Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Journal of Molecular Catalysis A: Chemical 269 (2007) 133–140
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Effect of precursor nature on the behavior of titanium-polysiloxane homogeneous catalysts in primary alkene epoxidation

G. Blanco-Brieva, M.C. Capel-Sanchez, J.M. Campos-Martin *, J.L.G. Fierro **

Instituto de Catálisis y Petroleoquímica, CSIC, c/Marie Curie, 2, Cantoblanco, 28049 Madrid, Spain[1]

Received 25 January 2006; received in revised form 8 January 2007; accepted 9 January 2007

Abstract

This work describes the synthesis, some structural characteristics and the performance of a series of titanium-containing polysiloxanes as homogeneous catalysts. These polysiloxanes were synthesized by mixing a titanium precursor, such as tetraisopropoxytitanium or tetrakis(2-ethylhexyloxy) titanium, with a silicon precursor of the trichloro(phenyl)silane, triethoxy(phenyl)silane or trimethoxy(phenyl)silane type in toluene solvent and then slowly hydrolyzing with water. Depending on the precursors, the polysiloxanes exhibited different physical properties; some of them were solids, while others were viscous liquids or even fluid liquids. These properties are related to the molecular weight of the polysiloxane, which is determined by the nature of the precursors. All the Ti-containing polysiloxanes were tested in the epoxidation reaction of oct-1-ene using EBHP (ethylbenzene hydroperoxide) as an oxidant. The reaction was selective to epoxide since in all cases the only product detected from the oct-1-ene was 1,2-epoxyoctane. The conversion profile of EBHP was found to depend not only on the amount of titanium incorporated into the polymeric structure but also on the symmetry and chemical environment of Ti^{IV} sites. It was observed that polysiloxanes containing tetrahedrally coordinated Ti^{IV} resulted in active catalysts whereas those in which titanium appeared in an octahedral environment were found to be inactive in alkene epoxidation.

Keywords: Epoxidation; Titanium; Homogeneous catalysis; Alkenes; Epoxidation

---

1. Introduction

Propylene epoxide (PO) cannot be obtained by a heterogeneously catalyzed procedure similar to that applied to ethylene [1], since over-oxidation is in this case predominant. This product at the root of the synthesis of polyether polyols used for the production of polyurethane foams, and also much used for the synthesis of propylene glycol for the elaboration of unsaturated polyester resins.

The world production of PO, which we estimate to be greater than 5 million metric tonnes per year, is increasing by more than 5% annually. Up until 1970–1980 this epoxide was produced from chlorohydrins essentially by stoichiometry routes [1]; at present catalytic routes are the most important. The oxidants are alkyl hydroperoxide. They act as *catalytic and highly selective*, but ways remains to be found to commercialize or recycle the alcohol co-product. For instance, when ethylbenzene hydroperoxide is employed as oxidant, the 1-phenylethanol obtained as a co-product is dehydrated to produce styrene [1].

Many different methods for the preparation of epoxides have been developed, but the most extensive industrial method is the oxidation of alkenes to the corresponding epoxide in liquid phase with organic hydroperoxides in the presence of a catalyst. Indeed, hydrocarbon-soluble coordination compounds of the transition metals can be employed as the homogeneous catalyst [2,3]. Other alternatives include the use of heterogeneous catalysts such as a chemical combination of titania–silica such as Ti/SiO_2, Tiβ and Ti-MCM-41 [4,5]. These catalysts showed high values of selectivity to epoxide but lower catalytic activity than homogeneous counterparts.

Although homogeneous titanium-containing epoxidation catalysts are known, the selectivity to the alkene oxide obtained with such catalysts is significantly lower than those obtained with the above heterogeneous catalysts, some improvements

---

* Corresponding author. Tel.: +34 91 5854948; fax: +34 915854760.
** Corresponding author.
E-mail addresses: j.m.campos@icp.csic.es (J.M. Campos-Martin), jlgfierro@icp.csic.es (J.L.G. Fierro).

[1] http://www.icp.csic.es/eac/index.htm.

1381-1169/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2007.01.013

having been found with polyorganometallosiloxane synthesized in a neutral solvent such as toluene [6]. The literature concerning use of these compounds as catalysts is collected in patents [7,8] and recent reviews [9,10]. However, selectivity and conversion are still lower than with heterogeneous catalysts [6] because these compounds trend to dimerize [11–16], allowing the formation of Ti–O–Ti bridges. This bond induces steric hindrance at the titanium site producing a detrimental effect on catalytic performance [14]. Some elegant procedures to avoid this drawback using elastomeric polysiloxane networks or poly-methyl silsesquioxane have been implemented [17,18].

It is now widely accepted that the active site for epoxidation in titanium-containing materials is of tetrahedral nature [4,5]. This makes it very important to have a method for catalyst preparation that will avoid the formation of titanium in octahedral coordination. In previous work, we have reported the synthesis process of titanium-polysiloxanes with very high yield to epoxide [19,20]. Here we describe the effect of precursors on the catalytic behavior of titanium-polysiloxanes in the epoxidation of alkenes with ethylbenzene hydroperoxide.

2. Experimental

The catalysts were prepared in the following manner: a titanium (IV) precursor (1.25 mmol) was added to 100 ml of toluene under a nitrogen atmosphere and the solution was stirred for 15 min at room temperature. Then, a silicon precursor (50 mmol) was added. Following this, water (6 ml) was added dropwise for 2 h and a clear solution was obtained. When a halogenated precursor was employed, sodium carbonate (80 mmol) was added to neutralize the HCl by-product and excess Na_2CO_3 was removed by centrifugation at 6000 rpm for 20 min. The solvent was removed at 363 K under reduced pressure. For comparative purposes, three titanium-free polysiloxane samples were prepared according to the above procedure but in the absence of titanium precursor (labeled B1, B2 and B3).

Gel permeation chromatography (GPC) analysis of M_w/M_n was done on an Agilent 1100 Series equipped with a Refractive Index Detector. A 8 mm × 300 mm PLgel column was used with toluene at a flow rate of 0.8 ml/min. Retention times were calibrated against polystyrene standards: between 250 and 70,000 g/mol. FT-IR spectra were recorded using 128 scans accumulated at a resolution of $4\,\text{cm}^{-1}$ on a Nicolet 510 FT-IR spectrophotometer using KBr wafers containing 1% of the sample. UV–vis total reflectance spectra measurements were performed on AvaSpec-2048 fiber optic spectrophotometer, using $BaSO_4$ as a reference. The samples were analyzed under ambient conditions. Photoelectron spectra (XPS) were recorded using a VG Escalab 200R spectrometer equipped with an Mg Kα ($h\nu = 1253.6$ eV) anode and a hemispherical analyzer operating at a constant pass energy (20 eV) mode. Prior to analysis, the samples were outgassed at room temperature for 1 h at 10^{-6} mbar. The C 1s line from the aromatic ring of polysiloxane structure at 284.9 eV was used as an internal standard. In addition, quantitative analysis was also provided by the XPS technique. For this purpose, the area under the peaks were estimated by calculating the integral of each peak after smoothing and subtraction of the "S-shaped" background, after which the atomic surface contents were estimated from the areas of the peaks, corrected using the corresponding sensitivity factors [21].

Catalytic epoxidation of oct-1-ene with ethylbenzene hydroperoxide (EBHP) was accomplished in a glass batch-reactor equipped with a magnetic stirrer and a condenser. In a typical run, 45 g of alkene (0.4 mol) and 33 g of a solution of EBHP (33 wt%) in ethylbenzene, kindly provided by Repsol-YPF (0.08 mol of EBHP), were heated at 393 K, after which 0.3 g of catalyst was added. The concentration of EBHP was measured by standard iodometric titration. The remaining organic compounds were analyzed by GC-FID on a Hewlett Packard 6890-plus device equipped with an HP-WAX capillary column. These samples were pre-treated with triphenylphosphine to decompose the EBHP quantitatively to 1-phenylethanol before GC analysis. Ethylbenzene was used as internal standard in quantitative GC analysis. Selectivity to epoxide was based on the EBHP consumed. We decide to select oct-1-ene because it is well known that primary aliphatic alkenes are the most difficult to epoxidize and hence it is a useful model to describe the reactivity in the epoxidation of propene to propene oxide (PO), in the industrial process of PO production [1]. We employed execs of alkene, because at the PO process the most costly reactant is the hydroperoxide.

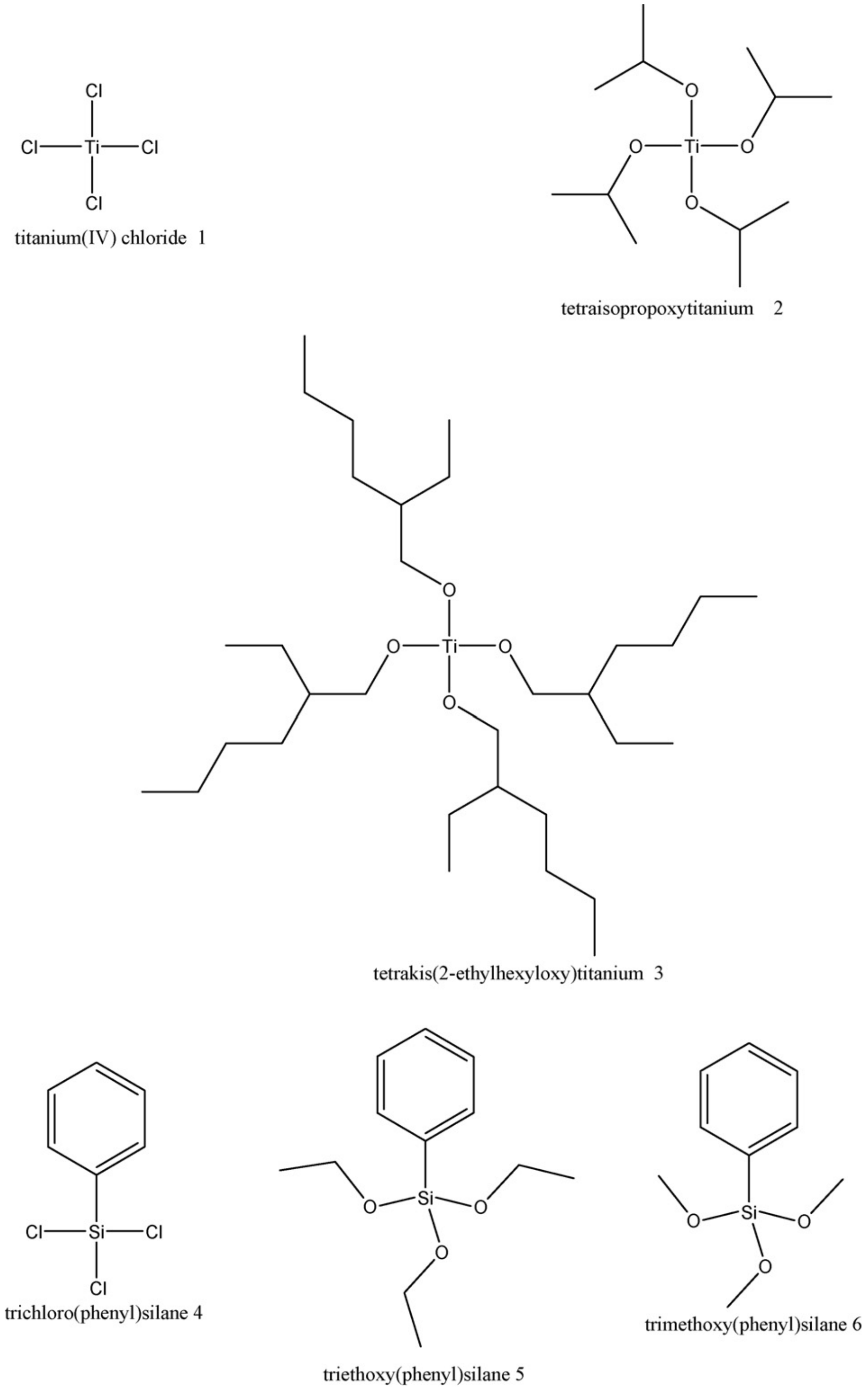
Epoxide selectivity was related to the hydroperoxide converted according to the equation:

$$S\,(\%) = \frac{[\text{Epoxide}]}{[\text{EBHP}]_0 - [\text{EBHP}]} \times 100 \qquad (1)$$

where epoxide represents 1,2-epoxyoctane; the subscript 0 stands for initial values, and all concentrations are expressed on a molar basis. No other by-products such as diol or ethers derivates from the oct-1-ene were detected. In all reactions, the carbon balance was higher than 98% for oct-1-ene and EBHP, respectively.

3. Results and discussion

Samples were prepared using several precursors (Scheme 1), as shown in Table 1. The Ti-loading of the catalysts varied among the samples (Table 1), depending on the nature of the precursors. When a chlorinated silicon precursor was employed, the highest degree of titanium incorporation into polymer structure was obtained when **1** was employed as the titanium precursor. This effect can be attributed to the differences in the hydrolysis rate of the titanium precursor. Thus, the catalyst prepared from the titanium alkoxides (**2** and **3**), which exhibit dissimilar reactivity from the hydrolysis to **4** (silicon precursor), produced inefficient titanium incorporation, because the differences in the hydrolysis rate may lead to separate reactions of silicon and titanium precursors, with the subsequent loss of titanium. The amount of titanium incorporated followed the order: **1** ≫ **2** > **3**, which is related to the hydrolysis rate. This effect was less evident when the silicon precursor was **5**, because the lower hydrolysis rate of this precursor masked the differences in the hydrolysis rate of the titanium precursors.



Scheme 1. Precursors employed for synthesis of titanium-polysiloxanes.

The use of different precursors led to marked disparity in the physical properties of the polysiloxane synthesized; some were solids while others were viscous liquids or fluid liquids (Table 2), and these physical properties are related to the molecular weight determined by GPC. Ti-polysiloxanes showed a higher molecular weight than the Ti-free polysiloxane counterparts. This effect can be attributed to the catalytic properties of titanium (IV) in esterification reactions, which facilitate the reaction between Si–OH and R–O–Si, favouring growth of the polysiloxanes chain. The molecular weights were also related to the nature of precursors. The polysiloxanes synthesized with chlorinated precursors (**4**) exhibited a higher molecular weight than their counterpart **5**, while the lowest value was obtained for the samples prepared with **6**. This effect was evident on com-

Table 1
Precursors, titanium-loading and labeling of samples

Sample	Ti precursor	Si precursor	Ti (wt%)
B-1		PhSiCl[a]	–
G-1	TiCl$_4$	PhSiCl[a]	0.9
G-2	Ti(iPro)$_4$[b]	PhSiCl[a]	0.1
G-3	Ti(EtHex)$_4$[c]	PhSiCl[a]	0.3
B-2		PhSiEt[d]	–
G-4	Ti(iPro)$_4$[b]	PhSiEt[d]	0.8
G-5	TiCl$_4$	PhSiEt[d]	0.03
G-9	Ti(EtHex)$_4$[c]	PhSiEt[d]	0.9
B-3		PhSiMet[e]	–
G-6	Ti(EtHex)$_4$[c]	PhSiMet[e]	1.0
G-7	Ti(iPro)$_4$[b]	PhSiMet[e]	1.0
G-8	TiCl$_4$	PhSiMet[e]	1.5

[a] PhSiCl: trichloro(phenyl)silane.
[b] Ti(iPro)$_4$: tetraisopropoxytitanium.
[c] Ti(EtHex)$_4$: tetrakis(2-ethylhexyloxy)titanium.
[d] PhSiEt: triethoxy(phenyl)silane.
[e] PhSiMet: trimethoxy(phenyl)silane.

paring the Ti-polysiloxanes G-1 and G-8 prepared with **4** and **5**, respectively; the sample prepared with the chlorinated had a molecular weight of 3208 and the former only 1839. This effect can be attributed to the differences in the hydrolysis rate of the precursor. However, another effect could be responsible for these differences, since during the hydrolysis of chlorinated precursors an amount of HCl was present, and it is well known that Brønsted acids catalyze the reactions between terminal –OH groups, favouring the formation of longer siloxane polymers, with the consequent increase in molecular weight. This process was inferred by checking the dissimilarity observed among G-6, G-7 and G-8 where the former had the highest molecular weight prepared using the chlorinated titanium precursor (**1**).

The IR spectra of these titanopolysiloxanes (Figs. 1–3) displayed bands characteristic of the aromatic ring, several bands at 3200–3000 cm^{-1} characteristic of C–H stretching in aromatic rings [22], and three peaks at 1430, 1490 and 1595 cm^{-1} attributed to the stretching modes of the aromatic ring [22], as well as that of the Si–O bond, and a broad band between 1300 and 950 cm^{-1}. When titanium was introduced into the reaction mixture, a clear band located at 920 cm^{-1} – which is considered as fingerprint associated with asymmetric Ti–O–Si linkages in tetrahedral coordination – could also be discerned [23]. The intensity of this band was proportional to the titanium contents in the catalysts [24]. However, clear dissimilarities were observed when a different silicon precursor was employed. The spectra of polysiloxane synthesized with the chlorinated precursors (**4**) (Fig. 1) exhibited a broad band in the 3700–3200 cm^{-1} energy region with a shoulder at 3625 cm^{-1}, suggesting the presence of phenyl-bonded silanol [25]. The infrared spectrum of polysiloxane G-3 showed bands belonging to the C–O bonds of alkoxide groups (1460 cm^{-1}) and the C–H bonds of alkyl groups (2990–2800 cm^{-1}) [22], confirming the presence of (**2**), employed as a titanium precursor in the preparation of this catalyst. As stated above, hydrolysis of the titanium precursor was only partial because precursor (**2**) displayed the lowest hydrolysis rate of the three Ti-precursors employed.

Table 2
Molecular weight and physical aspect of the samples

Sample	Molecular weight (GPC)		Aspect
	Range	Maximum	
B-1	5100–1100	2796	White solid
G-1	10,200–2000	6022	White solid
G-2	9200–1500	5068	White solid
G-3	9700–1800	5790	White solid
B-2	150–60	120	Liquid
G-4	750–120	356	Viscous liquid
G-5	1200–350	678	Viscous liquid
G-9	800–210	482	Viscous liquid
B-3	170–65	119	Liquid
G-6	6500–1100	3361	White solid
G-7	8200–1200	4230	White solid
G-8	9500–1700	4730	White solid

Similar infrared spectra were obtained from the polysiloxanes prepared from precursor **6**. However, several weak peaks arising from the stretching vibration modes of the C–H bonds in alkyl groups (2990–2800 cm^{-1}) were observed. Clear bands belonging to non-hydrolyzed methoxy groups in precursor (**2**) were reported in Fig. 3. These bands were not only more intense in the titanium-free polysiloxane sample (B-3) but also a new band at 815 cm^{-1}, due to the vibration of Si–O–C [22] groups, was detected. This observation is consistent with the lower extent of the hydrolysis reaction of precursor **6**. This is in keeping with the GPC analysis of molecular weight, which showed that the formation of Si–O–Si linkages is favoured in the presence of titanium precursors.

The infrared spectra of the Ti-containing polysiloxanes prepared from precursor **5** were quite different from those of all the other samples (Fig. 3). In these spectra, no bands belonging to the stretching vibration of hydroxyl groups were observed. However, several intense bands arising from the stretching vibration of the C–H bonds of alkyl groups (2990–2800 cm^{-1}), together with a band at about 965 cm^{-1}—attributed to vibration of C–C–O bonds of the ethoxide groups [22] and another one at about 795 cm^{-1}, which can be assigned to vibrations of Si–O–C–C bonds [21]. These observations indicate that the extent of hydrolysis of precursor **5** was rather low, in agreement with its lower molecular weight determined by GPC measurements as compared to that of the other samples. In addition, no band around 920 cm^{-1} associated with asymmetric vibration of tetrahedral Si–O–Ti linkages was found which can be taken as conclusive that the extent of titanium incorporation to the polysiloxane structure was very low, if indeed it occurred.

The electronic spectra of blank samples – B-1, B-2 and B-3 – showed a band centered around 250 nm due to aromatic ring absorption. This band masks the typical of Ti^{IV} located in tetrahedral coordination [26]. These titanium species are the active sites in alkene epoxidation [4], and this reason the technique was not useful for the study of the titanium environment [20].

To avoid this pitfall, all the solid samples were analyzed by X-ray photoelectron spectroscopy (XPS) in order to explore the chemical state of titanium. The high-resolution photoelectron spectra of Ti 2p core-levels of the *in situ* outgassed samples (see for example Fig. 4) displayed the characteristic Ti $2p_{1/2}$–Ti

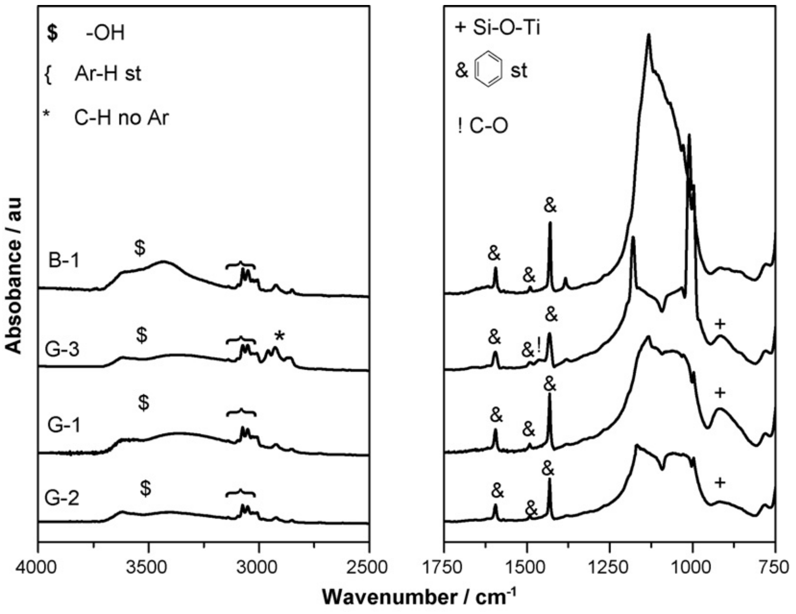


Fig. 1. Background IR spectra of the polysiloxane samples prepared with **4**.

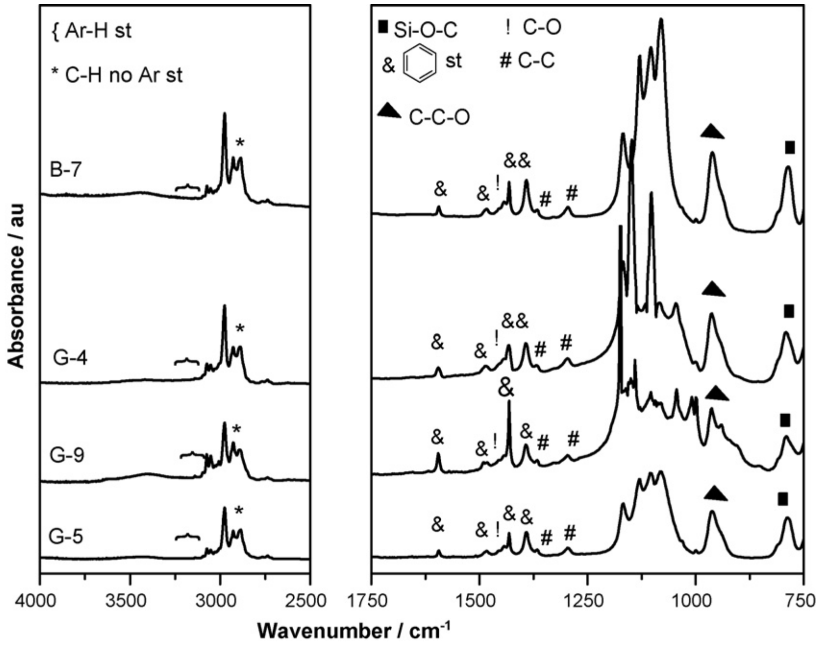


Fig. 2. Background IR spectra of the polysiloxane samples prepared with **5**.

$2p_{3/2}$ doublet. Although chemical information can be derived from each component, discussion should be based on the most intense Ti $2p_{3/2}$ component. Curve fitting of the Ti $2p_{3/2}$ core level revealed a component at a binding energy of 460.0 eV, which can be attributed to titanium in tetrahedral coordination [27], for the majority of the catalysts (Table 3). However, in the catalyst G-3 a minor additional component at a lower binding energy (458.5 eV) was detected, usually assigned to titanium in octahedral coordination [27].

All these data unequivocally demonstrate that titanium atoms had become incorporated into the polysiloxane structure as isolated sites in which every Ti^{IV} ion was tetrahedrally surrounded

Table 3
XPS data of the solid samples prepared

Sample	BE Ti $2p_{3/2}$ (eV)	Surface Ti/Si (atomic ratio)	Bulk Ti/Si (atomic ratio)
G-1	460.0	0.026	0.025
G-2	n.d.	n.d.	0.003
G-3	460.0 (86), 458.6 (14)	0.014	0.008
G-6	460.0	0.026	0.027
G-7	460.0	0.028	0.027
G-8	460.0	0.043	0.041

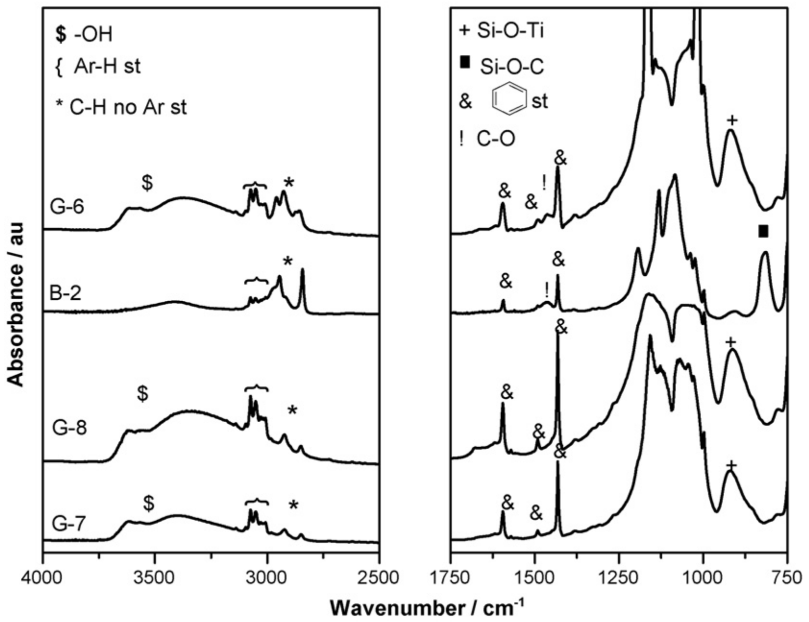


Fig. 3. Background IR spectra of the polysiloxane samples prepared with **6**.

by Ti–O–Si linkages. The only exception was sample G-3, which indeed showed great differences when synthesized from the type **4** silicon precursor and the type **3** titanium precursor as a consequence of the separate hydrolysis of the titanium precursor, resulting in the formation of Ti–O–Ti bonds with Ti^{IV} in octahedral coordination instead of tetrahedral Ti–O–Si linkages. Unfortunately, the sensitivity of the technique was insufficient to be able to record the Ti 2p spectrum of sample G-2 with a reasonable signal-to-noise ratio because of the very low Ti-content of this sample.

Surface analysis of the polysiloxane samples was done by photoelectron spectroscopy (XPS). Since the mean free path of photoelectrons in the solids is short (below 3 nm), XPS is a surface-sensitive characterization technique. Thus, it provides chemical information about the topmost few layers of the solid. The surface atomic ratios from the XPS intensity ratios were compared with those obtained by chemical analysis. These values are summarized in Table 3 and Fig. 5. With the exception of the G-3 sample, the XPS Si/Ti ratios for the Ti-polysiloxane samples approach the ratio for the bulk Si/Ti = 45 ratio derived from chemical analysis. This observation clearly indicates a homogeneous distribution of the titanium in the polysiloxane structure. The enrichment in titanium of the surface of sample G-3 could

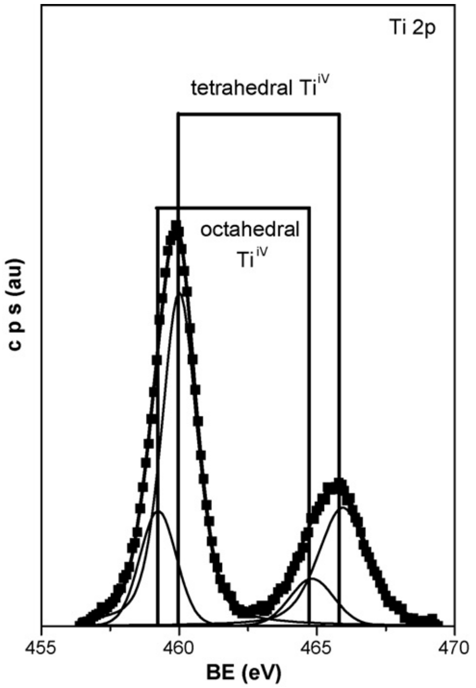


Fig. 4. Photoelectron spectrum of catalysts G-3 degassed at room temperature.

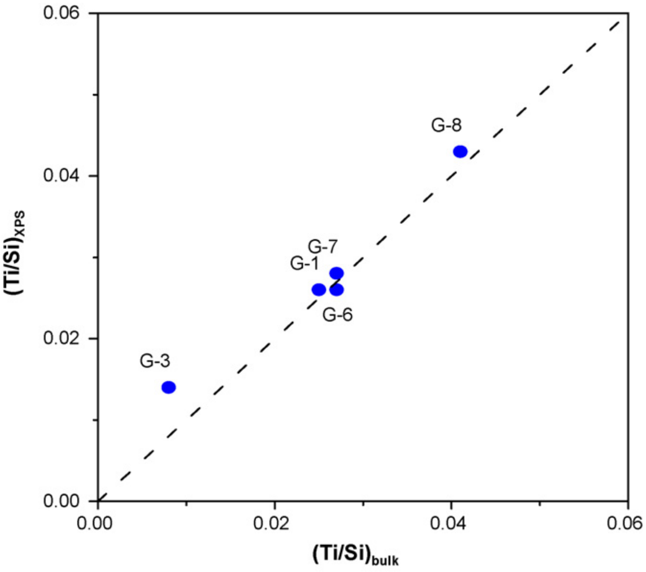


Fig. 5. Surface atomic ratio measured by XPS *vs*. bulk atomic ratio measured by chemical analysis.

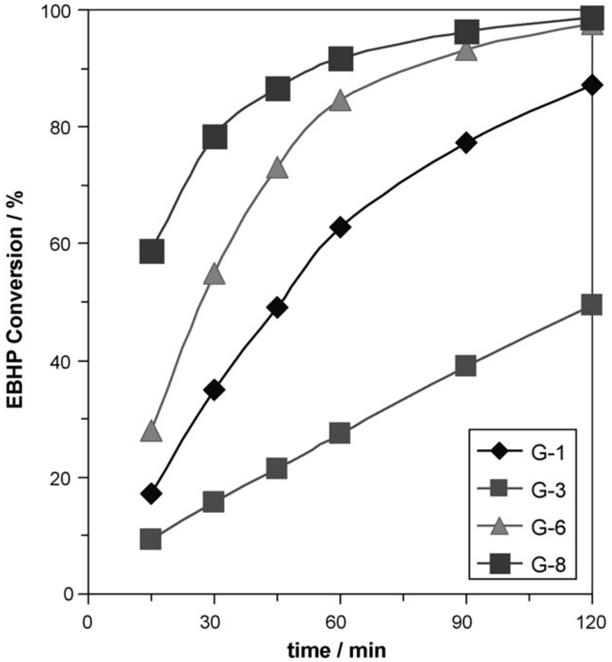


Fig. 6. Dependence of EBHP conversion *vs*. reaction time in the epoxidation of oct-1-ene at 383 K.

be related to the separate hydrolysis of the precursors, which produce the precipitation of small TiO_2 structures on the surface of the polysiloxane during the evaporation of the solvent in the synthesis process.

The conversion profiles of ethylbenzene hydroperoxide (EBHP) *versus* time were related to the titanium contents of the Ti-polysiloxane employed (Fig. 6, Table 4). The highest reaction rate was obtained with the catalyst G-8, which had 1.5 wt% of titanium, a very low conversion level being obtained with catalyst G-3 (0.3 wt% of Ti). However, this relationship could not be applied for the samples prepared from the silicon precursor **5**. These catalysts showed a very low conversion level despite their titanium contents (see G-4 and G-9). They were prepared with the silicon precursor with a very low hydrolysis rate and the polysiloxane was poorly developed, and owing to the different hydrolysis rate with the titanium precursors (**2**, **3**) the main part of the titanium was hydrolyzed separately, giving small aggregates of TiO_2 with the titanium in octahedral coordination; these Ti species were inactive in alkene epoxidation [4].

Table 4
Reaction data in the epoxidation of oct-1-ene by ethylbenzene hydroperoxide (EBHP) at 393 K after 2 h of reaction

Catalyst	% EBHP conversion	% Oct-1-ene conversion	% Selectivity of EBHP to epoxide
G-1	87	14.4	83
G-2	n.d.	–	–
G-3	49	6.3	64
G-4	59	3.3	28
G-5	n.d.	–	–
G-9	75	4.2	28
G-6	98	15.7	80
G-7	95	14.6	77
G-8	99	15.2	77

The reaction was selective to epoxide respect to the alkene since in all cases the only product detected from the oct-1-ene was 1,2-epoxyoctane. However, the selectivity to epoxide based on the EBHP consumed differed among catalysts, the main product from EBHP decomposition was acetophenone. The lower selectivity values obtained with samples prepared from the silicon precursor **5** were also achieved with catalyst G-3, in which octahedrally coordinated titanium was present. These findings highlight the fact that EBHP preferentially decomposes on Ti^{IV} sites surrounded by an octahedron of oxygen ions, with the subsequent drop in the selectivity to epoxide. In contrast, samples G-1, G-6, G-7 and G-8, in which photoelectron spectroscopy revealed a tetrahedral coordination of titanium, exhibited a higher EBHP selectivity. It is worth mentioning that catalyst G-1 epoxide selectivity was somewhat higher than other samples, probably due, as described in the literature, to the chloride precursor itself, which usually yields more selective polysiloxanes catalysts [19,20]. Chloride precursors are prone to becoming incorporated into the polysiloxane structure and hence to yielding more selective species for alkene epoxidation with organic hydroperoxides.

4. Conclusions

(i) The coordination of Ti^{4+} ions (d^0 configuration) to incompletely polysiloxane structures to yield electrophilic metal sites. The incorporation of titanium into the polysiloxane structure largely depends on the ability of the precursors to become hydrolyzed during the synthesis step. (ii) Incomplete hydrolysis of phenyltriethoxysilane, as observed by FT-IR, yielded non-homogeneous titanopolysiloxanes in which a titanium phase was found to be separated from the polysiloxane structure. (iii) This kind of titanopolysiloxane containing a segregated titanium oxide phase exhibited very low activity and selectivity in the target epoxidation reaction. (iv) The best catalytic performance was achieved when both silicon and titanium precursors displayed similar hydrolysis rates and hence titanium became incorporated into the incompletely condensed polysiloxane network.

Acknowledgments

The authors acknowledge financial support from Repsol-YPF (Spain). GBB gratefully acknowledges a fellowship granted by Repsol-YPF. JMCM acknowledges financial support from the Ministerio de Ciencia y Tecnología (Spain) in the Ramon y Cajal Program.

References

[1] J.M. Kobe, W.E. Evans, R.L. June, M.F. Lemanski, in: I.T. Horváth (Ed.), Encyclopedia of Catalysis, vol. 3, Wiley–VCH, Weinhein, Germany, 2003, p. 246.
[2] M.L. Merlau, C.C. Borg-Breen, S.B.T. Nguyen, in: I.T. Horváth (Ed.), Encyclopedia of Catalysis, vol. 3, Wiley–VCH, Weinhein, Germany, 2003, p. 155.
[3] J.M. Brégeault, Dalton Trans. (2003) 3289.

[4] D.E. De Vos, B.F. Sels, P.A. Jacobs, Adv. Synth. Catal. 345 (4) (2003) 457.

[5] P. Ratnasamy, D. Srinivas, H. Knözinger, Adv. Catal. 48 (2004) 1.

[6] C.S. Bell, H.P. Wulf, Shell Oil Compamy, US 38735780, 1975.

[7] M. Crocker, R.H.H. Herold, Shell International Research, B.V., WO 9724344, 1997.

[8] R.A. van Santen, H.C.L. Abbenhuis, W. Vorstenbosch, Solvay Deutchland GmbH, WO 9846352, 1998.

[9] H.W. Roesky, G. Anantharaman, V. Jancik, S. Singh, V. Chandrasekhar, Chem. Eur. J. 10 (2004) 4106.

[10] H.C.L. Abbenhuis, Chem. Eur. J. 6 (2000) 25.

[11] P.P. Pescarmona, J.C. vander Waal, I.E. Maxwell, T. Maschmeyer, Angew. Chem., Int. Ed. 40 (4) (2001) 740.

[12] P.P. Pescarmona, J.C. vander Waal, T. Maschmeyer, Eur. J. Inorg. Chem. (2004) 978.

[13] T. Maschmeyer, M.C. Klunduk, C.M. Martín, J.M. Thomas, B.F.G. Johnson, Chem. Commun. (1997) 1847.

[14] B.F.G. Johnson, J.M. Thomas, T. Maschmeyer, M.C. Klunduk, Chem. Eur. J. 5 (5) (1999) 1481.

[15] S. Krijnen, H.C.L. Abbenhuis, R.W.J.M. Hassen, J.H.C. van Hooff, R.A. van Santen, Angew. Chem., Int. Ed. 37 (3) (1998) 356.

[16] M. Crocker, R.H.M. Herold, A.G. Orpen, M.T.A. Overgaag, J. Chem. Soc., Dalton Trans. (1999) 3791.

[17] K.I. Alder, D.C. Sherrington, J. Mater. Chem. 10 (2000) 1103.

[18] W.-C. Chen, L.-H. Lee, B.-F. Chen, C.-T. Yen, J. Mater. Chem. 12 (2002) 3644.

[19] G. Blanco-Brieva, J.M. Campos-Martin, M.P. de Frutos, J.L.G. Fierro, Chem. Commun. (2001) 2228.

[20] G. Blanco-Brieva, M.C. Capel-Sanchez, J.M. Campos-Martin, M.P. de Frutos, J.L.G. Fierro, E.J. Lede, L. Adrini, F.G. Requejo, Adv. Synth. Catal. 345 (2003) 1314.

[21] C.D. Wagner, L.E. Davis, M.V. Zeller, J.A. Taylor, R.M. Raymond, L.H. Gale, Surf. Interf. Anal. 3 (1981) 211.

[22] E. Pretsch, T. Clerc, J. Seibl, W. Simon, Tablas para la elucidación estructural de compuestos orgánicos por métodos espectroscópicos, Alambra, Madrid, Spain, 1980.

[23] G. Ricchiardi, A. Damin, S. Bordiga, C. Lamberti, G. Spano, F. Rivetti, A. Zecchina, J. Am. Chem. Soc. 123 (2001) 11409.

[24] A. Haoudi-Mazzah, P. Dhamelincourt, J. Gnado, A. Mazzah, J. Raman Spectrosc. 26 (1995) 1027.

[25] J.F. Brown, J. Am. Chem. Soc. 87 (1965) 4317.

[26] V.A. de la Peña-O’Shea, M.C. Capel-Sanchez, G. Blanco-Brieva, J.M. Campos-Martin, J.L.G. Fierro, Angew. Chem., Int. Ed. 42 (2003) 5851.

[27] T. Blasco, M.A. Camblor, J.L.G. Fierro, J. Perez-Pariente, Microp. Mater. 16 (1994) 109.