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Influence of solvent in the synthesis steps of titanium-supported amorphous silica epoxidation catalysts

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

Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, 28049 Madrid, Spain

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Abstract

A series of titanium-silica catalysts with relatively low Ti contents were prepared by dispersing titanium isopropoxide in a solvent (cyclohexanol, 1-phenylethanol, 1-hexanol, 2-(2-ethoxyethoxy)ethanol, diglyme, and acetophenone) and then mixing each solution with the silica substrate. The process consisting of the hydrolysis of the Ti precursor by the hydroxyl groups of the silica surface yielded catalysts containing Ti loadings of 0.8–3.0 wt%. The catalysts prepared were characterized using various spectroscopic techniques, including diffuse reflectance infrared Fourier transform (DRIFTS), ultraviolet–visible (UV–vis), and photoelectron (XPS) spectroscopic techniques. The catalytic activity of the catalysts studied was determined using liquid-phase epoxidation of 1-octene with hydrogen peroxide as a model reaction. All catalysts showed very high hydrogen peroxide consumption but the selectivity to the epoxide was seen to be strongly dependent upon the solvent used in the preparation. Only the catalyst prepared using cyclohexanol solvent, in which the titanium content was low (0.8 wt%) and the Ti(IV) ions were isolated tetrahedrally coordinated by oxide anions, exhibited very high (95%) selectivity to the epoxide. The other Ti/SiO_2 catalysts containing a higher amount of titanium (1.0–3.0 wt%), but less disperse and with Ti(IV) in an octahedral environment, exhibited poor performance in the target reaction.

Keywords: Amorphous titanium-silica catalysts; Catalyst preparation; 1-Octene epoxidation; Hydrogen peroxide oxidant; Diffuse reflectance spectroscopy; UV–vis spectroscopy; Photoelectron spectroscopy

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1. Introduction

Despite numerous reports in the literature, the epoxidation of terminal alkenes remains a challenge in petrochemistry. Many different methods have been developed for the preparation of epoxides. In particular, the epoxidation of alkenes with diluted hydrogen peroxide is one of the main goals in this field. In recent years, a large volume of work has been generated on titanium-substituted zeolites in the framework, including TS-1 [1–3], Ti-β [4–6], Ti-incorporated ordered mesoporous silica [7–9], and amorphous xerogels [10–12]. A common and major claim of all these works is the excellent performance of these catalysts in the epoxidation reactions of the olefinic substrates with hydrogen peroxide. However, despite good activity with alkyl hydroperoxides, the catalytic performance of all these solids with hydrogen peroxide is far from that of TS-1.

Another approach is the preparation of silica-supported titanium materials, first described by Shell [13]. More recently, titanium silica-supported catalysts have been reported to be active in the epoxidation reactions of alkenes with hydrogen peroxide, and the preparation of this type of material by treatment of silica with $Ti(OiPr)_4$ [14–16], TiF_4 [17,18], tetraneopentyltitanium [19,20], or ion-beam implantation [21,22] has been described. We have recently published our preliminary results in the epoxidation of linear alkenes with aqueous hydrogen peroxide using Ti supported on silica, with high efficiency [23,24]. This kind of catalyst seems to be more stable than other related catalysts in view of the low leaching level and the truly heterogeneous character of the epoxidation reaction [25,26].

Moreover, the performance of these catalysts is strongly dependent upon the titanium environment. It has been claimed that as regards the TS-1 structure, titanium is most commonly assumed to occupy a substitutional position in the zeolite framework, since X-ray diffraction (XRD) measurements have revealed that unit cell volume increases linearly with the Ti content, in good agreement

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* Corresponding author.
E-mail address: jlgfierro@icp.csic.es (J.L.G. Fierro).

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with the isomorphous substitution of Ti by Si at tetrahedral framework sites [27]. In addition, the local environment of Ti in TS-1 has been studied in depth using several techniques, such as diffuse reflectance-ultraviolet–visible (DRS-UV–vis) [28], Fourier transform-infrared (FT-IR), and Raman [29,30] spectroscopic techniques, powder neutron diffraction [31], and X-ray absorption spectroscopy [29,33]. All these studies confirmed that titanium is in a tetrahedral environment in TS-1. This finding was also observed in large-pore zeolites [4–6], Ti-incorporated ordered mesoporous silica (OMS) [7–9], and amorphous silica xerogels [10–12]. However, other authors [34] have subsequently claimed that amorphous silica can be used in the same way as OMS, and these ordered mesoporous materials do not show any clear advantages over silica in epoxidation reactions.

From scrutiny of all the above work, it is apparent that no systematic studies have addressed the influence of the solvent employed in the preparation of titanium-supported amorphous silica catalysts in the chemical environment of titanium. Previous exploratory work carried out in our laboratory indicated the strong dependence of the solvent used in the synthesis of the catalyst and the performance of these catalysts in the epoxidation of primary alkenes with hydrogen peroxide. Accordingly, this work was undertaken with the aim of investigating the role played by the solvent used in the preparation of titanium-supported amorphous silica catalysts in the chemical environment of titanium, which in turn is directly related to its performance in the target reaction.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared as follows. Titanium isopropoxide (Aldrich, reagent grade) (0.75 g) was dispersed in the solvent (150 mL). The solvents employed were cyclohexanol, 1-phenylethanol, 1-hexanol, 2-(2-etoxyetoxy)ethanol, diglyme, and acetophenone. The solution was heated to 423 K under stirring conditions and then silica (Grace Davison G-952, specific area, 310 $m^2\,g^{-1}$; pore volume, 1.5 $mL\,g^{-1}$) (5.0 g) was added to the solution and maintained under vigorous stirring at 423 K for 2 h. The solid thus obtained was filtered off and washed twice with 150 mL of hot solvent, dried at 383 K, and finally calcined at 773 K for 5 h. A titanium-silicalite (TS-1) sample, prepared as described by Taramaso et al. [1], was used as reference.

2.2. Characterization

The titanium contents of the Ti/SiO_2 of the catalysts were determined using inductively coupled plasma absorption spectrometry, with a Perkin-Elmer Optima 3300 DV instrument.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was carried out on a FT-IR Nicolet 510 instrument equipped with an integration sphere and a Harrick HVC-DRP environmentally controlled cell. The samples were prepared by mixing the catalyst with KBr (10 wt% catalyst). About 50 mg of the powdered mixture was packed into a sample holder and dried in situ at 773 K for 1 h while a helium flow (Air Liquide) was passed through the sample. A DRIFT spectrum of dry KBr was also recorded as background. Two hundred and fifty-six scans were accumulated at a spectral resolution of 4 cm^{-1} for each sample. All spectra were recorded at room temperature.

Ultraviolet–visible spectra were measured on a Shimadzu 2100 UV–vis spectrophotometer equipped with an integrating sphere. A $BaSO_4$ disc was used as reference. All spectra were acquired under ambient conditions.

X-ray photoelectron spectra were recorded on a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and a magnesium X-ray source (12 kV and 10 mA) ($Mg\text{-}K_\alpha = 1253.6$ eV). The powder samples were packed into small aluminum cylinders and mounted on a sample rod in the pretreatment chamber and outgassed at 773 K for 1 h. The base pressure of the ion-pumped analysis chamber was maintained below 3×10^{-9} mbar during data acquisition. Peak intensities were estimated by calculating the integral of each peak after smoothing and subtraction of the “S-shaped” background. All binding energies (BE) were referenced to the adventitious C 1s line at 284.9 eV. This reference gave BE values with an accuracy of ±0.1 eV.

2.3. Activity measurements

The epoxidation reactions were carried out batchwise in a mechanically stirred 250-mL thermostated glass reactor equipped with thermometer, reflux condenser, and a septum for withdrawing samples. In a typical run, alkene (0.2 mol), *tert*-butanol (11 g), and 1 g of catalyst were mixed in the reactor and the suspension was heated at 333 K. Then, 4 g of a 5 wt% organic solution of H_2O_2 (in 1-phenylethanol) was added dropwise to the reactor suspension while maintaining vigorous stirring over 0.5 h. The organic compounds were analyzed on a GC-FID Hewlett Packard 6890-plus device equipped with a HP-WAX capillary column. The hydrogen peroxide consumption was evaluated by standard iodometric titration, using a Radiometer VIT-90 titrator.

Epoxide selectivity was related to the hydrogen peroxide converted according to the equation,

$$S\,(\%) = 100 * [\text{epoxide}] \big/ \big([H_2O_2]_0 - [H_2O_2]\big), \qquad (1)$$

where epoxide represents the 1,2-epoxyoctane, the subscript 0 stands for initial values, and all concentrations are expressed on a molar basis. No other product derived from the olefin was detected.

3. Results

Five catalysts were prepared following the procedure described under Experimental using different oxygenated solvents. Table 1 summarizes both the type of solvent employed in the preparation of each catalyst and the amount of titanium incorporated. It is clear that the titanium content of the catalyst depends on the type of solvent used in the synthesis steps. This is seen on comparing the alcohol-prepared catalysts, which incorporate titanium amounts of approximately 1 wt%, whereas in that produced using other types of solvents, such as diglyme or acetophenone, titanium incorporation was almost quantitative.

The electronic spectra of the catalysts showed absorption associated with the ligand metal charge transfer (LMCT) from the oxygen to an empty orbital of the Ti(IV) ion: $Ti^{4+}O^{2-} \rightarrow Ti^{3+}O^{-}$. The wavelength at which this transition occurs is highly sensitive to the coordination of titanium sites, and in the literature this has been proposed as a probe to test titanium coordination [28–37]. As a general rule, LMCT in titanium compounds containing octahedrally coordinated Ti(IV) takes place at higher wavelengths than in compounds in which the titanium ions exhibit only a tetrahedral coordination. The electronic spectra of the catalysts differ markedly from that of that of the TS-1 reference (Fig. 1), which can be used as a model of isolated titanium ions coordinated tetrahedrally to oxide ions within a silica network. The spectrum of TS-1 exhibited a rather narrow absorption band centered at 215 nm, which is usually associated with isolated Ti(IV) in tetrahedral coordination. The silica-supported catalysts showed a larger absorption band shifted toward a higher wavelength. However, information about the true coordination of titanium species is complicated by the coordination of water molecules from the ambient to the titanium sites [24]. The hydration of Ti(IV) sites is also favored as a consequence of the hydrophilic character of the solid. In all the catalysts, the presence of TiO_2 clustering can be ruled out because no absorption at 370–410 nm was detected. In order to interpret the UV–visible spectra, the experimental absorption bands were fitted taking a sum of Gaussian lines. Three components were considered in the fit: (i) a band at 212 nm, attributed to isolated Ti(IV) species in tetrahedral coordination [28–37]; (ii) a band at 264 nm, associated with hydrated titanium species, also in tetrahedral coordination [38]; and (iii) a band at 312 nm, due to polymeric titanium species grown on the silica surface that did not reach the crystallographic order of the TiO_2 (anatase) structure. As can be seen, the electronic spectrum of the TS-1 sample displays almost exclusively the component of isolated Ti(IV) in tetrahedral coordination, with a minor component of tetrahedral, hydrated titanium species. The electronic spectrum of catalyst C1 can be fitted to a sum of two Gaussians at 212 and 264 nm in similar proportions. This finding can be attributed to the more hydrophilic character of the silica surface, facilitating the hydration of titanium. The electronic spectra of the C2, C3, and C4 catalysts showed an additional, low-intensity component at 312 nm, which can be taken as conclusive of the formation of TiO_2 clustering and/or polymeric two-dimensional titanium species. In particular, the spectra of catalysts C5 and C6 exhibited the component at 312 nm in a much more intense way than in the other samples. This observation points to the formation of a larger amount of octahedrally coordinated titanium species.

The relative proportions of each component are shown in Table 2. From these data, it is clear that the catalysts prepared in nonalcoholic solvents (C5 and C6) differ substantially from those prepared in alcoholic solvents (C1, C2, C3, and C4) because the peak responsible for octahedrally coordinated titanium species is much more intense. Among the catalysts prepared in the presence of alcohol, the one synthesized with cyclohexanol (C1) did not exhibit the formation

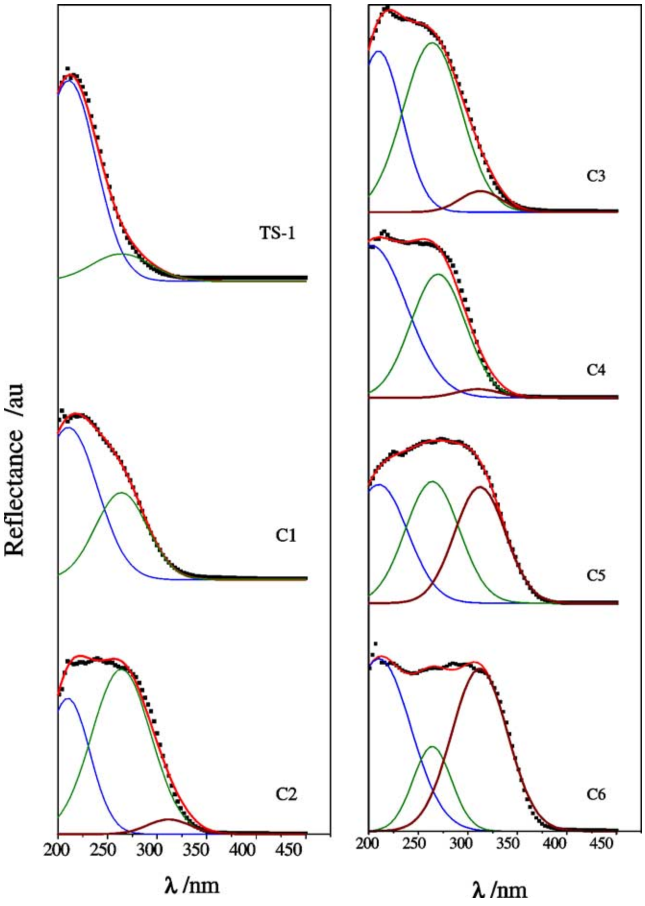

Fig. 1. DRS UV–vis spectra of samples synthesized.

Table 1
Labeling, titanium contents, and solvents employed in catalyst synthesis

Catalyst	Solvent	Ti (wt%)
C1	Cyclohexanol	0.8
C2	1-Phenylethanol	1.4
C3	1-Hexanol	1.0
C4	2-(2-Ethoxyethoxy)ethanol	1.2
C5	Diglyme	3.0
C6	Acetophenone	3.0

Table 2
Relative proportions of component peaks of DRS UV–vis of the catalysts synthesized

Catalyst	210 nm	264 nm	312 nm
TS-1	87	13	–
C1	66	44	–
C2	37	60	3
C3	41	54	5
C4	49	48	3
C5	30	30	40
C6	47	14	39

octahedrally coordinated titanium species, even in small proportions.

The DRIFT spectra of the in situ-dried silica-supported catalysts are similar; however, careful scrutiny reveals some differences. First, in the 4000–3000 cm^{-1} spectral region (Fig. 2), where stretching vibrations of hydroxyl groups appear, a broad band extending between 3000 and 3500 cm^{-1} can be discerned. This band comes from H-bridging hydroxyl (–Si–OH. . .O–Si–) groups and is accompanied by a sharp band at approximately 3700 cm^{-1} arising from isolated silanol (–Si–OH) groups. The proportion of isolated Si–OH groups with respect the H-bridging hydroxyl groups varies with the solvent used in catalyst preparation. Second, catalysts C5 and C6 exhibited a very small proportion of isolated –Si–OH groups, while this proportion increased substantially in catalysts C1, C2, C3, and C4 prepared in alcoholic media and, more specifically, when cyclohexanol was used as a solvent (C1).

The DRIFT spectra in the region of structural vibrations of the solid of the in situ-dried catalysts at 723 K were virtually the same, because the silica substrate was common to all the samples. Despite this general trend, some differentiating features can be observed following careful scrutiny of the 910–960 cm^{-1} energy region, where the Ti–O–Si vibrations usually appear [38,39]. It is stressed that this region is in general overshadowed by one vibration (rocking mode) of the –Si–OH groups at approximately 980 cm^{-1} [40,41], which hinders precise identification of the band at 910–960 cm^{-1}. In an attempt to identify the band responsible for titanium incorporation to the catalyst surface precisely, a fit of the experimental infrared spectrum was performed. A broad energy region between 600 and 1400 cm^{-1} was considered and nine Gaussian lines were introduced [42], whose assignment is as follows: symmetric stretching of Si–O–Si bands at 739, 792, and 832 cm^{-1}; a typical band of Si–O–Ti connectivity at 935 cm^{-1}; vibrations of Si–OH bonds at 980 cm^{-1}, and asymmetric Si–O–Si vibrations at approximately 1040, 1080, 1180, and 1228 cm^{-1}.

The fitted DRIFT spectra of the catalysts (Fig. 3) revealed significant differences in the band associated with Ti–O–Si

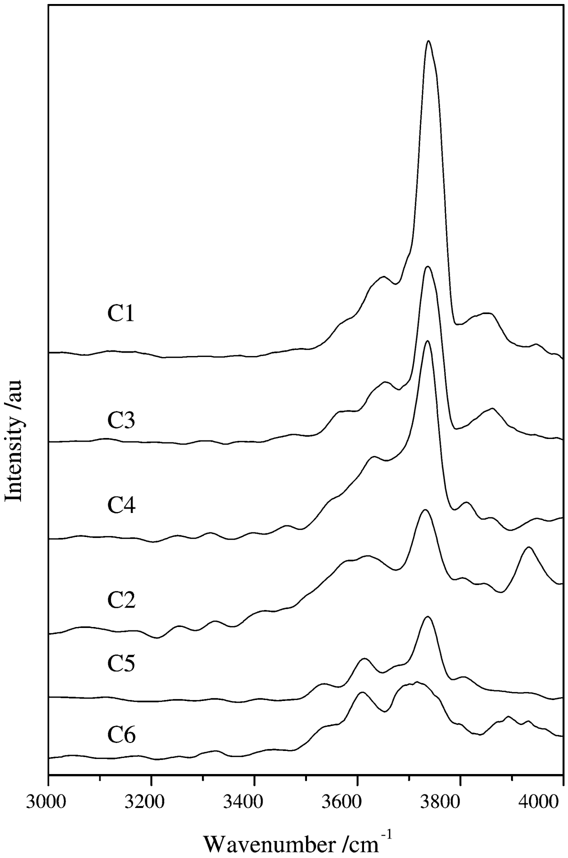

Fig. 2. DRIFT spectra of OH vibration regions of samples dried at 773 K.

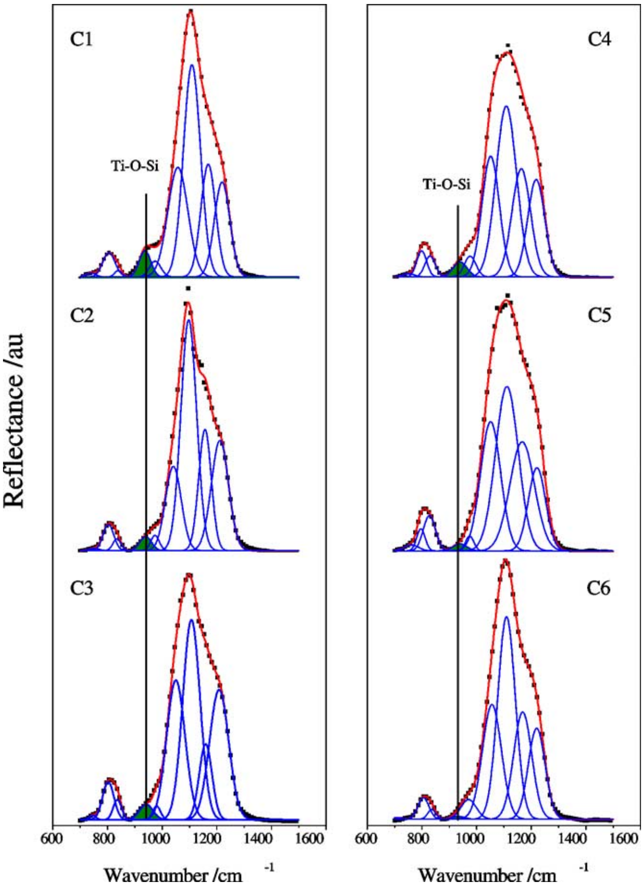

Fig. 3. DRIFTS of skeletal vibration regions of samples dried at 773 K.

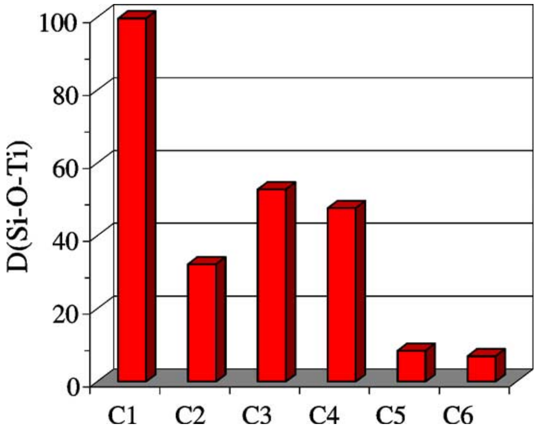

Fig. 4. Relative semiquantitative Ti dispersions (D) estimated from DRIFT spectra of samples dried at 773 K.

vibrations (935 cm^{-1}). Perhaps the most important finding was that changes did not correspond to the amount of titanium incorporated. The catalysts prepared using alcohol as a solvent (C1, C2, C3, and C4) exhibited a much higher relative intensity of this band than catalysts C5 and C6, even though the latter incorporated a larger amount of titanium. Such a difference is associated to titanium dispersion in the catalyst, because in the literature it has been proposed [42,43] that the ratio of the area of the fitted peaks at approximately 1200 cm^{-1} and that due to Ti–O–Si vibrations allows one to obtain semiquantitative values for titanium dispersion in silica. In order to calculate titanium dispersion, the following expression has been used [42],

$$D_{(\text{Si–O–Ti})} = [S_{(\text{Si–O–Ti})}/S_{(\text{Si–O–Si})}]x_{\text{Si}}/x_{\text{Ti}}, \tag{2}$$

where $S_{(\text{Si–O–Ti})}$ is the area of the fitted peak at approximately 935 cm^{-1} and $S_{(\text{Si–O–Si})}$ is the sum of the peak areas at approximately 1180 and 1228 cm^{-1}; x_{Si} and x_{Ti} are the molar proportions of Si and Ti, respectively.

The dispersion values of titanium in the catalysts (Fig. 4) show clear differences. While titanium dispersion was low for catalysts C5 and C6, it increased in the catalysts prepared using alcohols in the synthesis (C2, C3, and C4) and, more specifically, for the sample prepared using cyclohexanol (C1), which exhibited the highest dispersion. All these findings are in agreement with the UV–vis spectra of the catalysts. Interestingly, catalysts C5 and C6, with low titanium dispersion (as derived from the above analysis of the DRIFT spectra), also exhibited an important contribution of surface polymeric (Ti–O–Ti–O–) titanium species in the electronic spectra. Indeed, the proportion of this kind of titanium species was much lower when alcohols were employed in the synthesis of the catalysts (C2, C3, and C4) or even absent in the catalysts prepared in the presence of cyclohexanol (C1), in which only a tetrahedrally hydrated, isolated titanium species was present.

High-resolution photoelectron spectra of the Ti 2p core levels of the catalysts in situ outgassed at 773 K were recorded. The spectra shown in Fig. 5 showed the characteristic spin-orbit splitting of Ti 2p levels (Ti $2p_{3/2}$ and Ti $2p_{1/2}$). Since chemical information can be derived from the analysis of binding energies of each level, attention will only be paid to the most intense Ti $2p_{3/2}$ component of the doublet. The peak fitting of the experimental Ti $2p_{3/2}$ component revealed two contributions: one at high binding energy (460.0 eV), typical of Ti (IV) coordinated tetrahedrally by oxide anions [44], and another one at lower binding energies (458.5 eV), which is the fingerprint of Ti(IV) octahedrally coordinated by oxide anions [44]. Most of the catalysts prepared with the SiO_2 support showed varying proportions of tetrahedral and octahedral titanium species. At first glance, it is clear that the catalysts prepared in an alcoholic medium (C2, C3, and C4) show a much lower proportion of octahedral than of tetrahedral titanium species, and, consistent with the expectations of the characterization data afforded by the UV–vis technique, catalysts C5 and C6 exhibited a larger proportion of titanium in octahedral coordination.

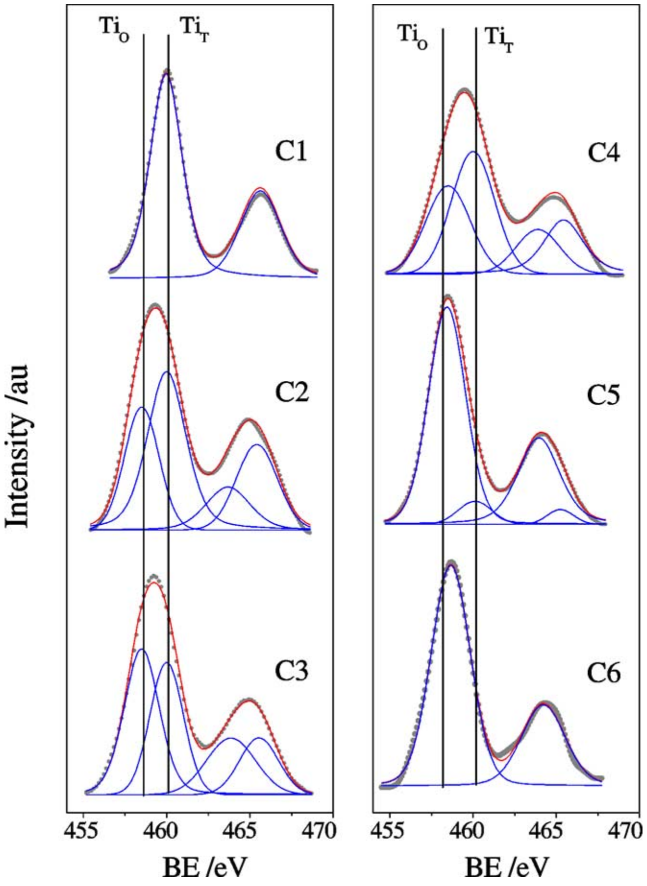

Fig. 5. XP spectra in Ti 2p core-level region of catalysts degassed in situ at 773 K.

All the catalysts were tested in a liquid phase 1-octene epoxidation reaction using hydrogen peroxide as oxidant agent. For the sake of simplicity and for comparative purposes, the reaction conditions were identical for all the catalysts. The hydrogen peroxide conversions and selectivity to epoxide of all the catalysts are shown in Table 3 and Fig. 6. All the Ti-containing silica catalysts showed very high con-

Table 3
Alkene epoxidation with hydrogen peroxide after 1 h of reaction ($T =$ 353 K)

Catalyst	H_2O_2 conversion (%)	Selectivity to epoxide (%)
C1	97	95
C2	99	55
C3	93	45
C4	99	54
C5	88	10
C6	97	20

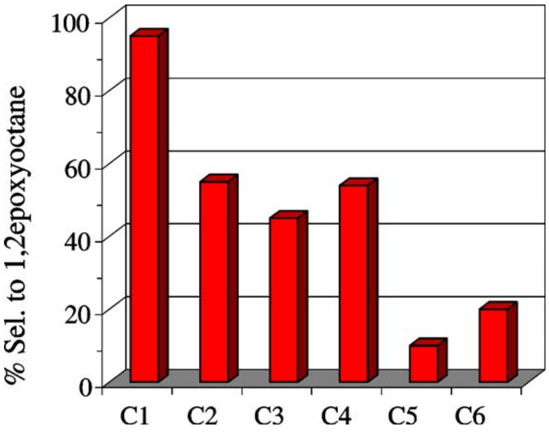

Fig. 6. Selectivity to 1,2-epoxyoctane during 1-octene epoxidation with hydrogen peroxide after 1 h of reaction ($T = 353$ K).

versions of hydrogen peroxide. In general, these catalysts presented a moderate selectivity to the epoxide, except catalyst C1, with which excellent epoxide selectivity was obtained. This trend in catalytic behavior is in complete accordance with the characterization data. Catalysts C5 and C6 with, a high proportion of octahedrally coordinated Ti(IV) species (UV–vis and XPS) and a rather low proportion of Ti–O–Si bridges (DRIFTS), exhibited a low selectivity to the epoxide. An intermediate situation was seen for catalysts C2, C3, and C4, in which a small proportion of octahedral titanium was developed, thus affording a moderate selectivity to epoxide. However, catalyst C1, in which the titanium coordination approaches that in TS-1, showed a very high hydrogen peroxide conversion and very good selectivity to epoxide.

In order to check the leaching of Ti species during the epoxidation reaction, as recommended in the literature [25,26], an experiment performed under similar reaction conditions was interrupted after 30 min. The hot liquid medium was removed with a syringe equipped with a filter and immediately transferred to another reactor already at the same temperature. The compositions were then monitored for another 1.5 h. No activity was found in the liquid phase alone after filtering out the catalyst from the reaction medium. It was clear that no hypothetical Ti species had leached out of the catalyst and the epoxidation reaction was stopped after catalyst removal, indicating that the activity of the catalyst can be only due to the Ti atoms incorporated onto the surface of the silica support.

4. Discussion

The results obtained in the present work on the structure and catalytic behavior of titanium-containing silica clearly indicate that the conditions employed in the synthesis step of the catalysts determine the surface structure of the catalytic component. More specifically, here attention was paid to only one of the variables involved in the genesis of this kind of catalyst; i.e., the solvent employed in the Ti-incorporation step.

As stated under Experimental, the samples were prepared by dispersing titanium isopropoxide in an organic solvent (cyclohexanol, 1-phenylethanol, 1-hexanol, 2-(2-ethoxyethoxy)ethanol, diglyme, and acetophenone) and then mixing the solution with the silica substrate. These solvents were selected in order to obtain quite different affinities between the Ti-isopropoxide precursor and the solvent, and therefore to determine hydrolysis rates of this precursor with the hydroxyl groups of the silica also different. One large difference observed was the amount of titanium incorporated to the silica substrate. The chemical analyses shown in Table 1 reveal that the highest Ti loading was achieved using acetophenone and diglyme solvents, but lower with alcohols. One tempting explanation of this behavior is the different chelating capacities of the polar groups of the solvent molecule with the titanium isopropoxide precursor in solution. The strongest interaction of alcohols with the Ti precursor in solution has a protective effect on this precursor, hindering its hydrolysis on the hydroxyl groups of the silica. This effect was more pronounced with cyclohexanol, which interacts strongly with titanium isopropoxide. The opposite occurred with the acetophenone and diglyme solvents.

On looking at the DRIFT spectra of the dried solids (Fig. 2), some insight into the preferential hydrolysis of the titanium precursor at the silica hydroxyl groups can be gained. One interesting observation derived from the DRIFT spectra was the very small proportion of isolated –Si–OH groups in samples C5 and C6, and its increase in catalysts C1, C2, C3, and C4 prepared in alcoholic media; most specifically, in sample C1 prepared in cyclohexanol. The DRIFT spectra in the region of the stretching frequencies of the hydroxyl groups throw some light on the hydrolysis of titanium isopropoxide and its preferential anchorage on the silica surface. As in sample C1, the –SiOH. . .OSi hydrogen bridges mostly disappeared, while the isolated Si–OH groups remained. It is inferred that hydrolysis takes place first at the bridging hydroxyl groups. If more titanium is available in solution, then all the surface hydroxyl groups are available and the process becomes less selective.

The chemical environment of titanium was studied following three complementary approaches DRS UV–vis, XPS, and DRIFTS within the framework vibrations of the solid. These techniques allow one to obtain structural information on nature of the active center at the microscopic level. They revealed that the catalysts synthesized in alcoholic medium, particularly in cyclohexanol, developed titanium tetrahedrally coordinated with oxide anions, which are the active sites for the epoxidation of olefins (see [24] and references therein). Nevertheless, the electronic spectra recorded from samples exposed to ambient atmosphere are strongly distorted by the water adsorbed onto the titanium center. Undoubtedly, the information gathered from the in situ DRIFTS and quasi-in situ XP spectra, in which the influence of chemisorbed water was avoided, is much more reliable [24]. Thus, selectivity to epoxide (Table 3) can be related to the dispersion of titanium ($D_{(\mathrm{Si–O–Ti})}$) (Fig. 4), and the amount of titanium in tetrahedral coordination (Fig. 5). It can clearly be seen that catalyst C1, with a $D_{(\mathrm{Si–O–Ti})}$ very high, in which titanium species are in a tetrahedral environment, also exhibited very high selectivity values of hydrogen peroxide. In an intermediate situation are the catalysts in which titanium appears as both tetrahedral and polymeric (octahedral) species (Fig. 5), and intermediate $D_{(\mathrm{Si–O–Ti})}$ values (Fig. 4) (catalysts C2, C3, and C4), which in turn showed moderate selectivities of hydrogen peroxide (Table 3). At the other extreme are the catalysts with a high proportion of octahedral Ti species and low dispersion ($D_{(\mathrm{Si–O–Ti})}$) values (catalysts C5 and C6), which proved to be highly active in the decomposition of hydrogen peroxide, with very low selectivity to the epoxide. This trend becomes more evident by comparing data in Figs. 4 and 6, which correspond to titanium dispersion measured by DRIFTS and selectivity to epoxide, respectively. The close similarity between titanium dispersion and selectivity points to a direct connection between active center environment and catalysts behavior. Thus, isolated Ti(IV) in isolated tetrahedrally coordinated positions with oxide anions is a necessary condition to have a selective system in the target reaction.

The combination of activity data with spectroscopic information reveals that careful attention must be exercised in the synthesis step of amorphous $\mathrm{Ti/SiO_2}$ catalysts in order to selectively incorporate titanium in tetrahedral coordination. Such a structure can be achieved by using cyclohexanol as solvent, which favors selective hydrolysis of the titanium precursor mainly on the H-bridging hydroxyl groups of the silica, resulting in isolated titanium species.

5. Conclusions

From the experimental work carried out on the synthesis of amorphous $\mathrm{Ti/SiO_2}$ catalysts, their spectroscopic characterization and testing in the liquid-phase epoxidation of 1-octene with hydrogen peroxide, the following conclusions can be drawn: (i) The amount of titanium incorporated to the silica depends strongly on the solvent used in the hydrolysis/anchorage step of the Ti precursor, cyclohexanol being the most effective of the solvents examined. (ii) All the Ti-containing silica catalysts exhibited very high conversions of hydrogen peroxide; their selectivity to the epoxide was moderate, with the exception of catalyst C1, for which it was very high. (iii) Spectroscopic data (UV–vis and XPS) clearly indicated that tetrahedrally coordinated titanium is present in the catalysts prepared using alcohol solvents and, more specifically, in catalyst C1, synthesized in cyclohexanol. (iv) The tetrahedral Ti species isolated are directly connected to the selective formation of the epoxide, whereas the presence of some two-dimensional octahedrally coordinated Ti species is detrimental for epoxide selectivity. These results highlight the importance of using cyclohexanol in the synthesis of rather simple $\mathrm{Ti/SiO_2}$, but highly effective, epoxidation catalysts.

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