

**Direct synthesis of titanium substituted mesostructured materials using non-ionic surfactants and titanocene dichloride**

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## Abstract

Titanium-substituted mesoporous molecular sieves have been successfully synthesized using non-ionic surfactants and titanocene dichloride under strong acidic conditions. Structure-textural parameters of the synthesized materials were characterized by using X-ray diffraction and nitrogen adsorption techniques. The increasing of the gel solution pH allows an enhancement of titanium within the mesostructure without damage of textural properties and presence of extra-framework species. The high accessibility and dispersion of titanium centres has been proved by means of  $\text{NH}_3$  adsorption and DR UV-Vis spectroscopy, being compared with TS-1 material. The synthesized materials show high activity and selectivity in the selective epoxidation of 1-octene with ethylbenzylhydroperoxide as oxidant. Moreover, silylated samples promoted an increase of epoxide selectivity.

## 1. INTRODUCTION

Titanium-containing silica-based catalysts have played an important role on a large variety of oxidation processes during the last three decades and thus, there is a large knowledge about the synthesis of many kinds of titania-silica materials and their application to oxidation reactions as catalysts. In spite of this great experience, SiO<sub>2</sub>-TiO<sub>2</sub> materials are still a subject of interest for researchers as it can be inferred from the huge amount of information reported every year on this matter. The discovery of the Shell catalyst [1] and the development of the TS-1 zeolitic material [2], in the seventies and eighties respectively, have been the major breakthroughs in this field and nowadays they are still being used on an industrial scale as catalysts for oxidation reactions. On the other hand, these materials show some disadvantages which reduce their applicability range, as the high sensitivity of titanium species against water traces in the shell catalyst or the small pore size of the TS-1 material. The new silica-based ordered mesoporous materials with pore size distribution in the mesoporous range, such as MCM-41 [3] and SBA-15 [4,5], may be the solution for these restrictions. Although the gap between zeolites and macroporous supports was covered by amorphous silica like xerogels [6], mesostructured materials show many more advantages to be used as catalysts, mainly due to the uniform pore size that features them. Incorporation of metal species into the matrix of mesostructured materials has been raised by post-synthetic treatments [7-8] and direct synthesis procedures [3, 9], involving the addition of a metal precursor to the synthesis media. In this sense, it is widely known that the dispersion of the titanium centers, the accessibility of the substrates to them and the porous structure of the final material play a dramatic influence on the catalytic behavior of these catalysts. Moreover, these features can be controlled through the choice of the proper synthetic procedure and the titanium precursor. In this way it is noteworthy direct

synthesis procedures offers much more advantages than any other preparation method, as it usually leads to a more stable and dispersed metal species into the material as well as the functionalization of the silica can be carried out in only one step. Direct synthesis methods have been applied successfully to the preparation of Ti-MCM-41 [9-10] and Ti-HMS [11], but direct substitution of titanium species into the walls of SBA-15 materials seems to be more difficult, among various reasons, because of the strongly acidic media used during its synthesis. Nevertheless, the interest for synthesizing Ti-SBA-15 instead of any other material belies on its higher hydrothermal stability, compared to MCM materials, and the possibility to be obtained with a higher mesostructured pore size, a crucial property when using bulky substrates. Currently, some articles have reported the use of a direct synthesis method in order to obtain Ti-SBA-15 materials. The first successfully attempt in this sense was reported by Newalkar et al. [12] using a direct synthesis method involving microwave thermal conditions and  $\text{TiCl}_4$  as metal precursor. The materials so obtained does not present anatase domains up to achieve a Si/Ti content around 20 which confirms the right isomorphic substitution of the framework titanium species. Nevertheless, the materials so obtained have not been tested in oxidation reactions so there is still a question mark over their catalytic behavior. Later, Li et al. [13] reported a new approach for the direct synthesis of Ti-SBA-15 using tetramethoxysilane and titanium isopropoxide as starting materials. This strategy, carried out in the presence of fluoride atoms in order to control the hydrolysis and condensation rates of the precursors, leads to materials with a good mesoscopic array and narrow pore size distributions, but poorly functionalized with titanium species as well as anatase domains appear when titanium content raises from a molar ratio of  $\text{Si/Ti} = 100$  in the synthesis mixture. Kholdeeva et al. [14] published a conventional hydrothermal procedure for the synthesis of highly ordered Ti-SBA-15, using  $\text{TiOSO}_4$

and  $\text{Na}_2\text{Si}_2\text{O}_5$  as metal and silicon precursors respectively. Although the titanium content is greatly increased compared to previous works, all the samples contain a high proportion of anatase domains which is a consequence of the low titanium dispersion into the silica matrix leading to a material with low-accessible titanium centers. Ti-SBA-15 has been also synthesized by means of ultrasonic irradiation using TEOS and titanium isopropoxide as precursors and tested in the oxidation of 2,6-di-tert-butylphenol [15]. The highest Ti content was 1.5 (wt. %) starting with synthesis mixtures containing a Si/Ti molar ratio of 3 (that means theoretical Ti content of 17 wt. % in case of complete incorporation). Recently, a method based on the adjusting of pH up to 7.5 after co-condensation of titanium ( $\text{TiCl}_4$ ) and silica (TEOS) species followed by a hydrothermal treatment has been reported [16]. A large amount of Ti species was introduced into SBA-15 materials up to Si/Ti molar ratios of 22 but the materials showed broad DR-UV-Vis spectra denoting the presence of penta- or hexa-coordinated species and no catalytic activity was reported. Summarizing, all the works described in literature using non-ionic surfactants and strong acidic-conditions have afforded materials with titanium centres buried into the silica matrix and in most of cases the catalytic activity has been poorly described. Titanocene dichloride has proved to be an interesting compound to be used as metal precursor for the synthesis of Ti-functionalized materials due to its inherent stability in comparison with conventional titanium sources such as  $\text{TiCl}_4$  or  $\text{Ti}(\text{OR})_4$ . Thomas and coworkers [7] demonstrated the protective effect of the Cp ligands, which prevents the formation of anatase domains and thus contributes to get higher dispersion degrees of the metallic centers, in the synthesis of Ti-MCM-41 materials anchoring the titanium species by post-synthetic procedures. Additionally, Coluccia et al. [10] have used the same titanium compound for the one-step synthesis of Ti-TLCT silica. In this later research it has been concluded

the hydrophobic nature of the Cp rings allows the location of titanium species into the micelles of the organic surfactant during the synthesis of the mesostructured silica, avoiding the attack of the mineralization agent to the titanium compound. In this way the so-obtained Ti-functionalized silica shows more accessible metal centers than when using other titanium precursors. In this work, we present a similar procedure to that reported by Coluccia and co-workers [10] for the direct synthesis of Ti-containing mesostructured materials using block-copolymer surfactants under strong acidic conditions and  $(\text{Cp})_2\text{TiCl}_2$  as titanium precursor. Under these synthetic conditions the challenge is the preparation of Ti substituted mesostructured materials with the maximum titanium content and absence of anatase accompanied with high accessibility of metal center for catalytic purposes. The synthesized materials have shown excellent catalytic activity in the liquid phase epoxidation of 1-octene with ethylbenzylhydroperoxide towards the corresponding epoxide. Likewise, the accessibility of active centers has been proved by means of thermal programmed desorption of ammonia molecules.

## **2. EXPERIMENTAL SECTION**

### **2.1 Samples preparation**

2.1.1 *Synthesis of Ti-substituted mesostructured materials.* The Ti-SBA-15 materials were synthesized using tetraethylorthosilicate (TEOS, Aldrich) and titanocene dichloride ( $\text{Cp}_2\text{TiCl}_2$ ; Aldrich) as silicon and titanium precursors. Different triblock copolymers (Pluronic 123,  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ; Brij56,  $\text{C}_{16}\text{EO}_{10}$ ; Brij76,  $\text{C}_{18}\text{EO}_{10}$ , all of them supplied from Aldrich) were used as structure-directing agents. Concentrated HCl aqueous solution was used as the acid source. The typical synthetic procedure of Ti-

substituted materials was as follows: 4 g of surfactant was dissolved in 125 ml of an aqueous solution of hydrochloric acid with varied concentrations. The solution was then heated up to 40°C (50 °C for Brij type surfactants) before adding the appropriate amount of titanium precursor. Prior to the addition of TEOS, a prehydrolysis time of 180 minutes was fixed. The resulting mixture was stirred at 40°C for 20 additional hours and hydrothermally aged at different temperatures and times under static conditions. After the synthesis, the solid product was recovered by filtration and air-dried overnight.

*2.1.2 Surfactant removal procedures.* The polymeric template was removed from as-made silica-based mesoporous materials through different techniques including thermal treatments and low-temperature solvent extraction. The thermal treatment consists on calcining the as-synthesized silica materials for 7 hours at 550 °C under air atmosphere. Analogously, following the method reported by Zhao et al. [4], block copolymer was removed from as-made materials by washing with ethanol under reflux in a magnetically stirred flask for 24 hours (1.5 g. of as-synthesized material per 400 ml. of ethanol).

*2.1.3 Silanization procedure.* The surface of the calcined / extracted silica-based materials has been end-capped with hexamethyldisilazane (HMDS) through a modified grafting procedure reported elsewhere [17]. In a typical preparation an appropriate amount of HMDS was dissolved in 200 g. of toluene followed by addition of the outgassed silica material (HMDS/ raw material mass ratio of 0.6). The resultant suspension was stirred at room temperature during 1 hour under nitrogen atmosphere allowing the diffusion of the silylating agent into the porous structure of the silica material. Thereafter, silylated product was recovered by filtration and intensively washed with toluene to remove nonreacted disilazane. Finally the material was dried at 200°C in an air flow during 4 hours.

2.1.4 *Other materials.* With the purpose of comparison, pure silica SBA-15 and TS-1 were synthesized according to procedures reported in literature [6,18]. Anatase, used as reference material, was supplied by Grace. A Ti/SiO<sub>2</sub> catalyst was prepared according to the procedure reported in the literature [19].

## 2.2 Samples characterisation

X-ray powder diffraction (XRD) data were acquired on a PHILIPS diffractometer using Cu K $\alpha$  radiation. Typically, the data were collected from 0.6 to 50.0° (2 $\theta$ ) 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. Nitrogen adsorption-desorption isotherms were collected using an adsorption porosimeter (Micromeritics, TRISTAR 3000) at 77K. The surface areas were calculated by the B.E.T. method. Pore sizes distributions were obtained applying the B.J.H. model assuming cylindrical geometry for the pores and using a Harkins-Jura expression for the multilayer thickness, specifically obtained for SBA-15 type materials. The pore volume was taken at P/P<sub>0</sub>= 0.985 single point. Transmission electron microscopy (TEM) microphotographs were carried out on a PHILIPS TECNAI-20 electron microscope operating at 200 kV. Titanium content was determined by ICP-atomic emission spectroscopy. The samples (100 mg) were dissolved in aqueous hydrofluoric acid. After dissolution, the sample was 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 <sup>29</sup>Si NMR experiments were performed on a VARIAN-Infinity 400 spectrometer operating at a frequency of 79.4 MHz with the



following conditions: magic-angle spinning at 6 kHz;  $\pi/2$  pulse, 4.5  $\mu\text{s}$ ; a repetition delay of 15 s; and 3,000 scans. Spectrum was referenced to tetramethylsilane.

Ammonia temperature programmed desorption (TPD) experiments were carried out in a Micromeritics 2910 (TPD/TPR) equipment. Previously, the samples were outgassed under a helium flow (50  $\text{Nml min}^{-1}$ ) with a heating rate of 15  $^{\circ}\text{C min}^{-1}$  up to 560  $^{\circ}\text{C}$  and kept at this temperature for 30 min. After cooling to 60  $^{\circ}\text{C}$ , an ammonia flow of 35  $\text{Nml min}^{-1}$  was passed through the sample for 30 min. The physisorbed ammonia was removed by flowing helium at 60  $^{\circ}\text{C}$  for 90 min. The chemically adsorbed ammonia was determined by increasing the temperature up to 560  $^{\circ}\text{C}$  with a heating rate of 15  $^{\circ}\text{C min}^{-1}$ , being kept this temperature for 30 min. The ammonia concentration in the effluent helium stream was measured through a thermal conductivity detector (TCD).

### **2.3 Catalytic tests**

The catalytic tests of 1-octene epoxidation were carried out in a batch reactor equipped with a temperature controller and pressure gauge at 110  $^{\circ}\text{C}$  for different reaction times hour under stirring. Catalysts and 1-octene (catalyst : 1-octene mass ratio of 0.02; mass catalyst of 1.0 g) were charged into the teflon-lined reactor and the system was heated up to 110  $^{\circ}\text{C}$ . Once the temperature reached 110 $^{\circ}\text{C}$ , the required amount of oxidant was added. Ethylbenzylhydroperoxide (EBHP; 35 wt. % ethylbenzene solution supplied by Repsol) was used as oxidant (EBHP (35 wt. %): 1-octene mass ratio of 0.7). Then, aliquots were withdrawn after 1 and 2 hours during the reaction course with the purpose of monitoring the evolution of oxidant conversion and oxidant selectivity towards the epoxide formation. Peroxide conversion was measured by iodometric titration whereas reaction products were analyzed by means of chromatography analysis.

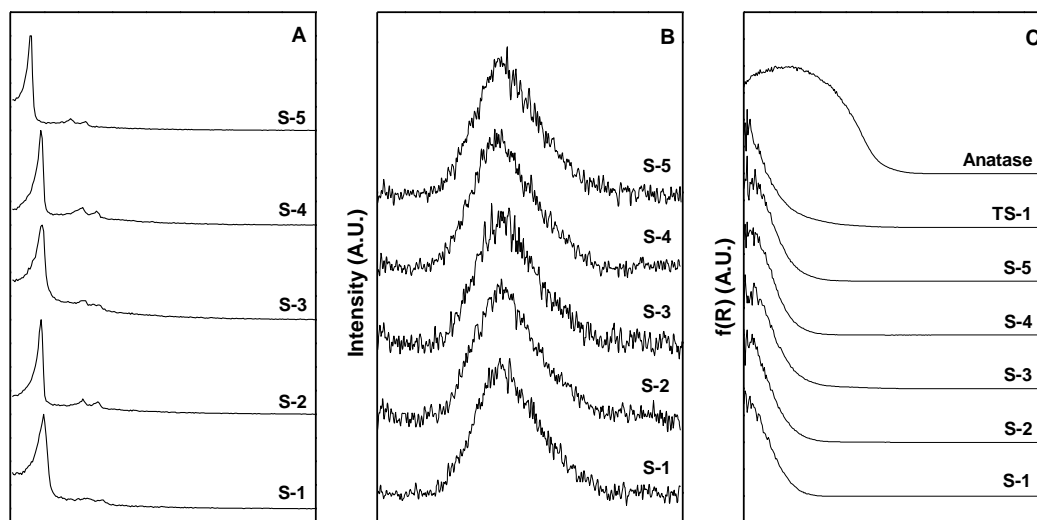
### 3. RESULTS AND DISCUSSION

#### 3.1 Titanium incorporation

Different synthetic strategies have been undergone with the purpose of incorporating the maximum content of titanium atoms effectively attached within the silica mesostructure synthesized under strong acid conditions in presence of non-ionic surfactants.

Initially, several Ti-substituted mesostructured material were prepared accordingly to the reported synthetic conditions for pure silica SBA-15 [4,5], using a stepping-up titanium content in the initial mixture (Samples S-1, S-2 and S-3. Table 1). Figure 1A presents the XRD patterns obtained for the synthesized materials with different titanium loadings. All the samples show the typical diffraction pattern of a mesostructured material with a p6mmc-type hexagonal ordering. The strong signal detected at lower angle values is assigned to the (100) reflection and it is accompanied with the reflections (110) and (200) which confirm the high mesoscopic order of the materials regardless of the amount of titanium precursor. These results are in contrast to that reported by Chen et al. [20] where poor mesoscopic order was obtained under similar conditions but using  $\text{TiCl}_3$  instead of titanocene dichloride as metal precursor. Moreover, X-ray diffractograms obtained for high angle range (Figure 1B) show a single very broad peak about  $23^\circ$  characteristic of amorphous silica. No line characteristic of an anatase structure associated with  $\text{TiO}_2$  deposits is observed even for the highest titanium load. These results are in line with the DR UV-Vis spectra shown in Figure 1C where a strong absorption band centred at 210 nm is observed for all these samples confirming the absence of anatase and the incorporation of Ti centres in a tetrahedral environment within the silica structure [21]. Interestingly, Ti substituted

mesostructured materials depicts a signal with similar broadness to that shown by a comparative TS-1 sample (Si/Ti=72). Although the Ti contents are different, a good dispersion of Ti sites is clearly inferred for these Ti containing mesostructured samples.



**Figure 1.** XRD spectra (A) at low and (B) high angle and (C) DR UV-VIS spectra for calcined Ti-SBA-15 samples.

**Table 1. Physicochemical properties of calcined Ti-substituted mesostructured materials**

Sample	Synthesis Conditions					Textural properties			Chemical Composition	
	Surfactant	Si/Ti <sup>a</sup>	TEOS / Surf <sup>b</sup>	HCl <sup>c</sup>	Ageing <sup>d</sup> T (°C) / t (h)	S <sub>BET</sub> (m <sup>2</sup> /g)	D <sub>p</sub> <sup>e</sup> (Å)	V <sub>p</sub> <sup>f</sup> (cm <sup>3</sup> /g)	Si/Ti <sup>g</sup>	TiO <sub>2</sub> (%) <sup>h</sup>
S-1	Pluronic 123	40	47	1.9	100 / 24	723	94	1.05	332	0.4
S-2	Pluronic 123	20	47	1.9	100 / 24	808	93	1.20	147	0.9
S-3	Pluronic 123	13	47	1.9	100 / 24	763	94	1.10	120	1.1
S-4	Pluronic 123	20	47	0.5	100 / 24	818	90	0.99	130	1.0
S-5	Pluronic 123	13	47	0.5	100 / 24	809	92	0.95	94	1.4
S-6	Pluronic 123	20	47	1.9	60 / 24	562	62	0.61	147	0.9
S-7	Pluronic 123	20	47	1.9	150 / 24	372	139	1.11	21	5.9
S-8	Pluronic 123	20	47	1.9	80 / 72	750	79	1.15	130	1.0
S-9	Brij 56	20	47	1.9	100 / 24	829	37	0.93	332	0.4
S-10	Brij 76	20	47	1.9	100 / 24	868	42	1.04	265	0.5

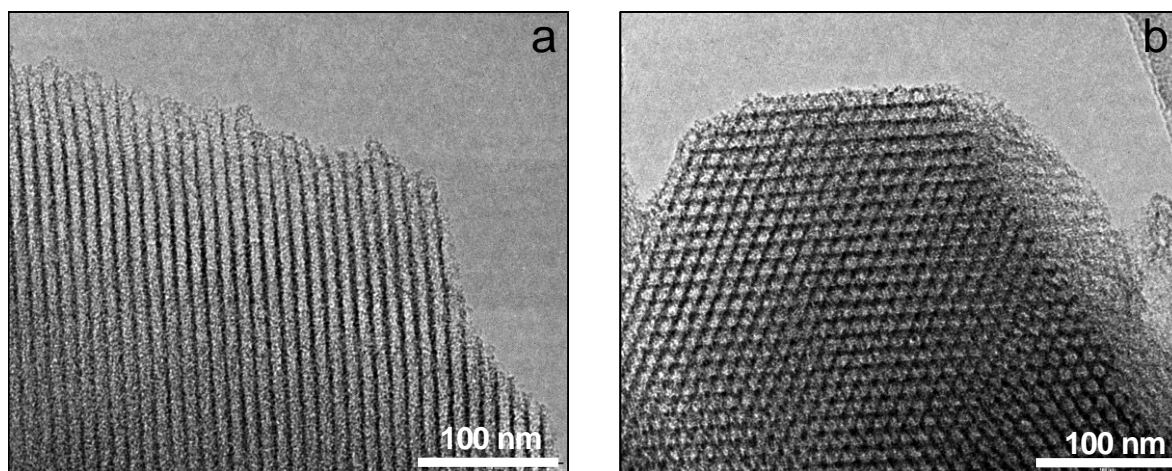
<sup>a</sup> Si/Ti molar ratio in the initial synthesis mixture; <sup>b</sup> TEOS/surfactant molar ratio in the initial synthesis; <sup>c</sup> Molar acid concentration in the synthesis mixture; <sup>d</sup> Ageing conditions. Temperature/Time; <sup>e</sup> Mean pore size using BJH model; <sup>f</sup> Total pore volume at P/P<sub>0</sub> of 0.985; <sup>g</sup> Si/Ti molar ration in the synthesised material after surfactant removal; <sup>h</sup> TiO<sub>2</sub> percentage in weight in the synthesized material after surfactant removal

The textural properties of the three samples are summarized in Table 1 (Samples S-1, S-2 and S-3). The incorporation of titanium into the framework of SBA-15 does not affect the pore diameter and pore volume. Additionally the pore diameter is larger than that conventionally obtained for pure silica SBA-15 (ca. 85 Å) indicating a possible swelling effect of the hydrophobic nature of the Cp rings. Similar increasing is obtained in the surfaces area of Ti-SBA-15 samples as compared with pure silica SBA-15 material (ca. 600 m<sup>2</sup>/g).

Chemical analysis of the calcined samples shown in Table 1 clearly indicate that the amount of Ti incorporated within the silica structure is much smaller than the amount added to the initial mixture. However it is clearly seen that the incorporation of Ti species enhances as the content in the initial mixture increases. The relative low incorporation efficiency of titanium atoms is related to the strong acidic conditions used for the synthesis of SBA materials. Under these conditions, Ti<sup>+4</sup> ions are greatly solubilized in aqueous media as well as the stability of Ti-O-Si bonds decreases [13]. However, results recently reported by Bao *et al.* [20], using TiCl<sub>3</sub> as titanium precursor under similar conditions to those used in this work, displayed just a Si/Ti ratio in the final product of 300 starting from Si/Ti of 20 in the gel solution, a similar initial content to that used in our contribution (see Table 1, sample S-2). This degree of incorporation is significantly lower to that showed in this work evidencing the beneficial effect of (Cp)<sub>2</sub>TiCl<sub>2</sub> for the improvement of titanium incorporation in strong acidic conditions.

With the purpose of increasing the titanium incorporation, the acid concentration was diminished up to 0.5 M (ca. pH 0.3) during the hydrolysis and condensation of silica and titanium precursors (S-4 and S-5 samples; Table 1). As the acidity of the gel solution decreases from 1.9 M to 0.5 M, the incorporation degree of titanium is clearly enhanced. Moreover, it is also found that Ti-SBA-15 samples obtained at weaker acidic

conditions show similar UV-VIS spectra (Figure 1. c), without any absorption band beyond than 250 nm indicating a good dispersion of Ti atoms in spite of increasing their content. Textural properties are preserved under weaker acidic conditions as it is clearly evidenced in Table 1 In the same sense Figure 2 displays TEM images of S-5 sample where it is evident the high mesoscopic ordering achieved for this sample.

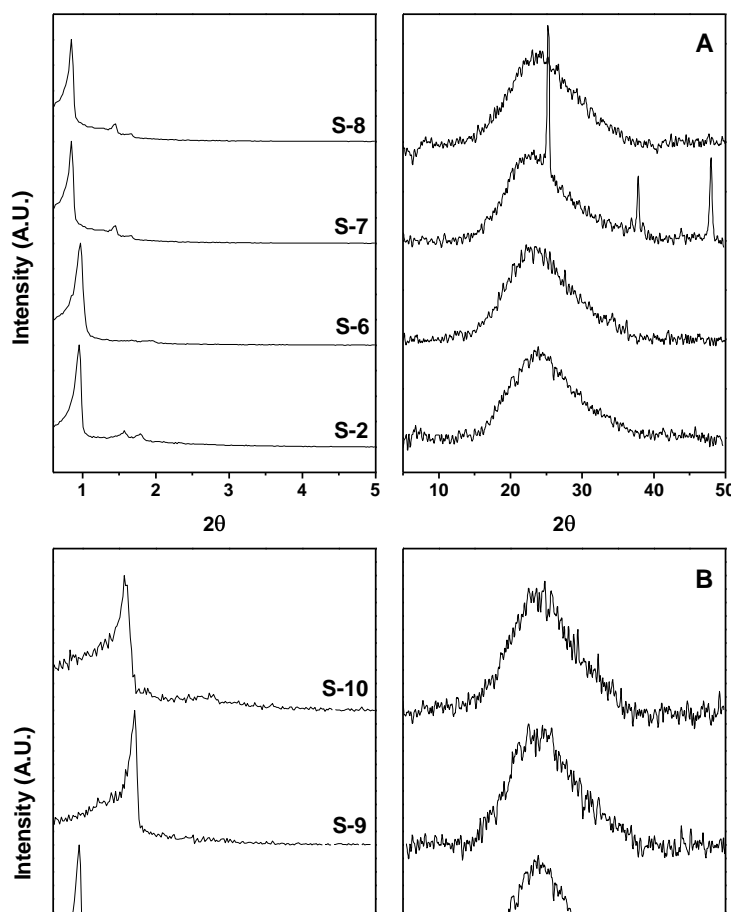


**Figure 2.** TEM images of calcined S-5 sample (a) in the direction of the pore axis and (b) in the direction perpendicular to the pore axis.

### 3.2 Tailoring of the pore size

Two different strategies have been used in this work to tune the pore size of these Ti-SBA-15 materials using  $Ti_2(Cp)_2$  as titanium precursor. Firstly ageing conditions were changed varying time and temperature. All the samples synthesized modifying ageing conditions show a very strong peak attributed to (1 0 0) spacings in low-angle range (Figure 3. A). However, the (1 1 0) and (2 0 0) diffractions are absent for the sample aged at lower temperatures (sample S-6), which indicates a low ordering of this material. Figure 3 also show the XRD spectra, recorded at high angle values, for the different samples where it is clearly evidenced that the increasing of temperature up to 150 °C promotes the precipitation of crystalline anatase domains. Chemical analyses of the calcined samples shown in Table 1 indicate that the amount of Ti incorporated

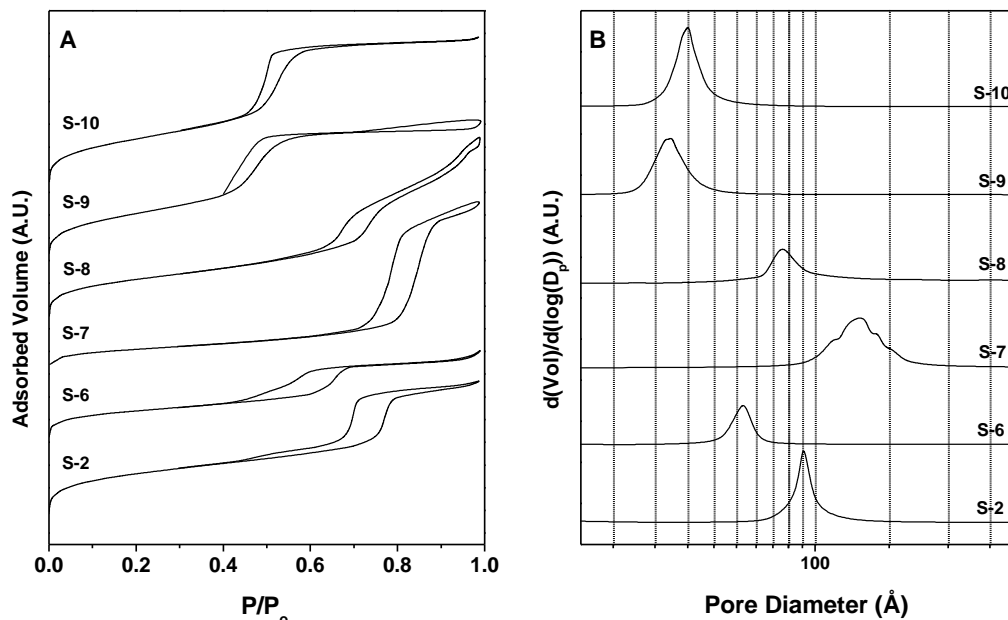
within the silica structure is kept constant with the ageing conditions (ca. 1 wt. %  $\text{TiO}_2$ ) except for sample S-7 (aged at 150 °C) where the large titanium content arise from the presence of anatase as evidenced in its XRD spectrum.



**Figure 3.** XRD spectra of calcined Ti-SBA-15 samples

The second approach for tuning pore size was to appoint low molecular weight surfactants such as Brij-56 and -76 (S-9 and S-10 samples). As expected, these materials show lower pore size that those samples synthesized using Pluronic 123 which is supported by the clear displacement of the (1 0 0) signal to high values in the XRD

pattern (see Figure 3. B). However, the use of these kind of surfactants have induced a lowering of titanium incorporation as shown in Table 1.



**Figure 4.** Nitrogen desorption / adsorption isotherms and pore size distribution in the mesoscopic range for calcined Ti-SBA-15 samples

Figure 4 shows the nitrogen adsorption-desorption isotherms recorded at 77 K for the different samples synthesized using both strategies of synthesis. All of them show type IV isotherms according to the I.U.P.A.C. classification with hysteresis loops characteristic of mesoporous solids. The surface areas, pore volumes and pore mean diameters are listed in Table 1. The results clearly indicate that increasing of temperature leads to an enhancement of pore diameter (comparing S-2, S-6, S-7 and S-8 samples). However, samples aged at low temperatures (S-6 and S-8) showed flat hysteresis loops compared to the steep hysteresis of S-2 and S-7 samples. The low surface area of S-7 sample accounts for the high amount of anatase precipitated on this material. Finally, the use of low molecular weight hydrophobic block polymer as surfactant have allowed obtaining well-defined pore size distribution with a mean pore



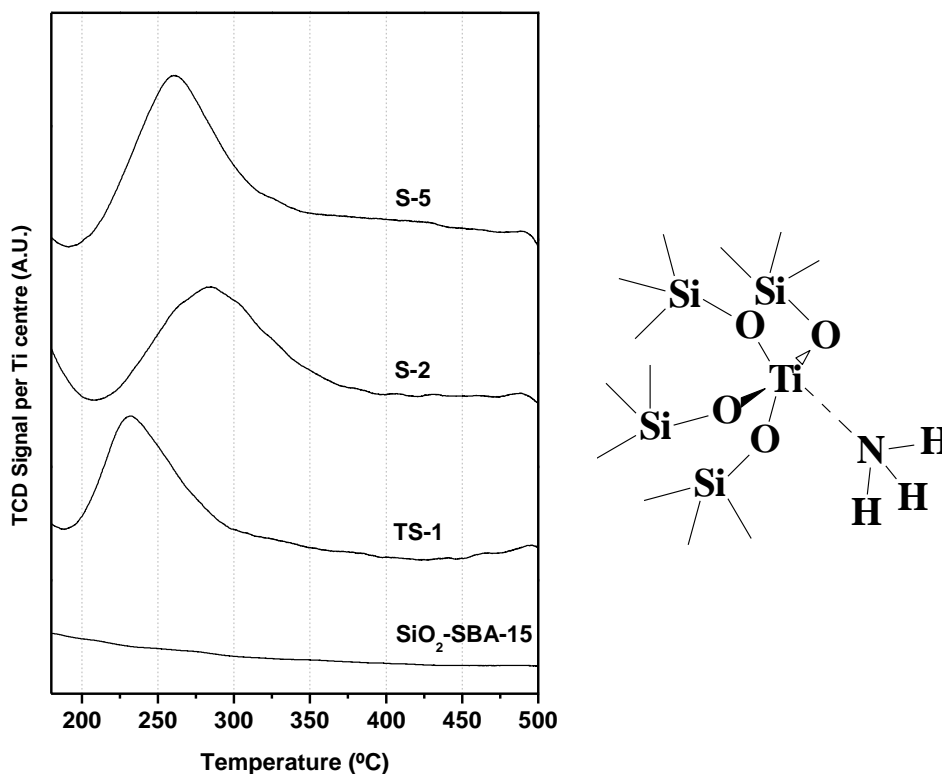
size of ca. 40 Å, which is significantly lower than the pore size obtained using Pluronic 123.

### 3.2 Accessibility of titanium centres

Different authors have claimed that an important amount of Ti species incorporated within SBA-15 type materials are buried in the thick amorphous walls and therefore they are not active for oxidation reactions [14,20]. However, little effort has been carried out to elucidate the accessibility of Ti sites in this kind of materials. Kholdeeva *et al.* [14] tried to clarify this matter by means of using FTIR spectroscopy and CO as molecular probe to be selectively adsorbed on the titanium centres of Ti-SBA-15. These authors concluded that the surface concentration of Ti atoms for Ti-SBA-15 materials was quite low under the specific synthesis conditions used in their work. In this contribution we have focused our attention in proving the high accessibility of Ti sites when titanocene dichloride is used as metal precursor. For this purpose ammonia TPD measurements were carried out.

Ammonia has been previously used as molecular probe to monitor the coordination sphere of Ti centres in Ti-grafted MCM-41 materials by means of FTIR, DR UV-VIS and photoluminescence spectroscopies [22]. The results of this research revealed that NH<sub>3</sub> is firmly adsorbed on Ti centres modifying their coordination sphere as previously it was observed for Ti-silicalite. Following this work, ammonia has been used in the present contribution to evidence the accessibility of Ti centres in the Ti-SBA-15 samples. The amount of NH<sub>3</sub> molecules interacting with titanium centres has been monitored by a TCD detector through temperature controlled desorption. Figure 5 displays TPD profiles of calcined Ti-SBA-15 samples (S-2 and S-5 samples) as well as pure silica SBA-15 and TS-1 as reference samples. In order to obtain a quantitative comparison among all the samples, TCD signal has been normalized per Ti centre. The

desorption pattern of titanium substituted materials consists on a clear signal over 225°C, which is completely absent in pure silica SBA-15 sample, confirming the interaction of Ti centres with ammonia molecules. Additionally, higher desorption temperatures are found for Ti-SBA-15 samples than in the case of TS-1 sample which could be related with a stronger interaction of Ti centres in these samples as compared to those located in the zeolite. In the same sense, the similarity found in the TCD signal areas achieved for TS-1 and Ti-SBA-15 samples evidence the high accessibility of Ti centres for the latter and confirms the benefit of using  $(Cp)_2TiCl_2$  as precursor in order to enhance the titanium accessibility.



**Figure 5.**  $NH_3$  TPD of titanium-containing samples and pure silica SBA-15.

### 3.4 Modification of surface properties and catalytic activity

As-made Ti-SBA-15 samples have been treated by means of different post-synthetic treatments such as: thermal calcination, thermal calcination followed by silanization,

surfactant extraction with ethanol under reflux and finally solvent-extraction followed by silanization. These different preparation procedures lead materials with distinct surface properties, since extraction, calcination and silylation steps make changes in the concentration of surface silanol groups and thus, hydrophilic character of silica samples is completely modified [23]. Physicochemical properties of the so-prepared materials are summarized in Table 2.

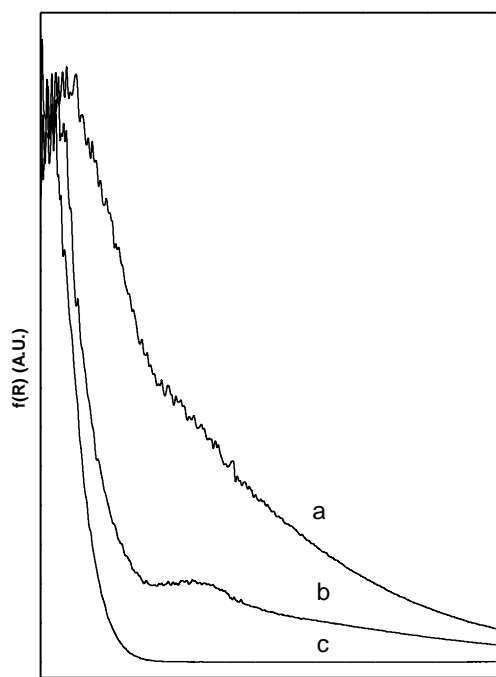
**Table 2. Physicochemical properties of Ti-substituted mesostructured materials after different post-synthetical treatments**

Sample	Post-synthetical treatment	Textural properties			TiO <sub>2</sub> (%) <sup>c</sup>
		S <sub>BET</sub> (m <sup>2</sup> /g)	D <sub>p</sub> (Å) <sup>a</sup>	V <sub>p</sub> (cm <sup>3</sup> /g) <sup>b</sup>	
S-4	Calcinated	818	90	0.99	1.0
S-11	Extracted	776	102	0.96	1.0
S-12	Calcined / silylated	533	84	0.71	0.8
S-13	Extracted / silylated	571	98	0.78	0.8

<sup>a</sup> Mean pore size using BJH model; <sup>b</sup> Total pore volume measured at P/P<sub>0</sub> of 0.985; <sup>c</sup> TiO<sub>2</sub> percentage in weight in the synthesized material after post-synthetical treatment

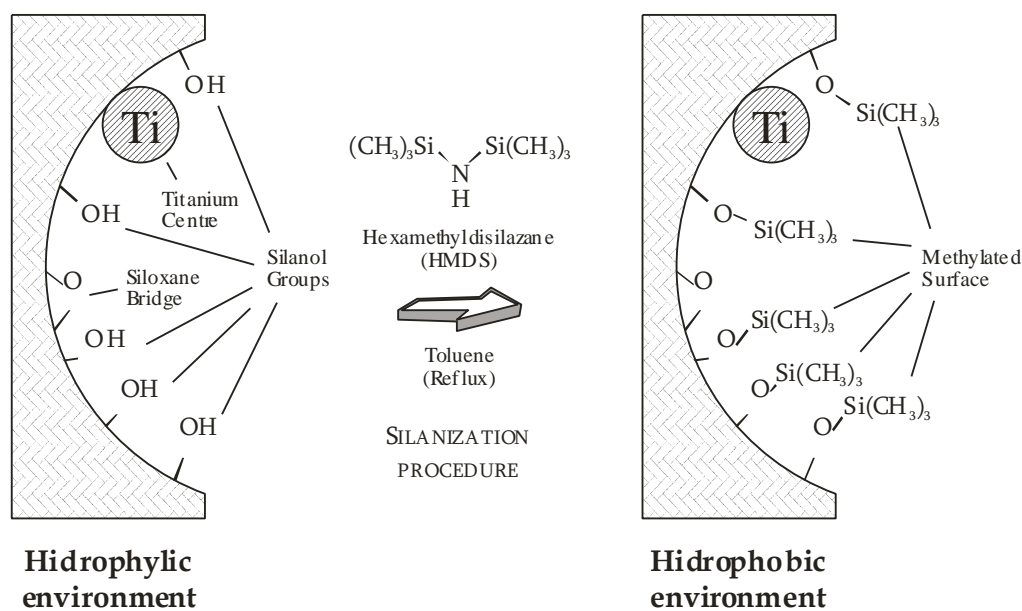
Thermal treatment allows the complete removal of surfactant and Cp ligands coordinated to titanium centres leading to the formation of titanium hydroxyl species [7]. On the other hand, the treatment of as-made Ti-SBA-15 materials with ethanol under reflux yields almost a complete removal of surfactant and the displacement of Cp ligands leading the formation of titanium ethoxide species attached onto the surface of silica. The displacement of Cp rings with ethanol groups is clearly seen in DR UV-Vis spectra depicted in Figure 6. DR UV-Vis spectrum of as-made Ti-SBA-15 displays a broad band corresponding to the absorption of Cp rings which is clearly reduced after solvent extraction. The remaining absorption band centred at ca. 300 nm could be attributed to extra-framework titanium but this signal is removed completely after

thermal treatment. Thus, this signal must be attributed to unreacted Cp ligands during extraction with solvents.



**Figure 6.** DR- UV-Vis spectra of (a) as-made Ti-SBA-15 (b) extracted Ti-SBA-15 (c) extracted Ti-SBA-15 followed by thermal treatment.

It has been widely described that the decreasing of the internal silanol groups in titanium-containing materials increase significantly the selectivity to the epoxide in epoxidation reactions [24-25]. Ti-SBA-15 materials after calcination and extraction have been silylated with hexamethyldisilazane. The data obtained from nitrogen adsorption isotherms before and after silanization are shown in Table 2. For both samples, calcined and extracted materials, the BET surface area, pore diameter and pore volume dropped upon silanization. This change on the textural parameters is attributed to the incorporation of trimethylsilyl groups onto the inner surface of the so-called materials (Figure 7).

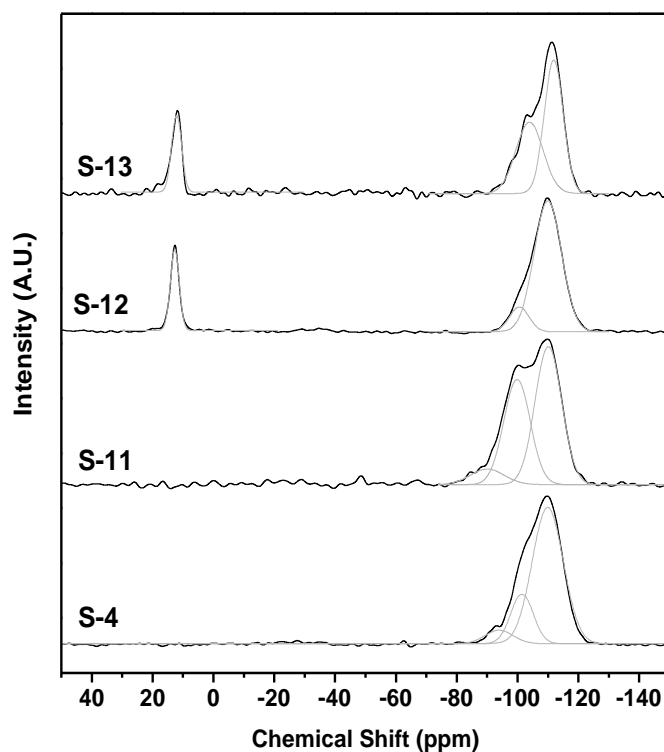


**Figure 7.** Silanization of Ti-SBA-15 samples using HMDS.

In order to evaluate the changes caused by the silanization step in the surface nature, the concentration of trimethylsilyl groups was measured by means of  $^{29}\text{Si}$  NMR technique (Figure 8). Before silanization, the  $^{29}\text{Si}$  NMR spectra of extracted and calcined materials (samples S-14 and S-11) exhibit up to three resonances, assigned to three different silicon species. The locations of these signals are -110 ppm for the  $\text{Q}^4$  silica species, -100 ppm for the  $\text{Q}^3$  environments and -90 ppm for the  $\text{Q}^2$  species. The material obtained through calcination procedures (sample S-4) displays a lower silanol content than the material obtained by surfactant extraction with solvents (sample S-11) due to the distinct procedure used for the surfactant removal in both samples. Unlike calcination, where high temperature conditions are employed, extraction with solvents require softer conditions preserving the silanol content of the starting material.

After silanization, a new signal, ascribed to the silicon atoms of trimethylsilyl group, appears at 12 ppm, whereas  $\text{Q}^3$  signal is significantly decreased and  $\text{Q}^2$  signal is completely removed. These results mean silanization procedure does not lead to a complete removal of the silanol groups, since  $\text{Q}^3$  signal remain present in the recorded

spectra (samples S-12 and S-13), but it causes a significant decrease on the surface silanol population. Thus, the hydrophilic character of the silica-based materials is changed by a hydrophobic nature. Any way, sample S-13, obtained from a material treated by extraction with solvents still displays a higher proportion of silanol groups than sample S-12, obtained from a calcined material.



**Figure 8.**  $^{29}\text{Si}$  NMR of titanium SBA-15 materials after different post-synthesis treatments

Catalytic activity of the different Ti-SBA-15 samples was studied using mild liquid-phase reaction conditions for the epoxidation of 1-octene with EBHP, used as oxidant reagent, being the catalytic results depicted in Table 3. Extracted samples have a similar activity and selectivity compared to that obtained for the calcined sample, even with enhanced selectivities. These catalytic results indicate that solvent extraction yields active material which is an important issue for prospective synthesis of organically modified materials where thermal treatment must be discarded. This catalytic behaviour

is particularly interesting from an economic point of view, since surfactant recover is a crucial step for the reduction of the costs in the preparation of mesostructured materials.

By the way, it has been also found that surface modification through silanization procedures improves significantly the Ti-SBA-15 catalyst selectivity to the epoxide with values over 90%. Moreover, the Ti-SBA-15 materials show a comparable catalytic performance to that obtained using the Ti/SiO<sub>2</sub> catalyst [19] and even the selectivity to the epoxide is greater for the mesostructured sample.

**Table 3. Oxidation of 1-octene over Ti-substituted mesostructured materials**

Sample	TiO <sub>2</sub> (%) <sup>a</sup>	X <sub>EBHP</sub> (%) <sup>b</sup>		S <sub>EBHP</sub> (%) <sup>c</sup>	
		1 h	2 h	1 h	2 h
S-4	1.0	43.2	60.3	73.1	71.8
S-11	1.0	49.6	63.6	80.0	78.5
S-12	0.8	41.2	52.0	88.4	96.7
S-13	0.8	52.3	68.0	92.7	92.6
Ti/SiO <sub>2</sub>	1.3	-	75.6	-	74.4
Ti/SiO <sub>2</sub> silylated	-	-	89.9	-	85.7

<sup>a</sup> TiO<sub>2</sub> percentage in weight of the catalyst; <sup>b</sup> Oxidant conversion; <sup>c</sup> Selectivity of oxidant toward the epoxide

Additionally, the high catalytic activity of these samples confirms the outstanding accessibility of titanium sites to the reactant molecules as it has been inferred from the NH<sub>3</sub> TPD measurements.

#### 4. Conclusions

Ti-incorporated materials using non-ionic surfactants and titanocene dichloride were successfully synthesized under strongly acidic conditions. The obtained materials possess highly ordered hexagonal structure and high surface areas. The UV-Vis

spectroscopy results indicate that titanium is present in highly dispersed state and has tetrahedral coordination. NH<sub>3</sub> adsorption measurements show a high accessibility of titanium species similar to that shown by TS-1 sample. These materials exhibit a high activity and selectivity in the epoxidation of 1-octene due to the presence of isolated and high accessible Ti sites in the mesostructured framework.

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