

# **Synthesis of titanium containing periodic mesoporous organosilica**

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**Abstract**

Organic-inorganic mesostructured materials were functionalized with titanium by direct synthesis under strong acidic conditions using non-ionic surfactants as structure directing agent and titanocene dichloride as titanium precursor. Materials with different organic content were synthesized with a high mesoscopic order and with incorporation of titanium species in isolated framework positions. The physicochemical properties of the synthesized samples were assessed by different characterization techniques including XRD,  $^{29}\text{Si}$  MAS-NMR, nitrogen adsorption/desorption experiments and DR UV-VIS spectroscopy.

## 1. INTRODUCTION

At the end of the nineties, materials composed of hybrid inorganic-organic frameworks with well ordered mesopores, designated as the periodic mesoporous organosilicas (PMO's), were discovered [1-3]. The synthesis strategy of periodic mesoporous materials is based on the condensation, in presence of the corresponding surfactant, of bis-(trialkoxysilyl)-alkylsilanes such as  $(R'O)_3\text{-Si-R-Si-(R'O)}_3$  in which the organic moiety (-R-) is doubly functionalized with two trialkoxysilyl groups ( $-\text{Si-(R'O)}_3$ ). However, few works have dealt with the incorporation of active metal species within the structure of the hybrid materials for prospective catalytic applications [4-5]. Titanium species have been recently incorporated to ethane bridged silica materials synthesized with cationic surfactants under basic conditions. These materials showed a good degree of the metal functionality incorporation, although the presence of octahedral titanium species was clearly evident [4-5]. Catalytic test showed that titanium functionalized PMO displayed a greater catalytic activity in the epoxidation of  $\alpha$ -pinene than free-organic silica-based Ti-MCM-41, being attributed to the improvement of the hydrophobic surface properties. Herein, we report for the first time the synthesis of titanium-containing organic-inorganic hybrid mesostructured materials under strong acidic conditions and using non-ionic surfactants as template.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials

Titanocene dichloride [ $\text{Cl}_2\text{TiCp}_2$ , 97%; ABCR] was used as titanium source for the synthesis of titanium functionalized mesostructured materials. Non-ionic surfactant [Pluronic 123,  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ,  $M=5800$ ; Aldrich] was used as structure-directing agent, Bis-triethoxysilyl ethane [ $(\text{CH}_3\text{CH}_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$ , BTSE, 96%; Gelest] and tetraethoxy silane [TEOS, 98%; Aldrich] as organic and silicon precursor. Concentrated HCl aqueous solution was used as the acid source.

### 2.2. Synthesis of materials

In a typical synthesis, 4g of tri-block copolymer were dissolved in 125mL of an aqueous solution of HCl 0.5M. The resultant mixture was then heated up to 40°C before adding the  $\text{Cl}_2\text{TiCp}_2$ . The metal species were prehydrolyzed for at least 3 hours, followed by the addition, in a unique step, of both the organic and inorganic silicon based precursors, BTSE and TEOS, respectively. The molar ratio BTSE:TEOS has been varied from 0:100 to 100:0. The resultant solution was then kept under stirring at 40°C for 20 hours and hydrothermally aged at 100°C for another 24 hours under static conditions. Finally, the solid was recovered by filtration and air-dried. The surfactant was removed following the method reported by Zhao et al. [6] washing the as-made material with ethanol under reflux for 24 h (1.5 g of material per 400 mL of ethanol). The solid was then recovered by filtration and dried in vacuum at 150°C overnight.

### 2.3. Samples characterization

X-ray powder diffraction (XRD) patterns were acquired on a PHILIPS X'PERT diffractometer using the  $\text{CuK}\alpha$  radiation. The diffractograms were collected in the range from 0.6° to 5.0° (2 $\theta$ ) using a step size of 0.02°. Diffuse reflectance ultraviolet spectra (DR-UV-

Vis) were collected in a VARIAN CARY-500 spectrophotometer equipped with a integration sphere accessory in the wavelength range from 200 to 600 nm. Nitrogen adsorption-desorption isotherms were collected using a manometric porosimeter (Micromeritics, TRISTAR 3000) at -196°C. The specific surface areas were calculated by the B.E.T. method whereas the pore size distributions were determined by the application of the B.J.H. method to the adsorption branch of the isotherm using a Harkins-Jura equation for the adsorbed multilayer thickness specially obtained for SBA-15 type materials [7]. Solid state  $^{29}\text{Si}$  MAS-NMR analyses were performed on a VARIAN INFINITY 400 spectrometer operating at 79.4 MHz under the following conditions: MAS at 6 kHz;  $\pi/2$  pulse, 4.5  $\mu\text{s}$ ; repetition delay, 15 s; 3000 scans. Spectra were referenced to tetramethylsilane. Titanium content was determined by ICP-atomic emission spectroscopy. The samples (100 mg) were dissolved in aqueous hydrofluoric acid (10 mL) and diluted in water up to 250 mL in a calibrated flask. Standard solution of Ti (1000  $\mu\text{g}\cdot\text{L}^{-1}$ ) was used for the calibration of the apparatus.

### 3. RESULTS AND DISCUSSION

Table 1 summarizes the synthesis conditions and physicochemical properties of synthesized materials after surfactant removal whereas XRD patterns are shown in Figure 1. All samples exhibit a clear diffraction peak typical of a  $p6mm$ -type hexagonal ordering. Organic-free titanium-containing material (S-0 sample) displays two additional peaks corresponding to the (110) and (200) diffractions, which indicates a high mesoscopic ordering degree. These diffraction signals disappear gradually with the increasing of the organic content within the silica framework.

The titanium environment has been assessed by means of diffuse reflectance UV-Vis spectroscopy. Spectra depicted in Figure 2 show a strong absorption band located at 210 nm for all the samples. This absorption band is attributed to Ti species in tetrahedral coordination within the silica structure [8]. The second band centered at 325 nm is usually ascribed to the presence of titanium oxide domains resulting in low dispersion of the metal species. However, this absorption band is removed completely after thermal treatment of the samples (Figure 2 (II)). Hence, this second absorption is a consequence of the coordination of residual cyclopentadienyl rings to the titanium site that remain attached even after the removal of the surfactant by washing with ethanol [9]. It is noteworthy, the intensity of this signal increases for the materials with the higher organic content, suggesting a lower extension of the ligand exchange during extraction as a result of the protective effect of the organic nature of the walls. Likewise, the narrow band in the DR UV-Vis spectra for calcined samples evidence the presence of highly dispersed tetrahedral titanium sites in the samples.

Table 1

Physicochemical properties of Ti-containing mesostructured materials synthesized with different organic contents

Sample	Synthesis conditions		Chemical composition		Textural properties			
	Ratio <sup>a</sup>	T/(T+Q)	Ti(%) <sup>b</sup>	T/(T+Q) <sup>c</sup>	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ ) <sup>d</sup>	$D_{\text{P}}$ ( $\text{\AA}$ ) <sup>e</sup>	$V_{\text{P}}$ ( $\text{cm}^3/\text{g}$ ) <sup>f</sup>	$W_{\text{t}}$ ( $\text{\AA}$ ) <sup>g</sup>
S-0	100:0	0.00	0.59	0.00	776.0	102.0	0.96	37
S-1	66:33	0.50	0.21	0.42	622.2	79.0	0.95	51
S-2	40:60	0.75	0.15	0.76	773.6	78.1	1.02	53
S-3	0:100	1.00	0.17	1.00	821.7	64.0	1.30	64

<sup>a</sup> Molar ratio between different silica sources; TEOS:BTSE. <sup>b</sup> Titanium percentage in weight in the synthesized material after surfactant removal; 4 % Ti:SiO<sub>2</sub> mass ratio in the synthesis medium. <sup>c</sup> Ratio of T and Q signals from <sup>29</sup>Si MAS-NMR. <sup>d</sup> Determined by the B.E.T. method. <sup>e</sup> Calculated by means of the B.J.H. method using the K.J.S. correction. <sup>f</sup> Total pore volume recorded at P/P<sub>0</sub>=0.985. <sup>g</sup> Wall thickness calculated from XRD and N<sub>2</sub> adsorption analysis ( $W_t = a_0 - D_p$ ;  $a_0 = 2 d(100) / \sqrt{3}$ ).

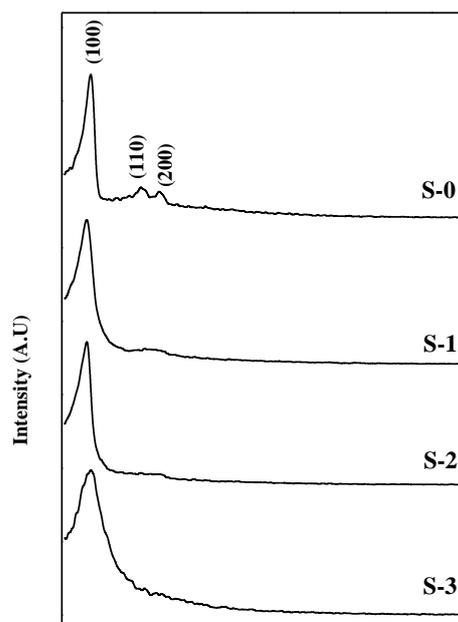


Fig. 1. XRD patterns at low angle of Ti-containing mesostructured materials synthesized with different organic contents

Nitrogen adsorption/desorption isotherms of extracted titanium-containing samples with different organic contents are shown in the Fig. 3 (I). It is clear the change from a type IV isotherm with a pure H1 hysteresis loop obtained for the free-organic siliceous material S-0, to a H1+H3 mixed hysteresis loop, according to the IUPAC classification, recorded for the pure PMO sample S-3. Moreover, the importance of the H3 type hysteresis loop grows as the organic content increases whereas H1 type loop diminishes, indicating a loss of mesostructured porosity in favour of the secondary porous system. The appearance of H3 type hysteresis loops is usually attributed to the presence of slit-shaped pores which origin interparticular adsorption [10]. This secondary porous system is not typical from SBA-15 type materials and would be related with the gradual increase of the total pore volume as the organic content increases in the materials (see Table 1).

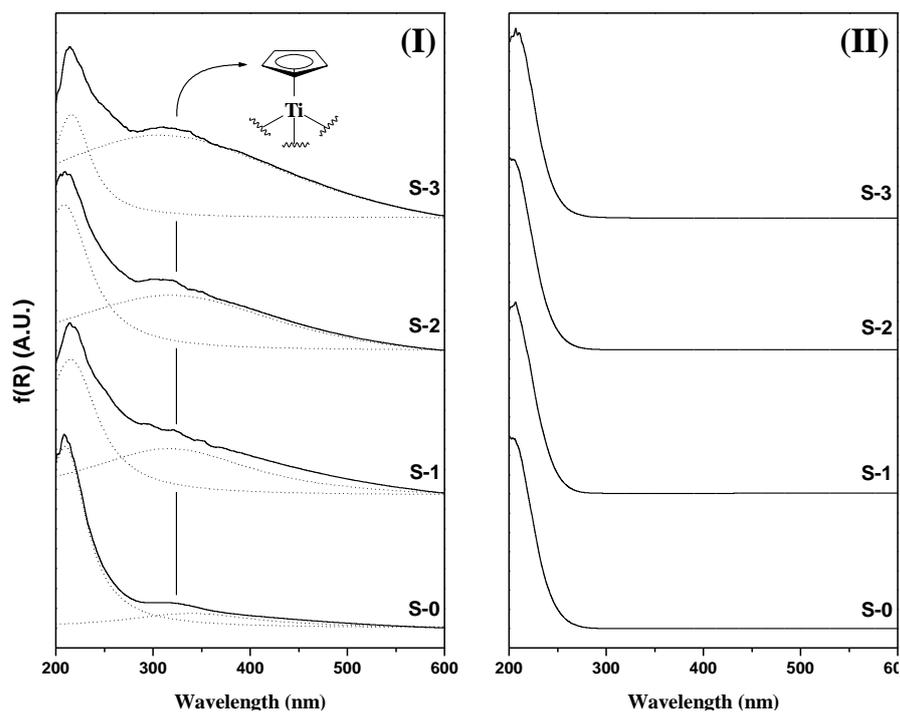


Fig. 2. DR-UV-Vis spectra of Ti-containing mesostructured materials synthesized with different organic contents before (I) and after calcination (II).

Pore size distributions in the mesoscopic range are shown in Fig. 3 (II). A clear lowering of the pore size is readily evidenced with the increasing of the organosilicon precursor amount in the synthesis medium. Since  $d(100)$  spacing values remains almost constant (see Figure 1), the pore wall thickness necessarily increases with the content of the organosilicon precursor. The presence of organosilicon species in the synthesis medium dramatically influences on the silica-surfactant interactions, which results in changes in the mesoscopic and textural properties of the synthesized Ti-PMO materials.

Chemical analyses of the samples depicted in Table 1 indicate that the amount of titanium incorporated to the silica structure is much smaller than that added to the initial mixture. The low incorporation efficiency of titanium atoms must be related to the strong acidic conditions used in the synthesis of triblock copolymer templated silicas. Under these conditions,  $Ti^{4+}$  ions are greatly solubilized in aqueous media as well as the stability of Ti-O-Si bond decreases [11]. Additionally, it has been observed even lower metal incorporation efficiency for the PMO samples as compared to the silica-based material, which might be related with the decrease of the number of reaction points between the titanium and the silicon precursor. Note that some leaching of titanium might occur during surfactant removal due to the hydrophobic character of the titanium precursor, which make possible a deep interaction of  $Cl_2TiCp_2$  and structure directing agent, thus the removal of the polymeric template can lead to a partial extraction of the supported titanium species.

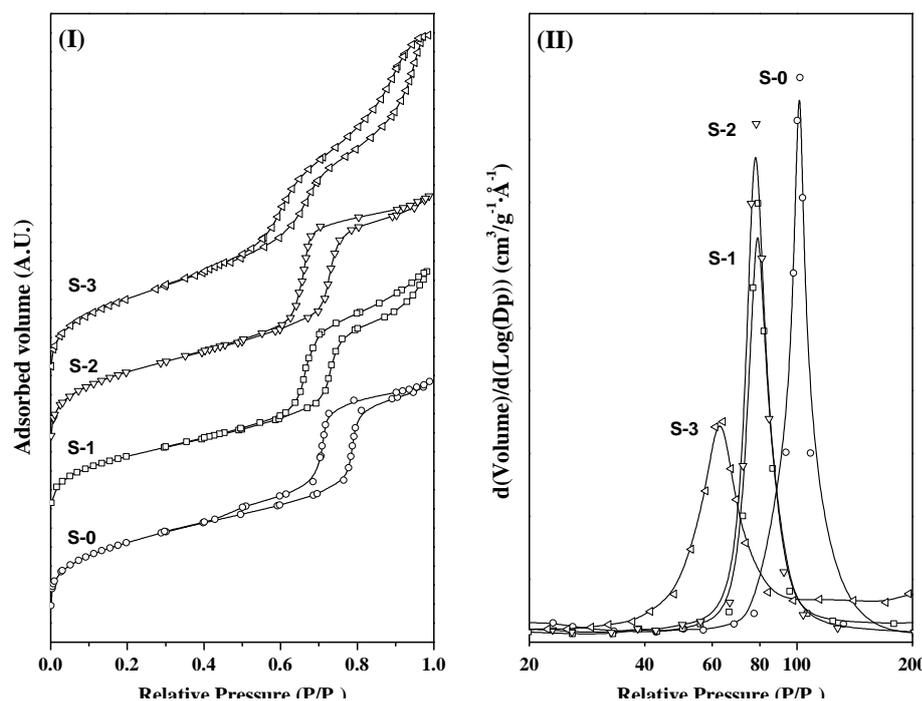


Fig. 3. (I) Nitrogen adsorption-desorption isotherms and (II) pore size distributions in the mesoscopic range for different Ti-containing mesostructured materials synthesized with different organic contents

Figure 4 shows the  $^{29}\text{Si}$  MAS-NMR spectra as well as their deconvolution recorded for the synthesized titanium containing SBA-15 type materials. The  $^{29}\text{Si}$  MAS-NMR spectra of the sample S-0, the free-organic siliceous material, exhibit 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 sample S-3, which has been synthesized only from BTSE, presents only T groups related with a silicon atom directly bonded to carbon species, resulting from the incorporation to the mesostructured material of the organosilicon precursors. Two different T groups can be inferred: silicon species linked to a hydroxyl group ( $\text{T}^2$  species,  $\delta = -45$  to  $-60$  ppm) and silicon atoms coordinated to three silicon atoms through oxygen bondings ( $\text{T}^3$  species,  $\delta = -60$  to  $-70$  ppm). Both types of signals can be observed in the other two materials (S-1 and S-2 samples) as a consequence of the use of TEOS and BTSE as silicon precursors. Moreover, T : (T+Q) ratio of the extracted materials correlate fairly well with the theoretical synthesis values indicating a high incorporation degree of the organic species. Ti-PMO materials with high loading of organic groups within the silica framework are expected to have enhanced hydrophobic properties.

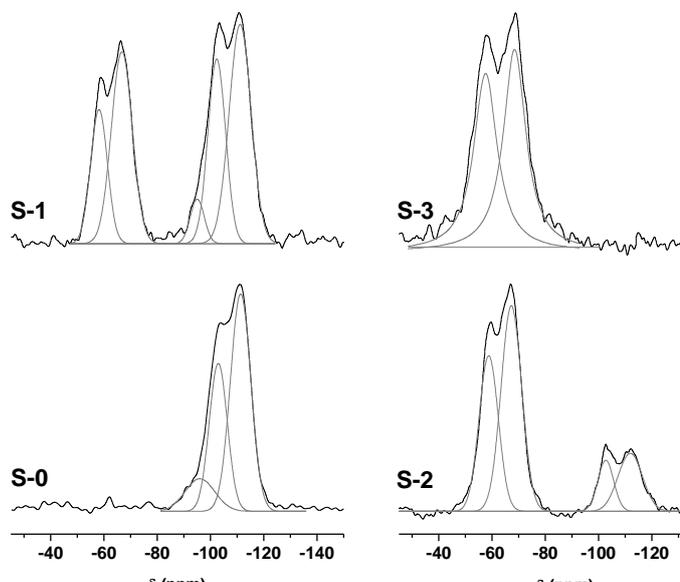


Fig. 4.  $^{29}\text{Si}$  MAS-NMR spectra of extracted Ti-containing PMO materials.

### 3. CONCLUSIONS

Highly periodic mesoporous organosilica materials functionalized with titanium have been successfully synthesized under strong acidic conditions and using non-ionic surfactants for the first time. These materials have tetrahedrally coordinated titanium atoms in a hydrophobic microenvironment. Further research is being carried out to explore their catalytic performance in the epoxidation of alkenes in liquid phase and correlate with their enhanced hydrophobic nature.

### REFERENCES

- [1] S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna and O. Terasaki, *J. Am. Chem. Soc.*, 121 (1999) 9611.
- [2] B.J. Melde, B.T. Holland, C.F. Blandford and A. Stein, *Chem. Mater.*, 11 (1999) 3302.
- [3] T. Asefa, M.J. Mac Lachlan, N. Coombs and G.A. Ozin, *Nature*, 402 (1999) 867.
- [4] M.P. Kapoor, A. Bhaumik, S. Inagaki, K. Kuraoka and T. Yazawa, *J. Mater. Chem.*, 12 (2002) 3078.
- [5] W. Cho, J.-W. Park and C.S. Ha, *Mater. Lett.*, 58 (2004) 2551.
- [6] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka and G.D. Stucky, *Science*, 279 (1998) 548.
- [7] R. van Grieken, G. Calleja, G.D. Stucky, J.A. Melero, R.A. García and J. Iglesias, *Langmuir*, 19 (2003) 3966.
- [8] W. Zhang, J. Wang, P.T. Tanev and T.J. Pinnavaia, *Chem. Comm.*, (1996) 979.
- [9] J.A. Melero, J.M. Arsuaga, P. de Frutos, J. Iglesias, J. Sainz and S. Blazquez, *Microporous Mesoporous Mater.*, 86 (2005) 364.
- [10] F. Rouquerol, J. Rouquerol and K. Sing, *Adsorption by powders & porous solids*, Academic Press, London, 1999, pp. 193-217.
- [11] W.H. Zhang, J. Lu, B. Han, M. Li, J. Xiu, P. Ying and C. Li, *Chem. Mater.*, 14 (2002) 3413.

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