

Titanium *K*-Edge XANES Analysis to Unravel the Local Structure of Alkene Epoxidation Titanium-Polysiloxane Homogeneous Catalysts

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Received: July 4, 2003; Accepted: October 6, 2003

Abstract: We describe the synthesis of highly effective homogeneous catalysts for the epoxidation of alkenes with organic hydroperoxide and their detailed characterization with the X-ray absorption near-edge spectroscopy (XANES) technique. Prepeaks at Ti *K*-edge XANES spectra of the catalysts showed a shift towards higher photon energy and a simultaneous drop in relative intensity with the increasing number of nearest oxygen neighbours around titanium. PCA analysis of Ti *K*-edge XANES spectra revealed that the catalysts can be grouped in four distinct regions according to their structural characteristics. These structural differences revealed by Ti *K*-edge XANES spectra can be ascribed to the procedure employed in catalyst synthesis. In a pre-

liminary attempt to explain catalytic performance, FTIR, UV-visible and XPS spectroscopic techniques were used to characterize the chemical structures developed on the catalysts; however, no correlation between reactivity and surface and/or bulk structures was found. Only the Ti *K*-edge XANES spectra of these Ti-polysiloxanes afforded a successful description of the local structure of Ti^{IV} centers due to their sensitivity in distinguishing different electronic structures for Ti atoms even under slight variations in their surroundings.

Keywords: epoxidation; homogeneous catalysis; titanium; X-ray absorption spectroscopy

Introduction

Epoxides, in particular propylene oxide, are a class of commodity chemicals of enormous importance in the chemical industry. The oxidation of alkenes to the corresponding epoxide in the liquid phase with organic hydroperoxides in the presence of a catalyst is well known. Generally, hydrocarbon-soluble organometallic compounds of transition metals can be employed as homogeneous catalysts. Examples are vanadium or molybdenum compounds.^[1] Other alternatives include the use of heterogeneous catalysts such as a chemical combination of titania and silica such as Ti/SiO₂,^[2] Tiβ^[3] and Ti-mesoporous materials.^[4] These catalysts showed high values of selectivity to epoxide but lower catalytic activity. Although homogeneous titanium-containing epoxidation catalysts are known,^[5] the selectivity to the alkene oxide obtained with such catalysts is significantly lower than those obtained with the above heterogeneous catalysts, some improvements having been found with polyorganometallosiloxane synthesized in a neu-

tral solvent such as toluene.^[6] The literature concerning these compounds as catalysts is limited, although recently there has been rekindled interest in soluble titanium catalysts, crystallized in the form of patents^[7] and articles.^[8] However, selectivity and conversion are still lower than with heterogeneous catalysts^[6] and, despite more recent attempts with titano-silsesquioxanes,^[9] these compounds continue to be tedious, expensive and time-consuming to prepare. It is now widely accepted that the active site for epoxidation in titanium-containing materials is of a tetrahedral nature.^[2–4] This makes it very important to have a method for preparing the catalysts that will avoid the formation of titanium in octahedral coordination. Recently, we have reported the synthesis process of titanium-polysiloxanes to epoxide with very high yield.^[10]

However, since traditional spectroscopic techniques such as UV-Vis, XPS, FTIR and Raman only provide limited information about the nature of the active site, the use of X-ray absorption near-edge spectroscopy (XANES) emerges as being extremely useful to study

the coordination of titanium with oxide anions.^[11] On the other hand, PCA (Principal Components factorial Analysis) of XANES spectra constitutes a valuable tool for the systematic decomposition of the different contributions, to XANES experimental results, because of the presence of different kinds of Ti-sites.^[12] Such information allows both the synthesis route and the catalytic performance to be assessed.^[13]

Results and Discussion

Some samples were prepared using several precursors and solvents, as shown in Table 1. The Ti-loading of the catalysts was close to 1 wt % in all cases (Table 1). The IR spectra of these titanopolysiloxanes (Figure 1) displayed bands characteristics of the aromatic ring as well as of the Si–O bond. A clear band located at 920 cm^{−1}, associated with Ti–O–Si^[14] linkages, could also be discerned. A broad band in the 3700–3200 cm^{−1} energy region with a shoulder at 3625 cm^{−1} was observed, suggesting the presence of phenyl-bonded silanol.^[15] Catalysts G-3 and G-6 exhibited additional weak bands in the region from 1600 to 1200 cm^{−1} due to the presence of Hacac, which remains strongly adsorbed on the Ti^{IV} sites^[16] even after the titanopolysiloxane has been formed.

The electronic spectra of blank samples, B-1 and B-2 (Figure 2), showed a band centered around 250 nm due to aromatic ring absorption. This band masks the typical band of Ti^{IV} located in a slightly tetrahedral environment.^[17] Despite this, the electronic spectra of samples G-3 and G-6 proved to be different, showing an additional band at about 400 nm characteristic of Ti^{IV} in an octahedral environment.^[17] The origin of the octahedral coordination lies in the fact that Hacac binds to Ti^{IV} sites, as already confirmed by IR spectroscopy.

The photoelectron spectra of the Ti 2p core-level (Figure 3) showed a single component for the most intense Ti 2p_{3/2} peak at a binding energy of 460.1 eV,

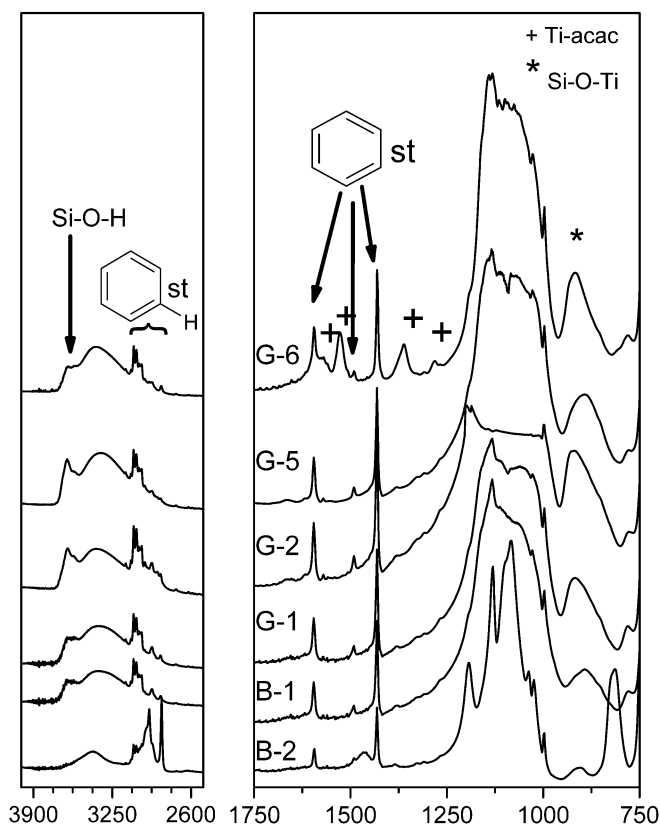


Figure 1. Background IR spectra of the polysiloxane samples.

corresponding to Ti^{IV} sites in tetrahedral coordination.^[18] No octahedrally coordinated Ti^{IV} species (binding energy of Ti 2p_{3/2} peak at around 459 eV)^[18] were observed in samples G-3 and G-6. A tentative explanation for this is that under the ultrahigh vacuum conditions required for conditioning the samples prior to recording the photoelectron spectra the Hacac ligands of samples G-3 and G-6 bound to the Ti^{IV} site may be lost, thereby changing the original coordination

Table 1. Catalysts prepared and titanium contents.

Catalyst	Ti Precursor	Si Precursor	Solvent	Ti % wt
G-1	TiCl ₄	PhSiCl ^[c]	Toluene	0.6
G-2	TiCl ₄	PhSiCl ^[c]	THF	0.9
G-3 ^[a]	TiCl ₄	PhSiCl ^[c]	Toluene	0.9
G-4	Ti(<i>i</i> -PrO) ₄ ^[b]	PhSiMet ^[d]	Toluene	1.1
G-5	Ti(<i>i</i> -PrO) ₄ ^[b]	PhSiMet ^[d]	THF	0.8
G-6 ^[a]	Ti(<i>i</i> -PrO) ₄ ^[b]	PhSiMet ^[d]	Toluene	1.1
B-1	–	PhSiCl ^[c]	Toluene	–
B-2	–	PhSiMet ^[d]	Toluene	–

^[a] Hacac was added during synthesis.

^[b] Ti(*i*-PrO)₄: titanium(IV) isopropoxide.

^[c] PhSiCl: phenyltrichlorosilane.

^[d] PhSiMet: phenyltrimethoxysilane.

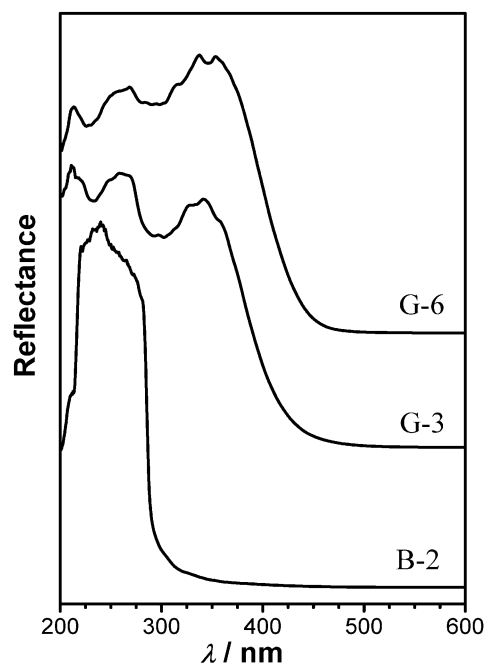


Figure 2. DRS UV-Vis spectra of blanks (B-1 and B-2) and catalysts G-3 and G-6, recorded under ambient conditions.

$\text{Ti}^{\text{IV}}_{\text{oct}} \rightarrow \text{Ti}^{\text{IV}}_{\text{tet}}$. This finding was confirmed by FTIR spectroscopy of outgassed G-3 and G-6, which did not exhibit bands from 1600 to 1200 cm^{-1} .

All the catalysts afforded high conversion levels of ethylbenzene hydroperoxide (EBHP); in most cases above 95% (Figure 4). However, the samples prepared from halogenated precursors exhibited conversion levels of EBHP that were even higher than with the alkoxide precursors (G-1 vs. G-4). The presence of compounds able to coordinate, such as the Hacac, with titanium during the preparation of titanopolysiloxanes elicited an enhancement in the selectivity to the epoxide (Figure 4b) (G-1 vs. G-2 and G-3, and G-4 vs. G-5 and G-6, respectively). The behaviour of the catalysts prepared with or without Hacac was different. Thus, the values of EBHP conversion and selectivity to epoxide were found to be very high for the catalysts prepared in the presence of ether (G-2 and G-5), and somewhat lower for those prepared in the presence of Hacac (G-3 and G-6), possibly because the Hacac molecule, which is still present in the coordination sphere of Ti^{IV} as confirmed by FTIR and DRS UV-Vis spectra, hinders the adsorption of reagents (hydroperoxide and alkene) on the active site, and the reaction rate therefore decreases. It is remarkable that the G-2 catalyst exhibited almost complete conversion of EBHP to epoxide.

Notwithstanding the foregoing, these reactivity trends cannot fully be interpreted on the basis of the spectroscopic information gathered by FTIR, DRS-UV-Visible techniques. To gain deeper insight into the catalyst structure at an almost atomic level, we recorded the Ti K-edge XANES spectra of these materials since they

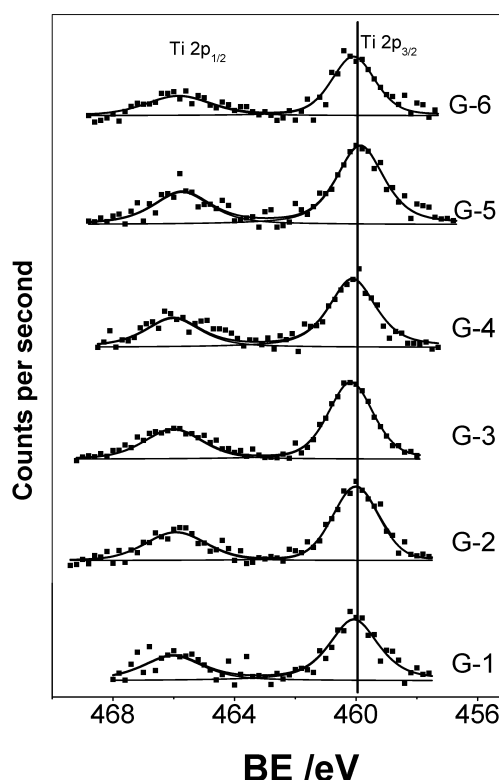


Figure 3. X-ray photoelectron spectra in the energy region of Ti 2p core-levels of the catalysts degassed at room temperature.

contain information about the electronic state of the X-ray absorbing Ti atom and about its surrounding local structure.

The Ti K-edge XANES spectra of each catalyst are shown in Figure 5a. All the samples displayed a well-defined absorption peak, whose intensity decreased in the order $\text{G-2} > \text{G-1} > \text{G-5} > \text{G-4} > \text{G-6} > \text{G-3}$. Simultaneously, the position in the energy scale shifted from 4969.8 eV in sample G-2 to 4970.4 eV in G-3. This shift towards higher energy and the relative drop in intensity in the Ti K XANES spectra mirror the common fact of an increase in the average number of nearest oxygen neighbours around the titanium. The Ti K XANES spectra were analyzed according to principal component factorial analysis (PCA).^[19–20] From the PCA analysis it became evident that XANES spectra could be generated by a set of four principal components. The confidence of the PCA analysis is based in the fact that more than 99.998% of the invariance in the data is given by those four factors, this point to the presence of four different Ti-sites. Figure 5b shows the abstract components of the absorbance, in which it becomes apparent that the first group of four is the most relevant. The contribution of the four principal components to the spectra of each sample can be represented in a three-dimensional Cartesian plot (Figure 6). This plot is generated by considering components 1 and 2 as the

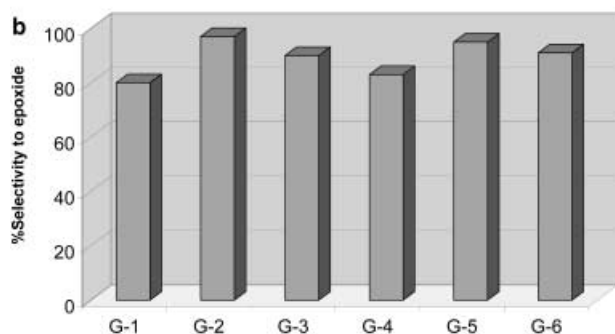
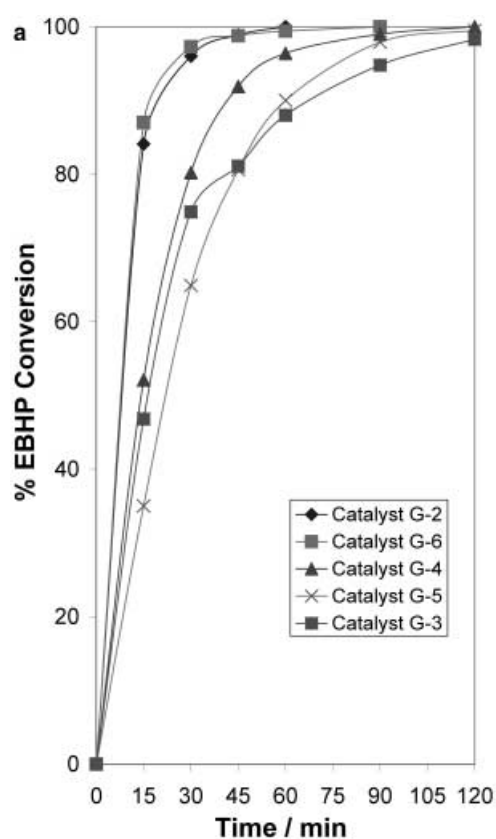


Figure 4. a) Dependence of EBHP conversion *versus* reaction time in the epoxidation of 1-octene at 388 K. b) Selectivity to 1,2-epoxyoctane during 1-octene epoxidation with ethylbenzene hydroperoxide at 90% conversion.

base axes and the third of the principal components as the height. All the catalysts can be grouped in four distinct regions: Region 1: catalysts G-2 and G-5; Region 2: catalysts G-3 and G-6; Region 3: catalyst G-4; and Region 4: catalyst G-1.

It should be noted that catalysts G1, G2, G4 and G5 are in the same plane while G3 and G6 are out of it. The fact that G3 and G6 are the only two catalysts to which Hacac was added during the synthesis procedure is an indication of the effect of this additive on the surroundings of Ti, presumably being responsible for the higher coordination at Ti sites.

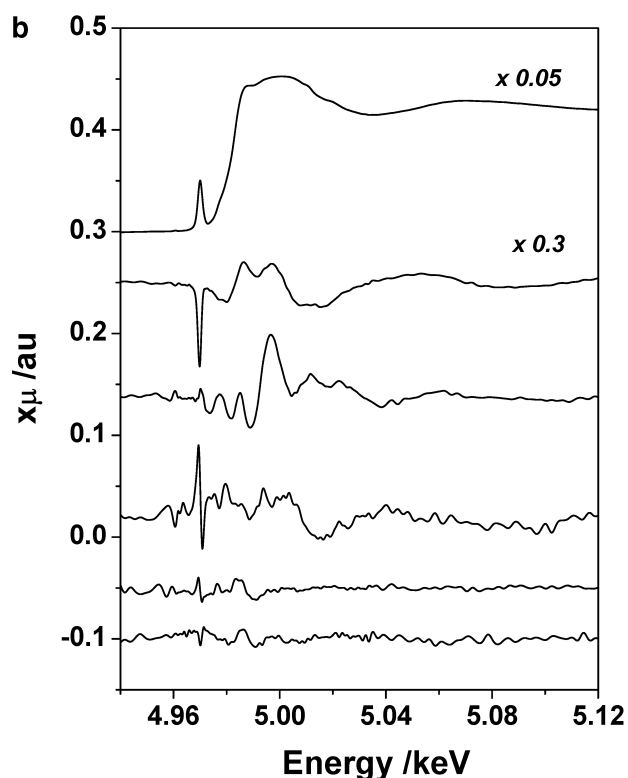
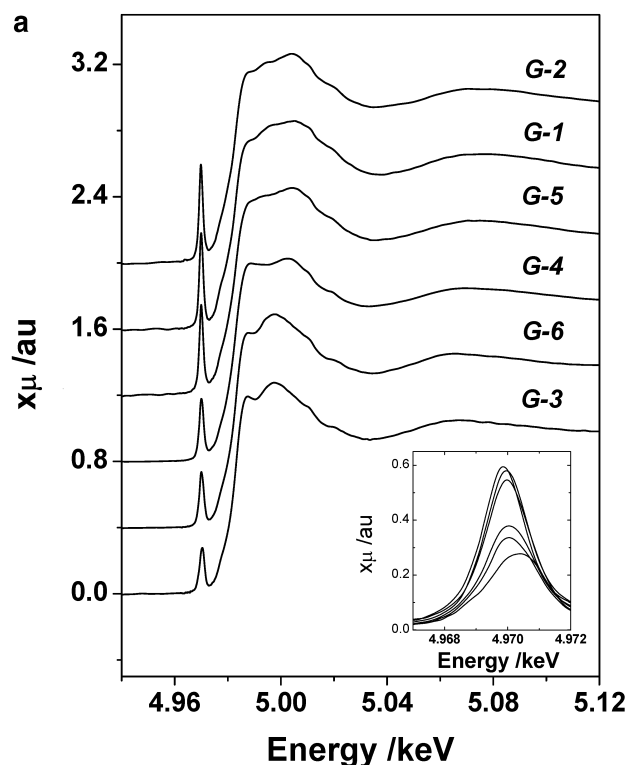


Figure 5. a) Ti-K-XANES of the samples. b) Absorbance-abtracted components determined by PCA analysis.

The Ti-K-XANES spectra of samples G-5 and G-2, whose components are grouped in region 1, exhibit an intense pre-peak which should be taken as being

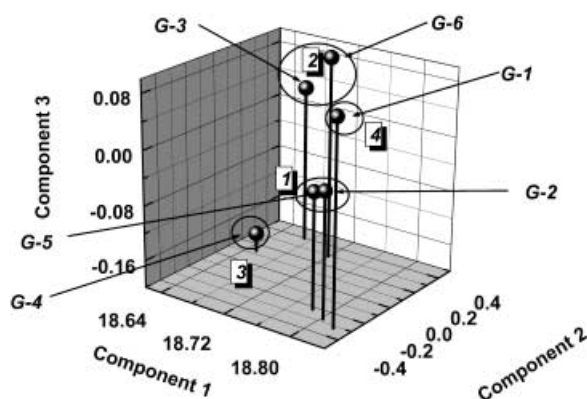


Figure 6. Contribution of three principal absorbance components in sample spectra.

indicative of tetrahedrally coordinated Ti^{IV} , with oxide ions as the major species (Figure 5). As illustrated in Figure 4, catalysts G-5 and G-2 displayed the best catalytic behaviour in the epoxidation reaction. Thus, it may be inferred that the active titanium species in the reaction has tetrahedral Ti^{IV} species; this is consistent with the large volume of work concerning catalytically active species of Ti-containing substrates. Region 2, which includes catalysts G-3 and G-6, may be essentially associated with octahedral species, since the respective Ti-K-XANES spectra exhibited less intense pre-peaks and their energy positions appeared shifted toward to higher energy (Figure 5). Therefore, the catalytic behaviour of samples G-3 and G-6 is reflected in a lower yield to epoxide (see Figure 4). Although the Ti-K-XANES spectrum of sample G-1 displays a pre-peak characteristic of Ti^{IV} in a coordination lower than 6 (Figure 5), its performance and the differences deriving from application of PCA analysis suggest the presence of a phase different to that related to region 1. In region 3, the Ti-K-XANES spectrum of sample G-4 displays a low intensity pre-peak, which is characteristic of octahedral Ti^{IV} , and hence exhibits a lower selectivity to epoxide than the other catalysts (Figures 4 and 5).

The structural differences revealed by Ti-K-XANES spectra can be ascribed to the procedure employed for catalyst synthesis. When a neutral solvent, such as toluene, is used, the halogenated precursor favours the formation of a non-active Ti^{IV} (with tetrahedral symmetry) species (G-1), while the alkoxide precursor yields octahedral Ti^{IV} active species (G-4). The use of THF solvent promotes the formation of a tetracoordinated Ti^{IV} species (G-2 and G-5). Finally, the incorporation of Hacac with toluene should apparently inhibit the formation of tetrahedral sites, while leading to Ti^{IV} in an octahedral environment (G-3 and G-6), but a different nature of species detected in the G-4 catalyst. Presumably, the tetracoordinated Ti^{IV} in these catalysts would increase the coordination number through chemisorption of Hacac molecules.

In conclusion, titanopolysiloxanes containing low amounts of titanium (0.6–1.1 wt %) have been synthesized using different titanium and silicon precursors. They were tested as homogeneous catalysts in the epoxidation reaction of 1-octene at 388 K with EBHP. Large differences in selectivity to epoxide were observed. In a first attempt to explain the catalytic performance, FTIR, UV-Vis and XPS spectroscopic techniques were used to characterize the chemical structures developed on the catalysts; however, no correlation between reactivity and surface and/or bulk structures was observed. Only the Ti K-edge XANES spectra of these Ti-polysiloxanes afforded a successful description of the local structure of Ti^{IV} centers, which in turn allowed us to rank catalyst reactivity. In particular, the XANES spectra of catalysts G-5 and G-2, which are the most selective in the epoxidation reaction, exhibited an intense pre-peak arising from the tetrahedrally coordinated Ti^{IV} species. By contrast, the XANES spectra of the less active G-3 and G-6 catalysts showed a drop in the intensity of the pre-peaks and a shift toward higher energies; both findings are associated with octahedral Ti^{IV} species due to Hacac chemisorption. Finally, in the G-1 sample, Ti sites are not active and are tetrahedrally coordinated while in the G-4 sample they are octahedrally coordinated with low selectivity.

Conclusion

Several Ti-polysiloxanes, containing low amounts of titanium (0.6–1.1%) were prepared using different solvents, and Ti- and Si-precursors. The structure at an almost atomic scale of these catalysts has been revealed by recording their Ti K-edge XANES spectra. The Ti K-edge XANES spectra of these polysiloxanes allowed us to successfully describe the local environment of the Ti^{IV} centers. This structure is directly related to their performance in the epoxidation reaction of 1-octene at 388 K with EBHP in a liquid, homogeneous phase. Only the catalysts which exhibited tetrahedrally coordinated Ti^{IV} species proved to be selective in the target reaction. Finally, we would like to emphasize that the structural differences among the catalysts, revealed by the Ti K-edge XANES spectra were induced by the procedure employed in the catalyst synthesis. Thus, these results can be exploited for the development of more efficient homogeneous Ti-polysiloxane catalysts.

Experimental Section

The catalysts were prepared in the following manner: a titanium(IV) precursor (titanium isopropoxide or titanium tetrachloride) (1.25 mmol) was added to the solvent (toluene or THF) (100 mL) under a nitrogen atmosphere and the solution was stirred for 15 min at rt. 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. Some samples were also prepared in the presence of Hacac, which was added together with the titanium precursor. For comparative purposes, two polysiloxane were prepared with two silicon precursors without the addition of a titanium precursor in toluene (called B1 and called B2).

FT-IR spectra were recorded with a resolution of 4 cm^{-1} on a Nicolet 510 FT-IR spectrophotometer using KBr wafers, containing 1% of the sample. UV-Vis diffuse reflectance spectra measurements were performed on a Shimadzu UV 2100 spectrophotometer equipped with an integrating sphere, using BaSO_4 as a reference. The samples were analyzed under ambient conditions. The reflection in percentage was measured and presented by the Kubelka–Munk–Schuster function. Photoelectron spectra (XPS) were recorded using a VG Escalab 200R spectrometer equipped with an $\text{MgK}\alpha$ ($h\nu = 1253.6\text{ eV}$) anode and a hemispherical analyzer operating in 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 at 284.9 eV was used as an internal standard; this reference gave BE values with an accuracy of 0.2 eV.

Catalytic epoxidation of 1-octene 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 an internal standard in quantitative GC analysis. Selectivity to epoxide was based on the EBHP consumed.

Ti-K-XAS data were collected at the XAS beam line at the Laboratorio Nacional de Luz Sincrotrón (LNLS), Campinas (Brazil). An Si(111) double-crystal monochromator with a slit aperture of 0.5 mm was used to obtain an estimated resolution of 1 eV. The anharmonicity of the beam was less than 1% since the critical energy of the ring was 2 keV.^[22] All spectra were recorded in the transmission mode using ionization chambers filled with air under pressure at ambient temperature. The calibration of the energy scale was monitored by simultaneously recording the spectra of a Ti foil placed just adjacent to the catalyst sample coupled with a third ionization chamber. All XAS spectra were recorded in the following energy regions: 4900–4960 eV (2 eV channel^{-1} , 2 s channel^{-1}), 4960–5005 eV ($0.2\text{ eV channel}^{-1}$, 2 s channel^{-1}) and 5005–5930 eV (2 eV channel^{-1} , 2 s channel^{-1}).

Acknowledgements

The authors acknowledge financial support from Repsol-YPF (Spain), the Fundación Antorchas (Argentina) and LNLS

Campinas (Brasil) under Project XAS #989/01. Three of us (GBB, MCCS and JMCM) gratefully acknowledge fellowships granted by Repsol-YPF.

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