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Journal of Catalysis 234 (2005) 488–495

JOURNAL OF CATALYSIS

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Influence of the textural properties of supports on the behaviour of titanium-supported amorphous silica epoxidation catalysts

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Received 16 February 2005; revised 29 April 2005; accepted 14 July 2005

Available online 11 August 2005

Abstract

A series of titanium–silica catalysts was prepared by grafting a titanium isopropoxide precursor on amorphous silica substrates with BET areas of 162–709 $m^2 g^{-1}$ and pore volumes of 0.5–1.4 $mL g^{-1}$. The grafting process, consisting of hydrolysis of the Ti precursor by the hydroxyl groups of the silica surface, yielded catalysts containing Ti loadings of 0.65–2.37 wt%. The textural properties of the Ti/SiO_2 catalysts were evaluated from the nitrogen adsorption–desorption isotherms, and their surface species were studied by ultraviolet–visible (UV–vis) spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and X-ray photoelectron spectroscopy (XPS) techniques. These catalysts were tested in the liquid phase epoxidation of oct-1-ene with hydrogen peroxide as a model reaction. All catalysts showed very high (95–98%) hydrogen peroxide consumption at 353 K after 1 h reaction time, but selectivity to the epoxide was strongly dependent on the pore volume of the silica substrate. Under these reaction conditions, an epoxide selectivity as high as 90–93% was reached on the catalysts with the largest pore volumes (1.4 $mL g^{-1}$). Spectroscopic techniques also revealed that Ti^{IV} ions coordinated tetrahedrally by oxide ions are essential to obtaining highly selective catalysts in the reaction.

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Keywords: Titanium–silica catalysts; Silica supports; Oct-1-ene epoxidation; Hydrogen peroxide oxidant; Diffuse reflectance spectroscopy; UV–vis spectroscopy; Photoelectron spectroscopy

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. A large volume of work has been generated on titanium-substituted zeolites in the framework, including TS-1, Ti-β, Ti-incorporated ordered mesoporous silica, and amorphous xerogels [1–3].

Another approach is the preparation of silica-supported titanium materials, first described by Shell [4]. 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 $Ti(OiPr)_4$ [5–7], TiF_4 [8,9], tetraneopentyltitanium [10,11] and ion-beam implantation [12,13] has been described. We have recently published our preliminary results on the epoxidation of linear alkenes with aqueous hydrogen peroxide using titanium-silica catalysts on silica, with high efficiency [14,15]. In view of the low leaching level and truly heterogeneous character of the epoxidation reaction [17,18], this kind of catalyst seems to be more stable than other related catalysts.

Other authors studied the performance of catalysts using dissimilar mesoporous supports, including amorphous silica and mesostructured silica (MCM-41), and found that using mesostructured systems is not required [19]. Recently, some used several catalytic systems containing titanium, including mixed oxides, mesostructured systems, and supported amorphous silica [20]. In all of this previous work, only a slight relationship was found between the behaviour of the

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doi:10.1016/j.jcat.2005.07.016

epoxidation reaction in liquid phase and the support characteristics.

Scrutinizing the previous studies, it becomes apparent that no systematic studies have addressed the influence of the textural characteristics of the supports used in the preparation of titanium-supported amorphous silica catalysts in the chemical environment of titanium. Earlier exploratory work carried out at our laboratory indicated a strong relationship between the support used in the synthesis of the catalyst and the performance of these catalysts in the epoxidation of primary alkenes with hydrogen peroxide. Accordingly, the present work was undertaken with the aim of investigating the role played by the textural properties of the supports used in the preparation of titanium-supported amorphous silica catalysts in the chemical environment of titanium, which in turn is directly related to their performance in the target reaction.

2. Experimental

2.1. Catalyst preparation

To prepare the catalysts, titanium isopropoxide (Aldrich, reagent grade) (0.75 g) was dispersed in cyclohexanol (150 mL). The solution was heated to 423 K under stirring conditions, and silica (5.0 g) was added to the solution, with the mixture 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. The solid was dried at 383 K, and finally calcined at 773 K for 5 h. For this study, seven commercial silica substrates with different textural properties were used (Table 1). The specific surface areas of these silica supports ranged from 175 to 725 $m^2\,g^{-1}$, and pore volume varied between 0.4 and 1.5 $mL\,g^{-1}$. With the exception of one silica sample showing some microporosity, all of the other samples were mesoporous.

Table 1
Samples prepared and textural characteristics of the supports employed

Catalyst	Silica	BET area ($m^2\,g^{-1}$)	Adsorbed volume ($mL\,g^{-1}$)	Ti (wt%)
MC1	Aerosil 200 (Degussa)	162	0.5	0.65
MC2	F-6 (Kjendel)	709	0.6	1.99
MC3	G-56 (Grace Davison)	257	1.0	0.97
MC4	G-57 (Grace Davison)	234	1.0	0.91
MC5	G-951 (Grace Davison)	601	1.0	2.37
MC6	G-952 (Grace Davison)	246	1.4	0.98
MC7	XPO2407 (Grace Davison)	213	1.4	0.82

2.2. Characterization

The titanium loadings of the Ti/SiO_2 catalysts were determined by inductively-coupled plasma absorption spectrometry using a Perkin–Elmer Optima 3300 DV instrument. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were recorded on a FT-IR Nicolet 510 spectrophotometer 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. A total of 256 scans were accumulated at a spectral resolution of 4 cm^{-1} for each sample. All spectra were recorded at room temperature.

Ultraviolet–visible light (UV–vis) spectra were recorded on a Avantes AVS-2048 fibreoptic spectrophotometer equipped with a reflection probe. $BaSO_4$ was used as reference. All spectra were acquired under ambient conditions.

XPS 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 aluminium 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 a Shirley background. All binding energies (BEs) 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 thermostatted glass-reactor equipped with a thermometer, a reflux condenser, and a septum for withdrawing samples. In a typical run, oct-1-ene (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 over 0.5 h. This procedure was adopted to simulate a CSTR, so that these catalytic activity data can then be extrapolated to an industrial process. We chose 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 for describing the reactivity in the epoxidation of propene to propene oxide (PO), in the industrial process of PO production without co-product [3]. We used an excess of alkene because in the PO process, the most costly reactant is hydrogen peroxide.

The organic compounds were analysed on a Hewlett Packard 6890-plus gas chromatography–flame ionisation detector (GC-FID) device equipped with a HP-WAX capillary column. 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 following equation:

$$S\ (\%) = 100 \times \frac{[\mathrm{Epoxide}]}{[\mathrm{H_2O_2}]_0 - [\mathrm{H_2O_2}]}, \tag{1}$$

where epoxide represents 1,2-epoxyoctane, the subscript 0 stands for initial values, and all concentrations are expressed on a molar basis. No other byproducts, such as diol or ethers, derivates from the oct-1-ene, were detected.

To check for any leaching of Ti species during the epoxidation reaction, an experiment was performed, as recommended in the literature [17,18], to study whether the liquid exhibited any reactivity. To accomplish this, the reaction was conducted under similar reaction conditions and then stopped after 30 min. The hot liquid medium was removed with a syringe equipped with a filter and immediately transferred to another reactor maintained at the same temperature. The compositions were then monitored over another 1.5 h. No activity was found in the liquid phase alone. This blank experiment indicates that no Ti species had leached out of the catalyst and that the epoxidation reaction was stopped after catalyst removal, indicating that the activity of the catalyst can only be due to the Ti atoms incorporated onto the surface of the silica support. In addition, the Ti-free silica substrates were tested in reaction, and no activity in the target reaction was observed.

3. Results

The nitrogen adsorption–desorption isotherms at 77 K of the various silica substrates exhibited different shapes and hysteresis loops due to their different textural properties (Fig. 1). The corresponding specific BET areas and pore volumes are shown in Table 1. With the exception of the Aerosil 200 silica support, all the other silica samples displayed a type IV isotherm of the IUPAC classification. The shapes of the isotherms of the F6 and G-951 silicas were between type I and type IV isotherms. The high BET area of these samples suggests the presence of micropores and also a certain contribution of the external surface; the contribution of the former was much more marked in the F6 than in the G-952 silica. All of the samples showed hysteresis loops, although of quite different character. The hysteresis loops corresponding to porous silicas (G-56, G-57, G-952, and XPO2407) were IUPAC type H1, characteristic of porous materials consisting of agglomerates or nearly uniform and regularly packed [21]. In contrast, the adsorption–desorption isotherm of silica G-952 displayed a slightly distorted hysteresis loop, indicative of the presence of pores of quite different sizes, some likely displaying an “ink bottle” shape. The hysteresis loop of sample F6 appeared at intermediate pressures, which can be associated with the presence of ink bottle-type pores. In contrast with the other silica substrates, the Aerosil 200 sample showed a type II isotherm typical of a nonporous sample.

As expected from the shapes and hysteresis loops of the different isotherms, pore size distributions also varied (Fig. 2). With the exception of the Aerosil 200 nonporous sample, which exhibited a very broad distribution situated at very high pore diameters, the other silica supports displayed well-defined pore size distributions. The smallest pore size (2–4 nm) was found for silica F-6; pore size range broadened (5–20 nm) for silica G-951. The other silica substrates (G-56, G-57, G-952, and XPO2407) displayed similar and relatively narrow pore size distributions. Specifically, the maximum distributions appeared at slightly lower pore sizes (ca. 15 nm) for samples G-56 and G-57, and increased slightly (ca. 25 nm) for samples XPO2407 and G-952.

The amount of titanium incorporated into the samples (Table 1) depended on the textural properties, although the surface density of titanium atoms was very similar in all samples. This finding can be ascribed to the fact that the titanium grafting procedure, which depends on the density of hydroxyl groups on the bare silica surface, is similar in all samples. Only the MC2 catalyst prepared from the F6 silica support showed a lower titanium surface density, probably because not much diffusion of solvated titanium precursor would likely occur in the narrow pores present in this support (cf. Figs. 1 and 2).

The electronic spectra of the Ti-loaded samples are shown in Fig. 3. These UV–vis spectra show absorption within the 200–300 nm energy region, characteristic of this type of catalyst [15,16]. In no case was a band observed located around 330 nm arising from octahedrally coordinated $\mathrm{Ti^{IV}}$ ions with oxide ions in an anatase-type structure. Further structural differences were observed on analysing the electronic spectra in greater depth. In particular, catalysts MC3, MC4, MC6, and MC7 displayed a narrower absorption band placed around 215 nm, typical of isolated $\mathrm{Ti^{IV}}$ ions in a tetrahedral environment of oxide ions [22]. An additional band at 250 nm was also observed, attributed to a tetrahedral species of titanium coordinated with water [22]. The other catalysts showed absorption peaks at a higher wavelength (275 nm), due to the presence of two-dimensional polymeric titanium species [15,16].

High-resolution photoelectron spectra of the Ti 2p core levels of the catalysts degassed in situ at 773 K were recorded. The spectra displayed the characteristic spin-orbit splitting of Ti 2p levels (Ti $2p_{3/2}$ and Ti $2p_{1/2}$). Because chemical information can be derived from analysis of the binding energies of each level, we focus only on the most intense Ti $2p_{3/2}$ component of the doublet. Peak fitting of the experimental Ti $2p_{3/2}$ component revealed two contributions, one at high binding energy (460.0 eV), typical of $\mathrm{Ti^{IV}}$ ions tetrahedrally coordinated by oxide anions [23], and another at lower binding energies (458.5 eV), the fingerprint

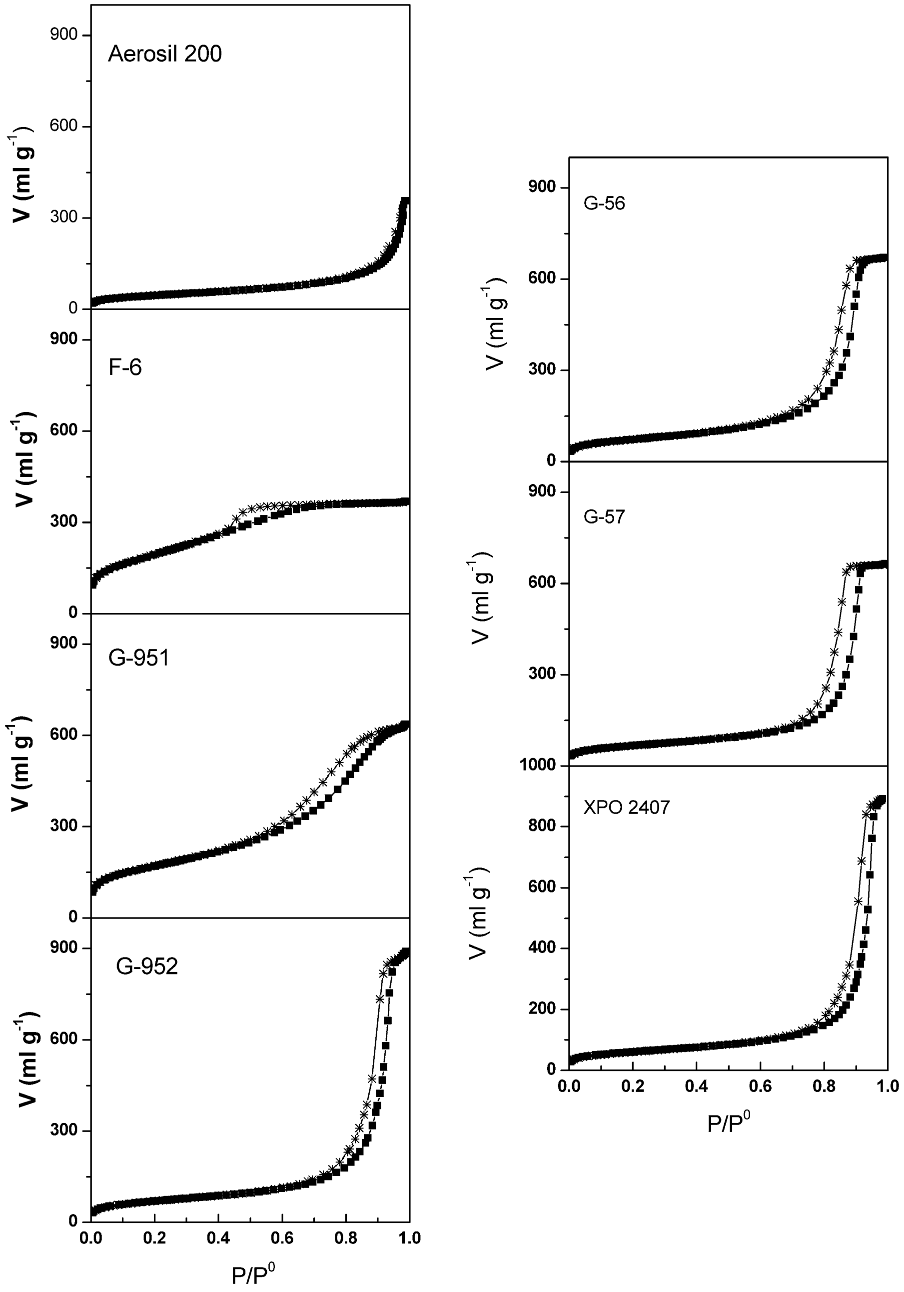

Fig. 1. Nitrogen isotherm at 77 K of the silica supports.

usually assigned to titanium in octahedral coordination or interaction with surface hydroxyl groups [23]. Most of the catalysts prepared with the SiO_2 support showed varying proportions of tetrahedral and octahedral titanium species. That there are differences in the catalysts is immediately apparent (Table 2). Catalysts MC3, MC4, MC6, and MC7 show a component only at 460 eV, typical of titanium in a tetrahedral environment [15,16,23], whereas catalysts MC1, MC2, and MC5 also exhibited a second component at 458.6 eV, assigned to titanium in an octahedral environment. These findings are consistent with the expectations of the characterisation data afforded by the UV–vis technique. Indeed, the electronic spectra of catalysts MC1, MC2, and MC5 exhibited a larger proportion of titanium in an octahedral coordination. It should be stressed that titanium oxide species were highly dispersed on the silica surface of all of the substrates used in this work. As a consequence of the high dispersion level of titanium in these samples, a direct correlation between the Ti/Si atomic ratio determined by XPS and titanium-loading determined by chemical analysis was obtained.

The DRIFTS spectra in the region of structural vibrations of the catalysts dried in situ at 723 K were virtually the same, because the silica substrate was common to all of the samples. Despite this general trend, however, some differentiating features were observed after careful analysis of the

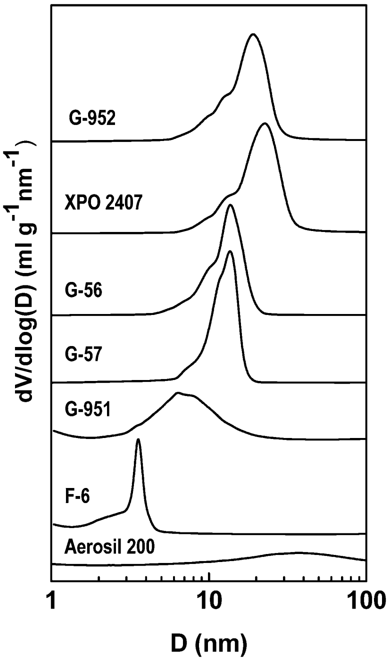

Fig. 2. Pore distribution using the BJH model to desorption branch of the 77 K nitrogen isotherm of the samples.

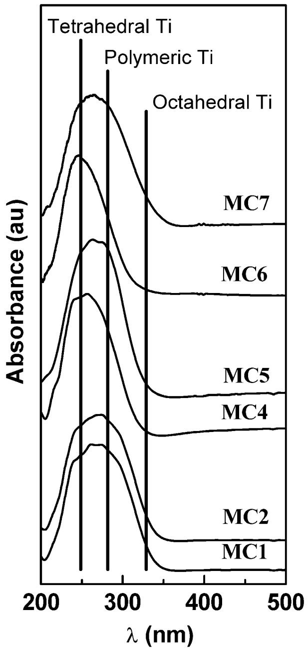

Fig. 3. DRS UV–vis spectra of the samples synthesized.

Table 2

Internal core binding energy of titanium and surface atomic ratio measured by XPS

Catalyst	BE Ti $2p_{3/2}$ (eV)	Ti/Si (atomic ratio)
MC1	458.9	0.0075
MC2	458.8 (46) 460.0 (54)	0.0172
MC3	460.0	0.0097
MC4	460.0	0.0110
MC5	458.7 (33) 459.9 (67)	0.0186
MC6	460.0	0.0114
MC7	460.0	0.0087

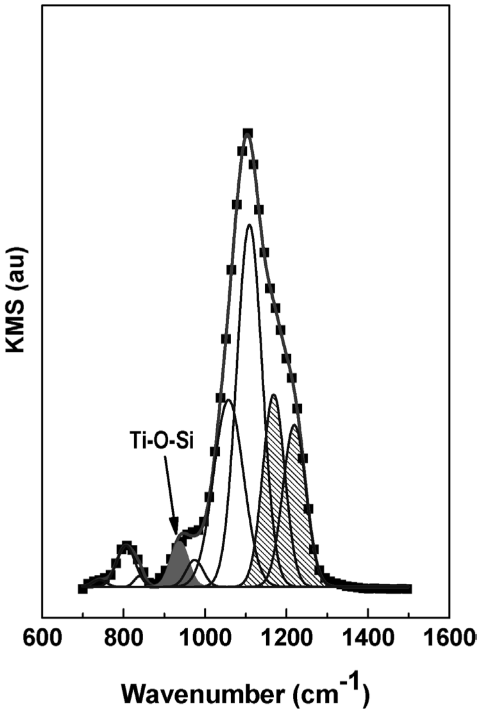

Fig. 4. DRIFTS of the skeletal vibration region of the MC7 catalyst dried at 773 K.

910–960 cm^{-1} energy region, where the Ti–O–Si vibrations usually appear [2,24]. Note that this region is in general overshadowed by one vibration (rocking mode) of the –Si–OH groups at approximately 980 cm^{-1} [25,26], which hinders precise identification of the band at 910–960 cm^{-1}. In an attempt to identify the band responsible for the precise titanium incorporation to the catalyst surface, a fitting of the experimental infrared spectrum was performed. A broad energy region at 600–1400 cm^{-1} was considered, and nine Gaussian lines were introduced [27], whose assignment was 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}.

Because Ti–O–Si bonds were developed during the grafting process of the silica surface with the Ti precursor, the DRIFTS spectra of the catalyst were recorded to assess their proportions in the different catalysts. The fitted DRIFTS spectra of the catalysts (see Fig. 4 as an example) revealed significant differences in the band associated with Ti–O–Si vibrations (935 cm^{-1}). Perhaps the most important finding was that the changes did not correspond to the amount of titanium incorporated. The catalysts prepared using a higher pore volume (MC6 and MC7) exhibited a much higher rela-

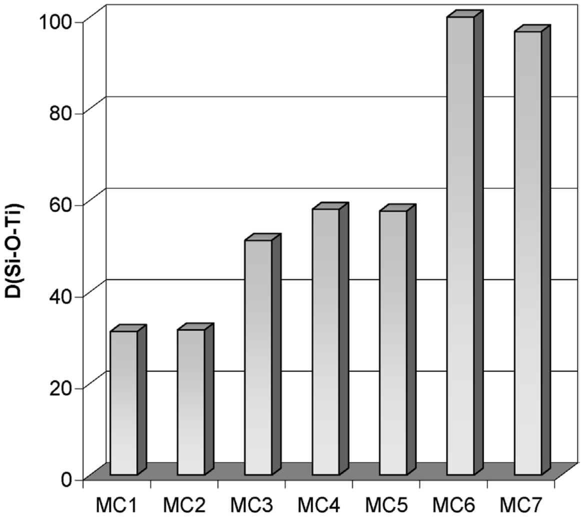

Fig. 5. Relative semiquantitative Ti dispersions (D) estimated from DRIFT spectra of samples dried at 773 K.

tive intensity of this band than did catalysts MC5 and MC2, even though the latter incorporated larger amounts of titanium. Such differences must be associated with titanium dispersion in the catalyst, because in the literature [16,26,27] it has been proposed 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. Titanium dispersion ($D_{(\text{Ti–O–Si})}$) was calculated using the following expression [16,27]:

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

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

The dispersion values of titanium in the catalysts (Fig. 5) show clear differences. Although titanium dispersion was low for catalysts MC1 and MC2, it increased in the catalysts prepared using supports with high pore volume (MC3 and MC4) and even more so for the samples prepared with the highest pore volume silica (MC6 and MC7), which exhibited the highest dispersion. These results are in agreement with the UV–vis spectra of the catalysts described earlier. Interestingly, catalysts MC1 and MC2, which had low titanium dispersion as derived from the foregoing analysis of the DRIFTS spectra, also exhibited an important contribution by surface polymeric (Ti–O–Ti–O–) titanium species in the electronic spectra. Indeed, the proportion of this type of titanium species was much lower when high-pore volume silica supports were used in the synthesis of the catalysts (MC3, MC4, and MC7) and was even absent in the catalysts prepared with the silica G-952 (MC6), in which only a tetrahedrally hydrated isolated titanium species was present.

All of the catalysts were tested in a liquid phase oct-1-ene epoxidation reaction using hydrogen peroxide as an oxidant agent. For the sake of simplicity and to facilitate comparison, the reaction conditions were identical for all of the catalysts. The hydrogen peroxide conversion and selectivity to epoxide of all of the catalysts are shown in Table 3. All of the Ti-containing silica catalysts showed very high hydrogen peroxide conversions; in general, these catalysts had a moderate or high selectivity to the epoxide. The highest efficiency values were achieved with the catalysts prepared with high-pore volume silica. This trend in catalytic behaviour is in complete accordance with the characterization data. Catalysts MC1, MC2, and MC5, with a high proportion of octahedrally coordinated Ti^{IV} ions (UV–vis and XPS) and a rather low proportion of Ti–O–Si bridges (DRIFTS), exhibited low selectivity to the epoxide. In catalysts MC3 and MC4, an intermediate proportion of Ti–O–Si bridges was developed, thus affording moderate selectivity to epoxide. However, catalysts MC6 and MC7, in which the titanium environment was the optimal one for this reaction [15,16], showed very high hydrogen peroxide conversion and very good selectivity to epoxide.

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

Catalyst	H_2O_2 conversion (%)	Oct-1-ene conversion (%)	Selectivity epoxide (%)
MC1	96	1.8	63
MC2	95	1.9	68
MC3	97	2.3	80
MC4	97	2.2	75
MC5	98	2.4	80
MC6	97	2.7	93
MC7	96	2.6	90

4. Discussion

The results obtained in the present work on the structure and catalytic behaviour of titanium-containing silica clearly demonstrate that the textural properties of the silica support used in the synthesis step of the catalysts determine the surface structure of the catalytic component. As stated in Section 2, the samples were prepared by dispersing titanium isopropoxide in an organic solvent, cyclohexanol, and then mixing the solution with the silica substrate. The Ti-isopropoxide precursor and the solvent have to migrate to the surface and then react with the surface hydroxyl groups of the silica. Some differences were observed in the amount of titanium incorporated to the silica substrate; however, the surface density of titanium atoms was very similar in all samples. A plausible explanation for this behaviour can be advanced assuming that the surface densities of the hydroxyl groups in all silica substrates are fairly similar.

The chemical environment of titanium was studied using three complementary approaches—UV–vis spectroscopy, XPS, and DRIFTS—within the framework vibrations of the solid. These techniques afford structural information about the nature of the active sites at a microscopic level. The spectroscopic data provided by these techniques revealed that

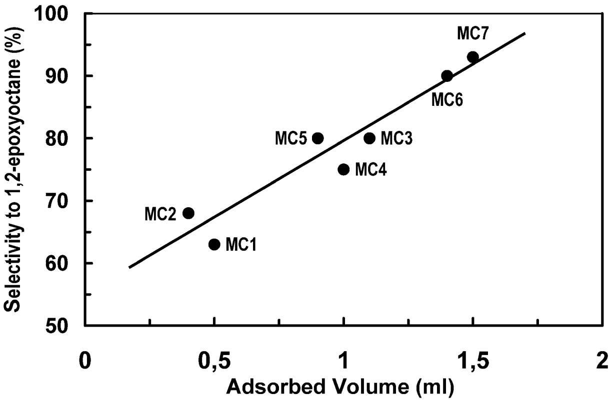

Fig. 6. Ratio of the pore volume of the silica support versus selectivity to epoxide in the epoxidation of oct-1-ene with hydrogen peroxide.

the catalysts synthesised with a high-pore volume supports developed titanium that was tetrahedrally coordinated with oxide anions, which are the active sites for the epoxidation of olefins [2,15]. Nevertheless, the electronic spectra of samples exposed to ambient atmosphere were strongly distorted as a consequence of the chemisorption of water molecules on the Ti^{IV} sites, which altered the original symmetry of the Ti^{IV} ions generated during the calcination step. The information gathered from the in situ DRIFTS and quasi-in situ XP spectra, in which the influence of chemisorbed water was avoided, is undoubtedly much more reliable [15]. These characterization data indicate a relationship between the texture of the support and nature of the titanium centres that can be attributed to diffusional differences during the preparation. Therefore, the catalysts prepared with supports with narrower pore size (MC1, MC2, and MC5) gave to the formation of bidimensional polymeric titanium species active in the decomposition of hydrogen peroxide. However, the characterization techniques (XPS and UV–vis) revealed no differences among catalysts with high pore diameter (MC3, MC4, MC6, and MC7).

Thus, the catalytic activity and the selectivity to epoxide (Table 3) can be related to the textural properties of the support (Table 1). Perhaps the most important finding is that selectivity to epoxide increased with increasing pore volume of the support. Our interpretation of this finding is that the greater pore volume could favour the accessibility of the titanium precursor to the H-bridging hydroxyl groups of the silica, with isolated titanium species developing.

In an attempt to quantify this effect, the pore volume determined from the N_2 adsorption–desorption isotherms at 77 K was plotted versus the selectivity to epoxide (Fig. 6). This plot revealed a close relationship between the pore volume of the samples and selectivity; a greater selectivity to epoxide was achieved in the samples displaying a higher pore volume. The difficulty in obtaining a perfectly carpeted inner surface of the pores by Ti–O–Si bonds in samples with lower pore volumes might well not be the only reason for the lower epoxide selectivity during the liquid phase epoxidation reaction. This observation is supported by the dispersion of titanium as measured by Fourier transform infrared spectroscopy; the catalysts prepared with higher-pore volume silicas displayed greater titanium dispersion (Fig. 5).

A combination of activity data with spectroscopic information reveals that care must be exercised in the synthesis step of amorphous Ti/SiO_2 catalysts to selectively incorporate titanium in tetrahedral coordination. Such a structure can be achieved using a high-pore volume silica support, which favours the accessibility of the titanium precursor to the H-bridging hydroxyl groups of the silica, with isolated titanium species developing.

5. Conclusions

Based on the joint use of textural and structural characterization techniques of the amorphous Ti/SiO_2 catalysts and their performance in the liquid phase epoxidation of oct-1-ene, the following conclusions can be drawn:

1. Using isopropoxide as the titanium precursor and cyclohexanol as the synthesis solvent, the amount of titanium incorporated will depend to a great extent on the specific BET of the silica substrate.
2. According to the UV–vis spectroscopy, DRIFTS, and XPS results, titanium species remain highly dispersed, and Ti^{IV} ions are located in a tetrahedral environment of oxide ions in all of the catalysts.
3. Although the surface density of Ti^{IV} ions is similar regardless of silica type, there are strong differences in selectivity to epoxide and a good relationship between pore volume and selectivity.

These results highlight the importance of selecting a silica substrate with a moderately high BET area (i.e., 200–250 $m^2\,g^{-1}$) but high pore volume, to prepare efficient and inexpensive Ti/SiO_2 epoxidation catalysts.

Acknowledgments

The authors gratefully acknowledge financial support and a fellowship (to MCCS) from Repsol-YPF, and financial support from the Ministerio de Ciencia y Tecnología (Spain) in the Ramon y Cajal Program (to JMCM).

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