosilicon precursor, assessed by means of ^{29}Si NMR spectroscopy (see supplementary data), is reduced from almost total incorporation for sample S6 (methylated sample) to 86% for sample S9 (butyl functionalized). This reduction in the organic content finally attached onto the surface of the materials is explained by the steric hindrances suffered by the larger organic functionalities. Thus, unlike small molecules, large alkylsilane moieties can not easily access to the micelles and thus the final incorporation of these functionalities is reduced.

Figure 4 displays the nitrogen adsorption-desorption isotherms (A), the calculated pore size distribution (B), the DR UV-Vis spectra (C) and the X-ray diffraction patterns (D) achieved for the materials functionalized with different alkyltriethoxysilanes. All the samples display type IV isotherms featured with very steep adsorption-desorption H1 hysteresis loops, indicating very narrow pore size distributions. Nevertheless the position of the inflection point at the adsorption branch is displaced to lower relative pressure values when increasing the size of the organosilicon precursor. This indicates the pore size of the mesostructured materials are clearly influenced by this synthesis variable. This can be clearly seen in the comparison of the pore size distributions (Figure 4(B)) of the prepared samples, where the longer alkyl chain, the smaller mean

pore size at the final material, because of the reduction of the free volume inside the pores.

The DR UV-Vis spectra recorded for the hydrophobized Ti-SBA-15 materials have also been achieved (Figure 4(C)) in order to determine the influence of the length of the alkyl chain at the organosilicon modifier on the environment of the supported titanium species. It is noteworthy how increasing the size of the alkyl chain at the organosilane precursor leads to an increasing of the intensity of the signal attributed to the presence of cyclopentadienyl ligands. As previously concluded, this fact is related to the presence of the organic functionality that repels the polar solvent used for the extraction of the structure directing agent. In this way, larger organic molecules, with a more pronounced hydrophobic nature, enhance this effect, and thus, the intensity of the UV signal related to Cp rings is increased. Following this reasoning, the hydrophobic behaviour of the surface of the organically functionalized Ti-SBA-15 materials is increased when using larger organic functionalities, as consequence of the more marked organic nature of the final materials.

The ordering degree of the synthesized materials has been assessed by means of XRD technique (Figure 4(D)). The size of the organosilicon precursor also influences the quality of the ordered structure because increasing the size of the organic functionality causes a decrease of the ordering degree, as it can be inferred from the reduction of the intensity at the d_{110} and d_{200} diffractions. This conclusion has also been obtained from TEM analysis (Figure 5). The materials prepared from small alkyl chains show the typical honeycomb structure of mesoporous SBA-15 materials. This perfect hexagonal array of mesopores is distorted when increasing the size of the organic moiety and thus, the butyl-functionalized sample S9 appears distorted to form almost a wormlike type structure, although some low range ordering remains visible. Back to the XRD analyses,

it is also noteworthy the displacement of the main diffraction signal through higher angle values, which means a reduction of the unit cell parameter (Table 1). This reduction involves a higher number of pores per volume in the materials when larger organic molecules are employed as modifying agents. Thus, using bulkier organic moieties seems to exert a similar influence than increasing the amount of the organosilane precursor in the synthesis media. In contrast, in this case the reductions observed for the mean pore size and unit cell parameter are very similar and thus, the wall thickness remains constant, probably because of the number of moles of the different organosilanes used for the hydrophobization of the samples was the same for all of the materials. This fact can be ascribed too, to the expansion of the corona area around the micelles. The use of larger alkyl chains allows better interpenetration between the pore wall and micelles. In this way, micelles get closer to their neighbours, causing the observed reduction in the unit cell parameter (see Table 1), but the expansion of the corona area corrects this effect keeping constant the pore wall thickness but at the expense of the pore size diameter.

3.4 Catalytic tests

The catalytic activity of the synthesized Ti-SBA-15 materials was assessed in the epoxidation of 1-octene with tert-butyl hydroperoxide as oxidant. Table 2 displays the catalytic results achieved with Ti-SBA-15 materials functionalized with different organic groups and prepared with a 6% wt. of titanium in the synthesis gel. The catalytic assay using non-functionalized Ti-SBA-15 material (sample SBA (6%); run 1) has also been included for reference purposes. All of the materials display catalytic activity in the epoxidation of the octene since substrate is converted in moderate to good extensions under the employed reaction conditions. 1,2-epoxyoctane was the sole product detected by gas chromatography so that a 100% selectivity of the catalyst in the

transformation of the olefin towards the oxirane has been assumed. In order to assess the heterogeneous nature of the supported titanium species, the reaction media used for the catalytic tests was analyzed by means of ICP-AES technique, looking for leached metal species. Negligible values under the quantification limit (0.005% in weight basis measured in accordance with the IUPAC recommendations [29]) were achieved on every case, confirming the high stability of the heterogenized metal species.

Non-functionalized Ti-SBA-15 material (sample SBA (6%)) yielded higher conversion of the reactants to those obtained using the organically modified materials, probably as consequence of the higher metal loading. Nevertheless, it is noteworthy for the hydrophobized materials, increasing the size of the organic functionality leads to increasing reactants conversions (Table 2, Runs 2 to 4) though the butyl functionalized material exhibits a much lower value for these reaction parameters. The increasing of the catalytic activity could be explained by a favoured adsorption process of the substrates onto the catalytic sites because of a more hydrophobic character of the surface because of the organic loading. On the other hand, the lower reactants conversion achieved for sample S9 could be attributed to an excessive dilution of the metal species.

Considering together the conversion of both reactants allows to calculate the efficiency in the use of the oxidant, which has been defined as the number of moles of reacted TBHP to lead a mole of the product. For comparison purposes the efficiency in the use of the oxidant and the turnover frequencies of the catalysts in the epoxidation reactions were calculated. The obtained values for this factor, as well as for the efficiency in the use of the oxidant, have been depicted in figure 6. Both parameters exhibit a clear correspondence with the number of atom carbons in the organic functionality of the hydrophobization agent. With regards the efficiency in the use of the oxidant, it is clear

the functionalization of the surface of the Ti-SBA-15 materials with organic groups leads to a beneficial effect over this parameter so that, the more hydrophobic behaviour, the more efficient use of the oxidant. The explanation for this behaviour is related to the access of the oxidant to surface hydroxyl functionalities in the catalytic materials. Hydroxyl groups are known to produce non-oxidative consumption of alkyl hydroperoxides [17], in other words, to decompose these chemicals without oxidizing the olefin. Thus, the organic functionalization through direct synthesis leads to changes on the hydrophilic / hydrophobic character of the surface. Thus, the interaction of the oxidant with hydroxyl groups is reduced because of the access of the oxidants to the surface is hindered by the organic functionalities and also they can be repelled because of the hydrophobic nature of the surface. Accordingly, the larger organic functionalities employed, the larger covered area, and lower interaction between oxidant and silanol groups. In this way, bulkier organic functionalities provides more hydrophobic behaviour and hinders the access of the hydroperoxide oxidant to the silanol groups, preventing its decomposition and enhancing the efficiency on its use.

Bearing in mind the titanium content of the samples, the differences observed between samples are even higher. Nevertheless, non-functionalized sample SBA (6%) display a higher catalytic activity than methylated sample S6, being the turnover frequency of the former higher than that achieved for sample S6. This could be attributed to a double effect introduced by the organic functionalities in the catalytic behaviour of these samples. On one hand, the access of reactants to titanium sites could be partially hindered because of partial covering by the alkyl functionalities, in a similar way the access of the oxidant to silanol groups are diffculted. On the other hand, the adsorption of the reactants onto the surface of the catalysts, next to titanium sites, is favoured when increasing the length of the alkyl chains, because of a more pronounced organic nature

of the surface, improving the intrinsic catalytic activity of the materials. Considering this, the catalytic results indicate small organic functionalities like methyl groups do not improve very much the adsorption process and thus the catalytic activity is not very much enhanced, but they can cover the titanium species, reducing in this way the overall catalytic activity of the material, which explains the lower TOF value achieved for this material compared with non functionalized Ti-SBA(6%) sample. Nevertheless, when the size of the organic functionality is increased, the beneficial aspects of a more marked hydrophobic microenvironment of titanium sites are noticeable, favouring the internal diffusion of reactants and products and finally leading to increasing catalytic activity per titanium site, overcoming the trouble of the covering of titanium species.

Finally, in order to probe the true heterogeneous nature and the stability of these catalysts, some reutilisation tests have been performed. Figure 7 shows the results achieved in the reutilisation reaction runs using sample S9 (butyl-functionalized Ti-SBA-15). This material has been selected for this test since this is the catalyst showing the highest intrinsic catalytic activity among the tested materials. The results achieved in the reutilisation assays do not evidence any loss in catalytic activity, which probes the heterogeneous nature of the catalyst as well as the stability of titanium species supported on the material.

4. Conclusions

The synthesis of organically modified Ti-SBA-15 materials in a single step leads samples with high dispersion of the metal species and enhanced hydrophobic behavior. Regarding the synthesis conditions, the order of the addition of the silicon precursor is a critical variable that has to be carefully controlled to achieve properly structured organically-modified Ti-SBA-15 materials. The amount of the organic functionality can

be increased up to 20% on a molar basis referred to the TEOS precursor but the resultant materials display poor structured mesophases. Increase of hydrophobization degree of titanium microenvironments can also be achieved by using large organosilane precursors. The catalytic activity of these organically modified Ti-SBA-15 materials is greatly influenced by the length of the alkyl chain at the organic functionalities. The larger organic functionalities attached to the final titanium-based catalysts, the higher catalytic activity per titanium site and efficiency in the use of alkyl hydroperoxides.

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Figure Captions

Figure 1. (A) DR UV-Vis spectra and (B) XRD patterns recorded for methylated Ti-SBA-15 materials prepared using different orders of addition of the silicon precursors.

Figure 2. Solid state ^{29}Si MAS-NMR analysis obtained for methylated Ti-SBA-15 materials with different organic loadings.

Figure 3. (A) N_2 adsorption-desorption isotherms at 77K, (B) Mesoscopic pore size distributions and (C) XRD patterns achieved for Ti-SBA-15 materials functionalized with different loadings of methyltriethoxysilane.

Figure 4. (A) N_2 adsorption-desorption isotherms at 77K, (B) Mesoscopic pore size distributions, (C) DR UV-Vis spectra and (D) XRD patterns obtained for organically modified Ti-SBA-15 materials functionalized with different organic groups.

Figure 5. TEM images recorded for Ti-SBA-15 materials functionalized with different alkyl groups.

Figure 6. Correlation between the efficiency in the use of the oxidant and turnover frequency with the size of the organic group attached on Ti-SBA-15 catalysts in the catalytic epoxidation of 1-octene.

Figure 7. Reutilisation tests carried out with sample S9 in the epoxidation of 1-octene with TBHP.

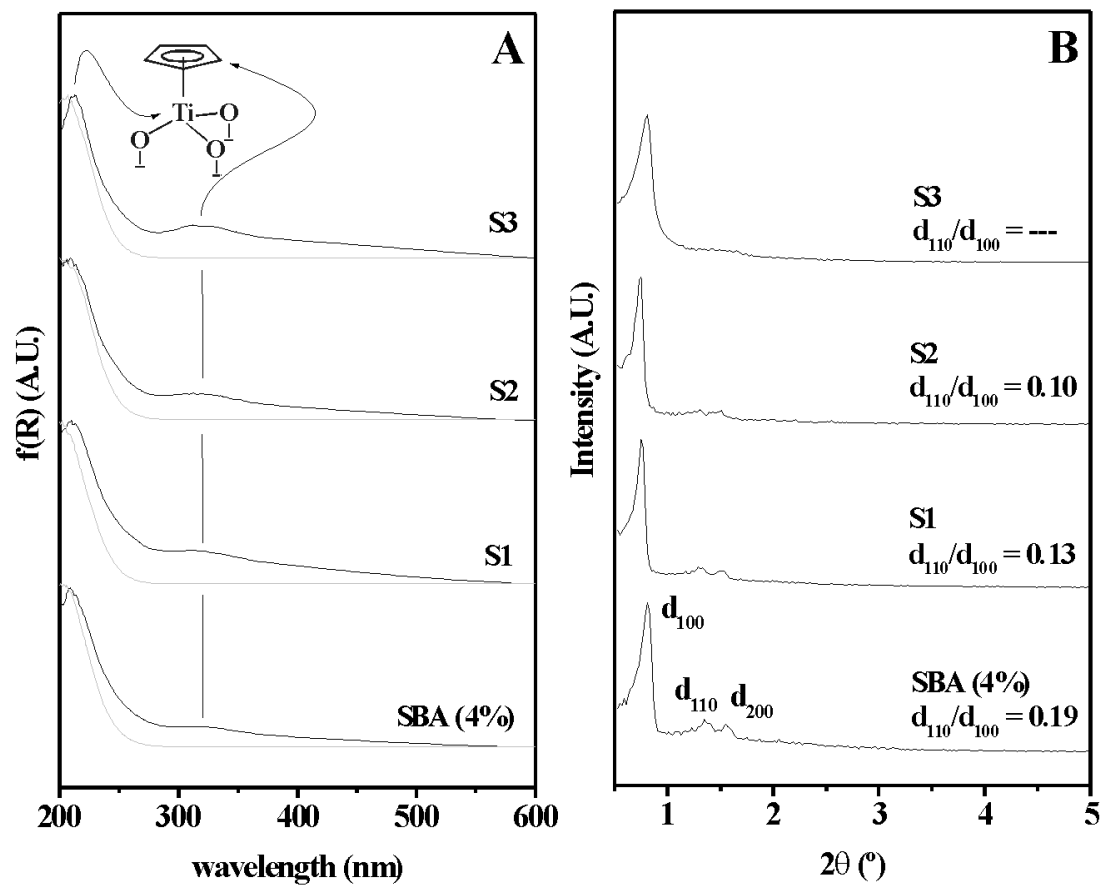


Figure 1.

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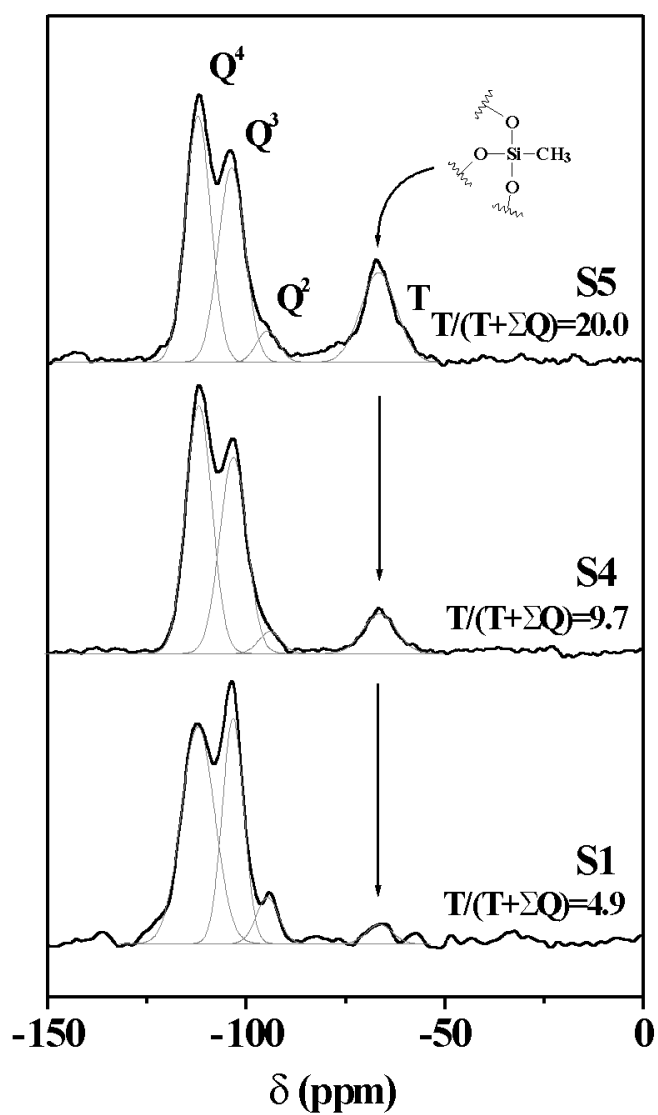


Figure 2.

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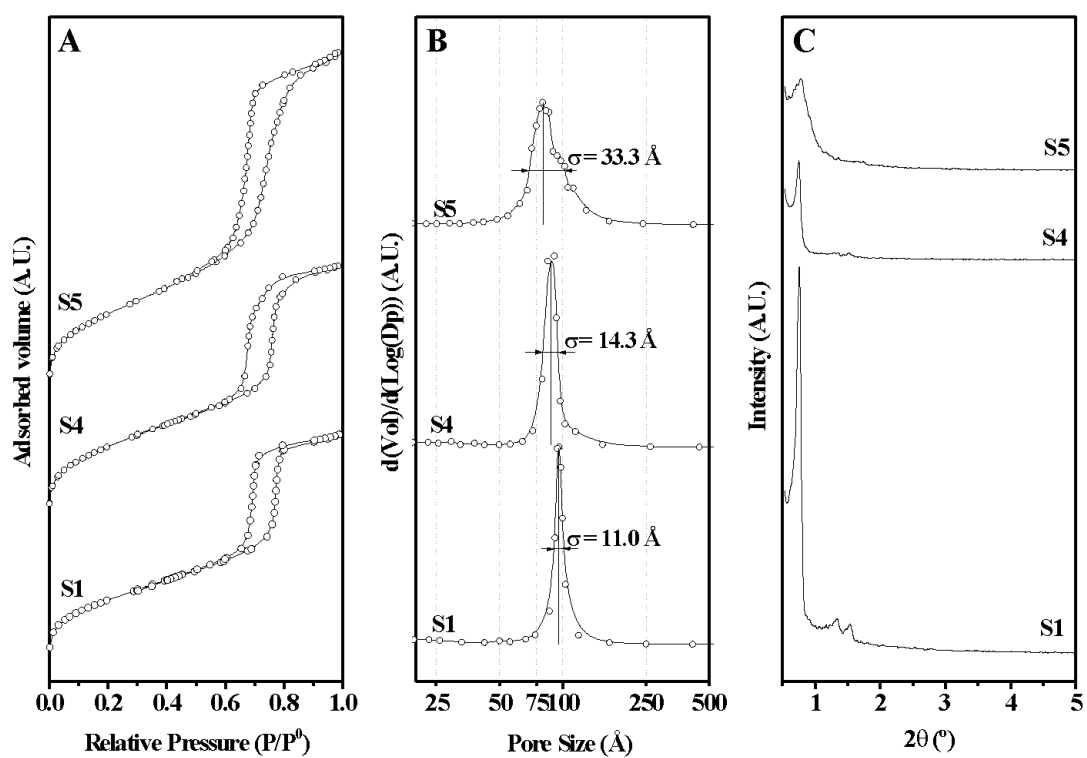


Figure 3

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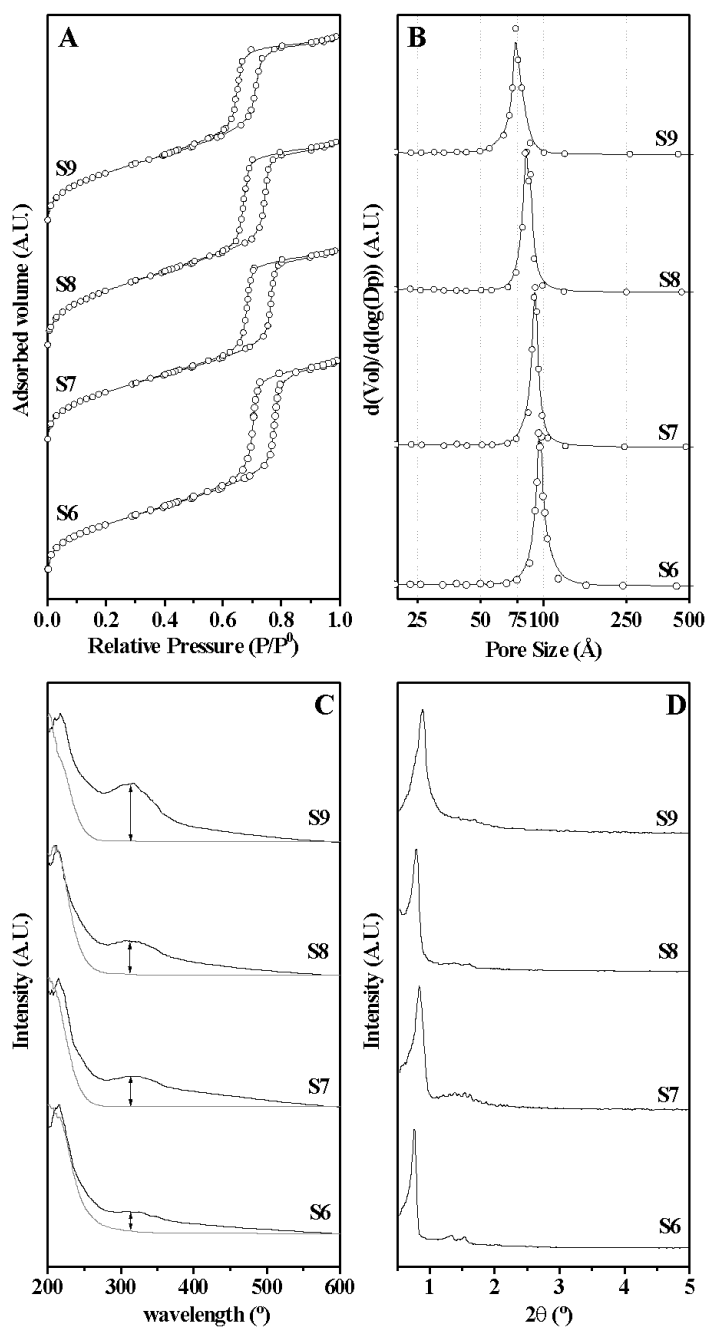


Figure 4

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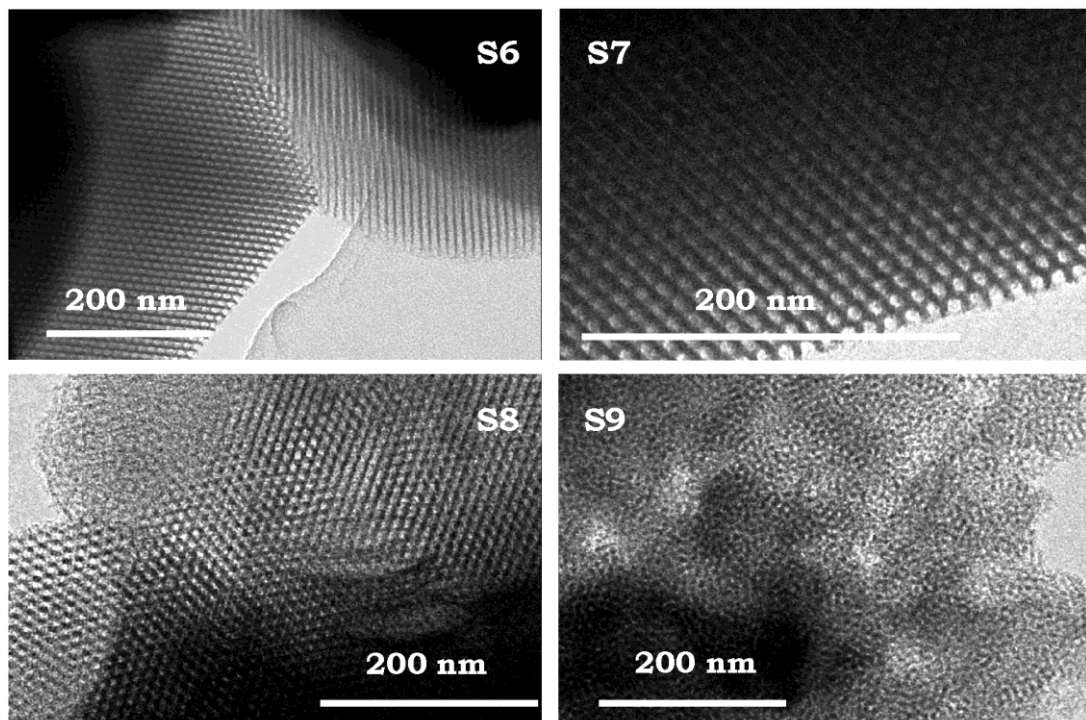


Figure 5.

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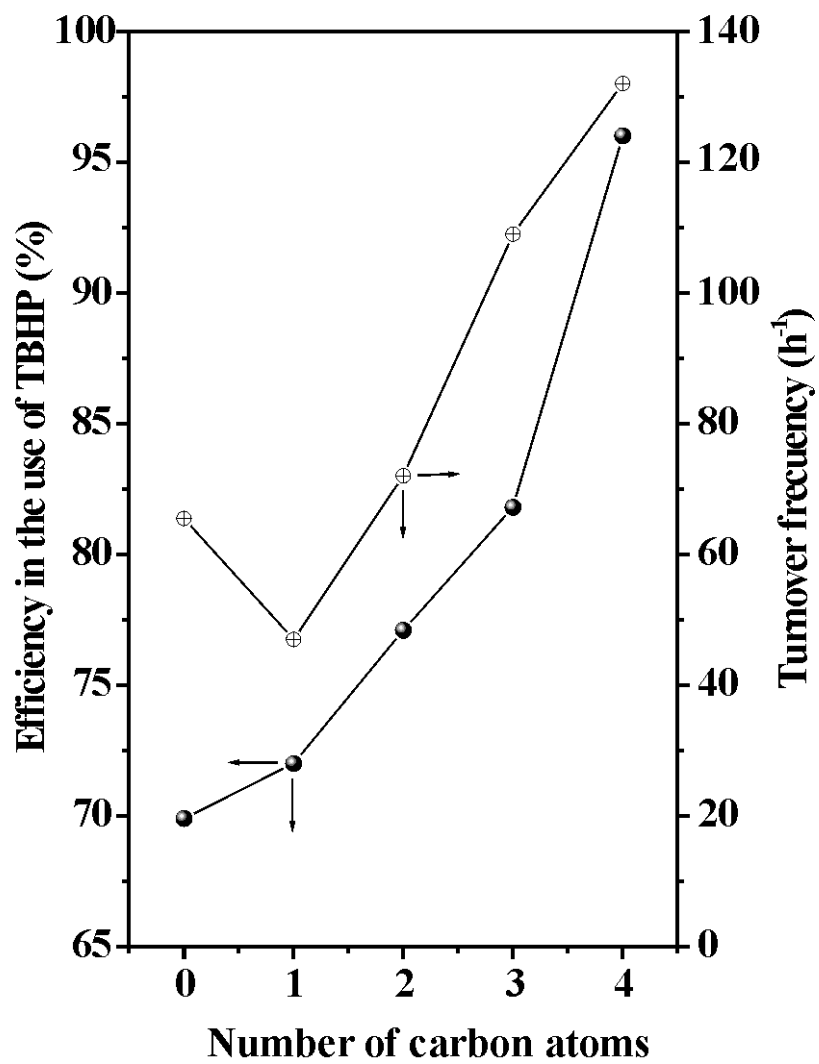


Figure 6

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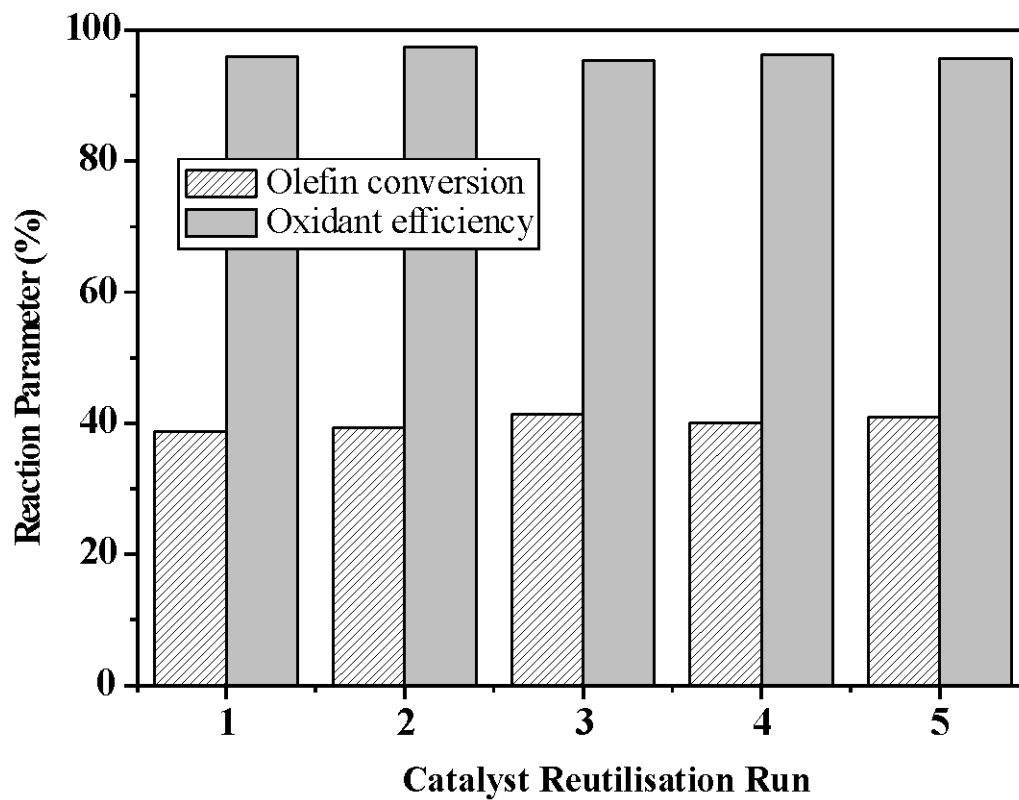
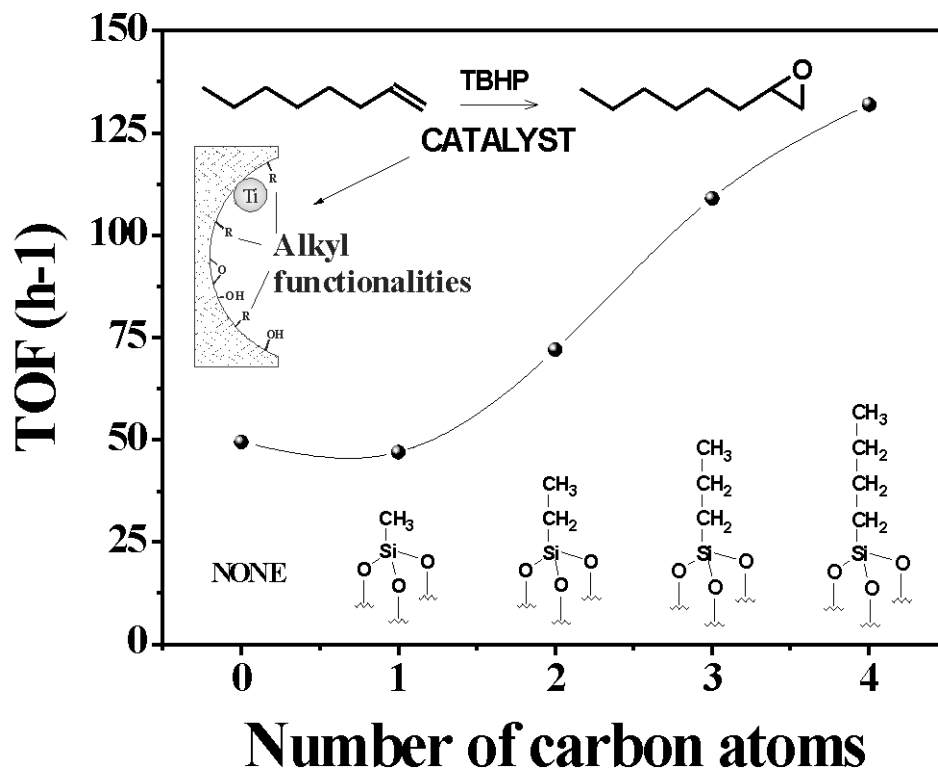


Figure 7

J. Iglesias



Graphical abstract

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Table 1. Synthesis conditions and physicochemical properties of organically-modified Ti-SBA-15 materials

Sample ^a	Synthesis conditions			Chemical composition			Textural properties			Structural parameters		
	Silicon precursors & order of addition	R-TES ₀ ^b (%)	Ti ₀ ^c (%)	Ti ^d (%)	R-TES ^e (%)	η_{R-TES} ^f (%)	Sg ^g (m ² /g)	Vp ^h (cm ³ /g)	Dp ⁱ (Å)	d ₁₀₀ ^j (Å)	a ₀ ^k (Å)	Wt ^l (Å)
SBA (4%)	TEOS	---	4.0	0.56	---	---	774	0.95	91	108	124	33
S1	TEOS / Met-TES	5.0	4.0	0.28	4.9	98.0	632	0.94	96	117	135	39
S2	TEOS & Met-TES	5.0	4.0	0.36	4.9	98.0	691	0.93	94	119	137	43
S3	Met-TES / TEOS	5.0	4.0	0.31	5.0	100.0	665	0.92	95	120	139	44
S4	TEOS / Met-TES	10.0	4.0	0.23	9.7	97.0	733	1.05	90	118	136	46
S5	TEOS / Met-TES	20.0	4.0	0.17	20.0	100.0	764	1.39	80	112	129	49

SBA (6%)	TEOS	---	6.0	0.67	---	---	825	1.25	103	112	130	27
S6	TEOS / Met-TES	5.0	6.0	0.61	4.8	96.0	651	1.02	96	118	136	40
S7	TEOS / Et-TES	5.0	6.0	0.45	4.6	92.0	678	0.93	91	116	134	43
S8	TEOS / Pr-TES	5.0	6.0	0.38	4.5	90.0	758	0.99	83	110	127	44
S9	TEOS / But-TES	5.0	6.0	0.25	4.3	86.0	676	0.90	74	101	117	43

^a All the materials were prepared starting with an initial titanium loading of 4% to 6% wt; ^b Initial organic functionality loading; ^c Initial titanium content in the synthesis gel in weight referred to the total silicon precursors expressed as silica; ^d Final titanium content in weight; ^e Final organic loading measured by ²⁹Si NMR; ^f Efficiency in the incorporation of the organic functionality; ^g Specific surface area measured by the BET method; ^h Total pore volume recorded at p/p0=0.985; ⁱ Mean pore size calculated by the BJH method applying the KJS correction; ^j Interplanar spacing measured by XRD; ^k Unit cell parameter calculated as $a_0=2/\sqrt{3}\cdot d_{100}$; ^l Pore wall thickness calculated as $wt = a_0-Dp$

Table 2. Catalytic results in the epoxidation of 1-octene with TBHP in presence of organically-modified Ti-SBA-15 catalysts.

Run ^a	Catalyst	Ti ^b (%)	X _{Octene} ^c (%)	X _{TBHP} ^d (%)	η _{TBHP} ^e (%)
1	SBA (6%)	0.67	44.9	51.8	69.3
2	S6	0.61	33.8	37.8	72.0
3	S7	0.45	38.9	41.7	77.1
4	S8	0.38	48.7	48.8	81.8
5	S9	0.25	38.8	33.8	96.0

^a Reactions carried out using Catalyst to substrate mass ratio of 12:1 and TBHP to 1-Octene molar ratio of 1.2:1, ^bTitanium content in weight basis; ^c 1-octene conversion; ^d TBHP conversion; ^e TBHP efficiency