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Catalytic sites in silica-supported titanium catalysts: silsesquioxane complexes as models

José M. Fraile *, José I. García, José A. Mayoral, Eugenio Vispe

Departamento de Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Instituto Universitario de Catálisis Homogénea,
Universidad de Zaragoza, C.S.I.C., E-50009 Zaragoza, Spain

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Abstract

The number of Si–O–Ti bonds in silica-supported titanium catalysts is an important parameter that affects activity and selectivity. Although comparisons between different catalysts can be made by infrared spectroscopy, estimation of the contribution of the different species is a difficult task. UV spectroscopy has been used to characterize three different titanium–silsesquioxane complexes. The wavelength in solution is highly dependent on the concentration, and broad bands are obtained by DRUV, at wavelengths that correlate with the number of Si–O–Ti bonds. The deconvolution of the DRUV spectra of silica-supported titanium catalysts allows identification of the three types of tetrahedral (pentacoordinated) species, together with octahedral species. These results correlate well with the known silanol densities of the different silica supports, and the catalytic activity and selectivity for epoxidation are clearly favored by the reduction in octahedral titanium and the increase in the number of tripodal species.

Keywords: Silsesquioxanes; Heterogeneous titanium catalysts; Epoxidation; Hydrogen peroxide; UV spectroscopy

1. Introduction

Heterogeneous titanium catalysts for alkene epoxidation require the presence of highly dispersed titanium centers [1]. This property can be achieved either by dispersion of titanium in a silica matrix or by grafting of titanium precursors to a silica support. Several authors have compared the performance of the two types of solids, and the supported catalysts are recognized as being more efficient than those containing the titanium centers in the matrix structure [2–4]. The preparation of silica-supported titanium catalysts requires the binding of the titanium precursor to the silanol groups of the surface. Taking into account the different relative positions of the silanols in silica [5], each titanium center can be bonded to one, two, or even three silicon atoms through Si–O–Ti bonds, leading to the formation of monopodal, bipodal, or tripodal species, respectively (Fig. 1). Although $Ti(OSiMe_3)_4$ has been used as a soluble model for titania–silica mixed oxides [6], the most used models for titanium catalysts have been titanium silsesquioxane complexes. These systems are consid-

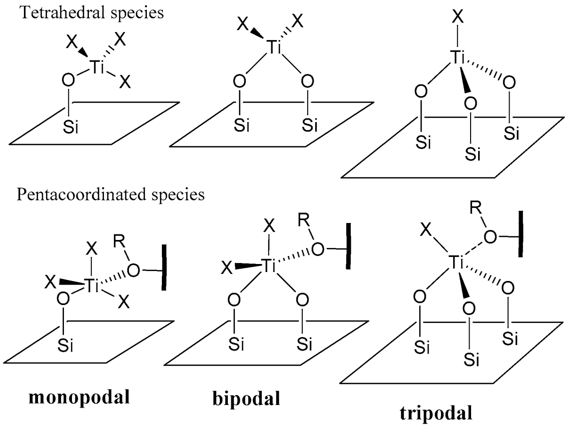

Fig. 1. Possible surface titanium species on silica.

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[*] Corresponding author. Fax: +34 976762077.
E-mail address: jmfraile@unizar.es (J.M. Fraile).

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ered appropriate as models for the silica surface because of the nature of the incompletely condensed silsesquioxanes [7–9], a suitability confirmed by our experience with silica-supported aluminum catalysts [10]. One of the main conclusions is that tripodal silsesquioxanes show much higher activity, by one order of magnitude, than bipodal ones for alkene epoxidation with alkyl hydroperoxides [11–13]. This result demonstrates the importance of the surface species control in the preparation of silica-supported titanium catalysts.

The characterization of this type of solid is not a simple task, if we take into account the different possible coordination states of titanium and the fact that the titanium precursor can produce oligomers (TiO_x) on the surface [14]. This difficulty is even greater if conditions similar to those used in the application of these systems are desired. In view of these problems, different spectroscopic techniques have been applied for this purpose.

Quantitative analysis of the released molecules in the preparation process is a useful tool, but it is usually applied to the preparation of small samples from gas-phase precursors and does not take into account the possible reactions between precursor molecules to form oligomers [15]. X-ray absorption spectroscopy (XAS) requires costly equipment and special facilities, factors that limit the utility of this technique. Moreover, the result obtained is an average of the absorption spectra of the different centers on the solid [16,17]. XPS provides valuable information mainly when the environment of titanium in the precursor is clearly different from that in the solid, as is the case in TiF_4 [18], but the high-vacuum conditions necessary for XPS analysis may modify the nature of the titanium centers [19]. The Si–O–Ti bonds give rise to an IR band at 940 cm^{-1}. The ratio between the areas of this band and that corresponding to Si–O–Si bonds in the 1200–1000 cm^{-1} range has been used to estimate the relative dispersion of titanium on different silica matrixes [20–22]. However, there is no way to determine the absolute number of these bonds. Furthermore, this determination is made more difficult by the superposition of the remaining Si–OH band. DR-UV spectra usually consist of a broad band with a maximum whose position depends on the degree of hydration of the solid [4,23]. The interpretation of the resulting spectrum is not straightforward, and disparate conclusions have been drawn by different authors. The conversion of Q^3 [$(SiO)_3$–Si–OH] into Q^4 [$(SiO)_3$–Si–OTi] silicon atoms by reaction of silanol groups with titanium can be followed by ^{29}Si-CP-MAS-NMR spectroscopy, but the cross-polarization enhancement of the signal precludes any quantitative determination of the different types of silicon [24].

In spite of the interest of silsesquioxanes as models for silica surface, the data obtained have usually been correlated with titanium centers in zeolites and similar crystalline materials [7–9,11–13], and so a direct comparison with titanium centers on amorphous silica supports is still lacking. In this paper we present the results of our recent studies in this area.

2. Experimental

2.1. Materials

Silsesquioxanes **1**–**3** were purchased from Aldrich. The silica supports were Merck60 (512 $m^2\,g^{-1}$), Degussa Aerosil 200 (200 $m^2\,g^{-1}$), and MCM-41 (802 $m^2\,g^{-1}$). Hydrophobic silica was prepared from Merck60 by treatment with dimethyloctadecylsilyl chloride [22]. Hydrophilic silicas were prepared from Merck60 by treatment with aqueous HCl or propionyl chloride in hexane [25]. Titanium catalysts on silicas [22,25–27] and MCM-41 [28] were prepared by previously described methods.

2.2. Characterization methods

Titanium and silicon analyses were carried out by plasma emission spectroscopy on a Perkin–Elmer Plasma 40 emission spectrometer. Elemental analyses were carried out with a Perkin–Elmer 2400 elemental analyzer. NMR spectra were recorded on a Bruker Avance 400 spectrometer. Infrared spectra were recorded on a Nicolet Avatar 360 FTIR spectrophotometer. Spectra of the silica-supported catalysts were taken from wafers diluted with KBr treated under vacuum ($<10^{-5}$ Torr) at 140 °C in a cell equipped with NaCl windows. UV spectra were recorded on a Unicam UV-4 spectrophotometer. For DR-UV measurements the spectrophotometer was equipped with a Spectralon RSA-UC-40 Labsphere integrating sphere. Samples were ground in a mortar and dried under vacuum at 140 °C overnight before measurements. The hot powder samples were placed in a home-made cell equipped with a quartz window. The spectra were recorded immediately to prevent significant moisture adsorption. Deconvolutions in gaussian curves were carried out with PeakFit 4.1. No restrictions were made for number or situation of peaks, and iterative processes were carried out until the adjust had a value of $r^2 > 0.99$.

2.3. Synthesis of titanium–silsesquioxane complexes

A solution of the corresponding silsesquioxane (**1**–**3**) (0.38 mmol) in anhydrous ethyl ether (20 ml) was slowly added (30 min) at room temperature to a solution of $Ti(O^iPr)_4$ (0.42 mmol) in the same solvent (20 ml) under an Ar atmosphere. The resulting solution was allowed to react for 30 min (in the case of **1**) to 2 h (in the case of **3**). The solution was concentrated under vacuum to half volume, and anhydrous acetonitrile (5 ml approx.) was added dropwise until a white microcrystalline precipitate was obtained. The solids were filtered off, washed with anhydrous acetonitrile (3 × 5 ml), and dried under vacuum. The pure titanium–silsesquioxane complexes were obtained by crystallization from chloroform (80% yield).

$[(c\text{-}C_5H_9)_7Si_8O_{13}Ti(O^iPr)_3]$ [**1**-$Ti(O^iPr)_3$]. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 3.81 (m, 3H), 1.93–1.64 (m, 20H), 1.63–1.34 (m, 36H), 1.34–1.06 (m, 18H), 1.00–0.85

(m, 7H). ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 77.23 ($OCHMe_2$), 27.28, 27.25, 27.00 and 26.93 (–CH_2–), 25.30 (–CH_3), 22.18, 22.13 and 22.06 (1:3:3, Si–CH). MS (FAB$^+$) m/z: 1140 (M$^+$), 963, 917. Analysis found: C, 46.06; H, 7.25; Si, 19.94; Ti, 4.15; calcd. for $C_{44}H_{84}O_{16}Si_8Ti$: C, 46.32; H, 7.37; Si, 19.65; Ti, 4.20.

[$(i\text{-}C_4H_9)_8Si_8O_{13}Ti(O^iPr)_2$] [**2**-Ti($O^iPr)_2$]. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 4.19 (m, 2H), 1.95–1.65 (m, 8H), 1.20 (d, 12H, J 6.13 Hz), 1.10–0.75 (m, 48H), 0.60–0.42 (m, 16H). ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 77.25 ($OCHMe_2$), 25.84, 25.78 and 25.68 (2:1:1, –CH_3 in ^{i}Bu), 25.30 (–CH_3), 24.06, 23.98 and 23.89 (1:2:1, –CH_2– in ^{i}Bu), 23.17 (–CH in ^{i}Bu). MS (FAB$^+$) m/z: 1054 (M$^+$), 936, 879, 822, 774, 717. Analysis found: C, 43.33; H, 8.22; Si, 21.35; Ti, 4.32; calcd. for $C_{38}H_{86}O_{15}Si_8Ti$: C, 43.27; H, 8.16; Si, 21.25; Ti, 4.55.

[$(i\text{-}C_4H_9)_7Si_7O_{12}Ti(O^iPr)$] [**3**-Ti($O^iPr$)]. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 4.05 (sept, 1H, J 6.13 Hz), 1.90–1.69 (m, 7H), 1.15 (d, 6H, J 6.13 Hz), 1.00–0.85 (m, 42H), 0.60–0.42 (m, 14H). ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 77.21 ($OCHMe_2$), 26.20, 25.93 and 25.69 (3:3:1, –CH_3 in ^{i}Bu), 25.30 (–CH_3), 23.91, 23.87 and 23.17 (3:3:1, –CH_2– in ^{i}Bu), 22.49 (–CH in ^{i}Bu). MS (FAB$^+$) m/z: 894 (M$^+$), 837, 794, 737. Analysis found: C, 41.36; H, 7.63; Si, 22.05; Ti, 5.29; calcd. for $C_{31}H_{70}O_{13}Si_7Ti$: C, 41.61; H, 7.83; Si, 21.92; Ti, 5.36.

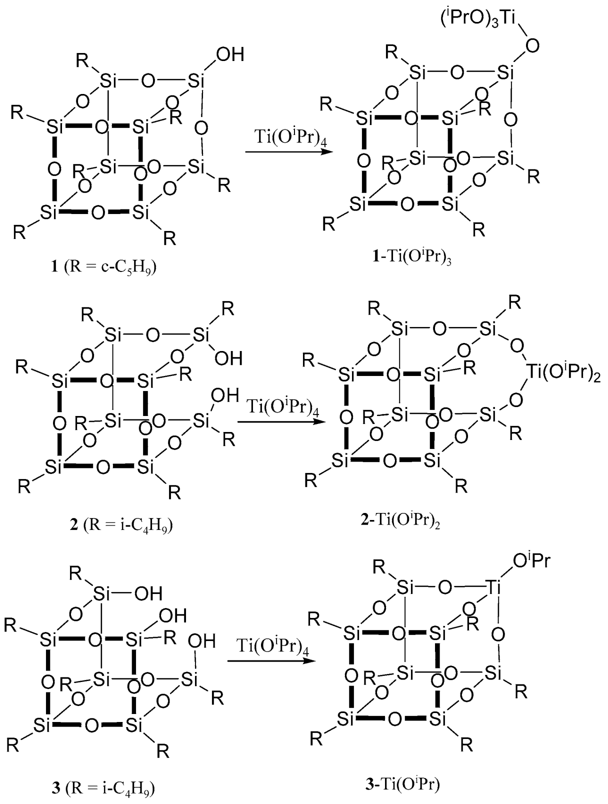
2.4. Epoxidation reactions with silica-supported catalysts

All of the catalysts were dried at 140 °C under vacuum for 12 h before use. All of the reagents and solvents (synthesis grade 99%) were used as received. The catalyst (200 mg) was added to a solution of the alkene (25 mmol) in *tert*-butanol (4 ml). The reaction mixture was heated at 80 °C, and H_2O_2 (0.28 ml, 30%, 2.5 mmol) diluted with *tert*-butanol (1 ml) was slowly added (2.5 h) with a syringe pump. Ethylene glycol dimethyl ether (1 ml, internal standard) was added, and the reaction mixture was stirred at 80 °C for an additional 5-h period. The catalyst was filtered off, washed with dichloromethane (5 × 5 ml), dried under vacuum, and reused under the same conditions. The yields were determined by GC on a Hewlett–Packard 5890 II, with a FID and helium as a carrier (20 psi), and a cross-linked methyl silicone column (25 m × 0.2 mm × 0.33 µm). The total conversion of H_2O_2 was confirmed by iodometric titration of the final solution.

3. Results and discussion

3.1. Synthesis and characterization of titanium–silsesquioxane complexes

3.1.1. Synthesis



Scheme 1. Synthesis of titanium–silsesquioxane complexes.

Given the different possibilities for the arrangement of silanol on the silica surface, three incompletely condensed silsesquioxanes (**1**–**3**) were chosen to model isolated (**1**), two-vicinal (**2**), and three-vicinal (**3**) silanols. The titanium-silsesquioxane complexes were prepared by reaction of the silsesquioxane with $Ti(O^iPr)_4$ in ether (Scheme 1), as described in the literature [11–13], in order to serve as models for monopodal, bipodal, and tripodal titanium centers. The compounds were fully characterized by elemental analysis and different spectroscopic techniques. The reaction of all of the silanol groups was confirmed by the complete disappearance of the broad band in the 3750–3000 cm^{-1} region of the IR spectra, together with the 0.1 ppm shift of the ^{13}C-NMR signals for the atoms directly bonded to Si. In all cases the isopropoxy groups were present, as shown by the septuplet (or multiplet) at around 4 ppm in the ^{1}H-NMR spectra, together with the new signals at 77 and 25–26 ppm in the ^{13}C-NMR spectra. All of these features, together with the consistent elemental analysis data (C, H, Si, Ti) and mass spectra, confirm the monomeric nature of the titanium–silsesquioxane complexes. After the structures had been confirmed, the titanium–silsesquioxane complexes were characterized by the spectroscopic techniques directly applied to the solid catalysts, namely, IR and UV.

3.1.2. IR spectra

The dispersion of titanium in titania–silica mixed oxides has been determined from the ratio between the areas of the IR bands corresponding to Si–O–Ti (around 940 cm^{-1}) and Si–O–Si connectivities in the 1200–1000 cm^{-1} range [20,

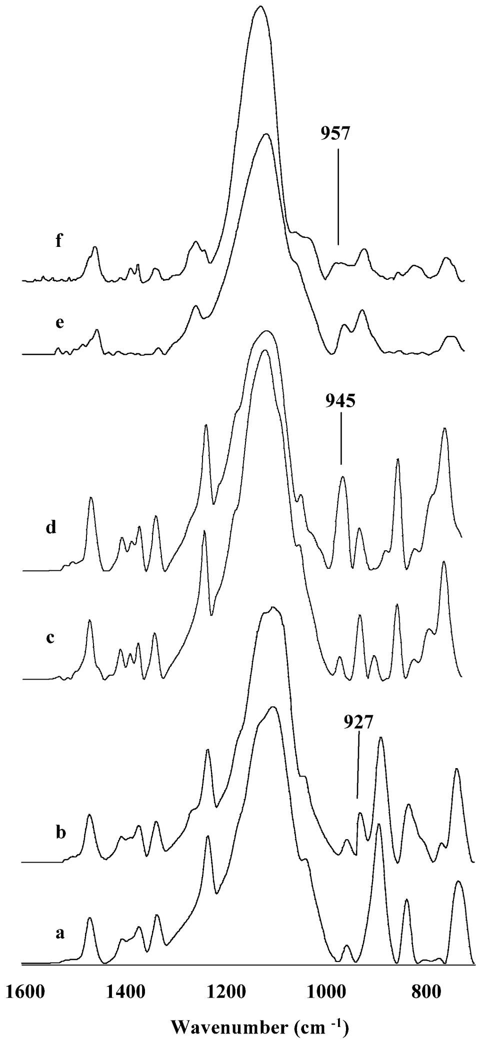


Fig. 2. IR spectra (1600–700 cm^{-1}) of the silsesquioxanes **1**–**3** and the corresponding titanium complexes: (a) **3**, (b) **3**-Ti(O^iPr), (c) **2**, (d) **2**-Ti(O^iPr)$_2$, (e) **1**, (f) **1**-Ti(O^iPr)$_3$.

21,29]. We have also applied this method to silica-supported titanium catalysts [22]. In the case of silsesquioxanes, a new band appears in the 960–925 cm^{-1} range upon the incorporation of titanium (Fig. 2), and this can be assigned to Si–O–Ti bonds. However, from the spectra it is clear that the intensity of the band is not directly related to the number of Si–O–Ti bonds. For example, the intensity of the band for the bipodal species **2**-Ti(O^iPr)$_2$ is higher than that of the tripodal complex **3**-Ti(O^iPr), despite the lower number of bonds. In fact, the wavenumbers are different for the three samples (927, 945, and 957 cm^{-1} for **3**-Ti(O^iPr), **2**-Ti(O^iPr)$_2$, and **1**-Ti(O^iPr)$_3$, respectively), and the bands are superimposed on others already present in the original silsesquioxanes. Thus, conclusions about the dispersion in silica-supported titanium catalysts by this method are not conclusive.

3.1.3. UV spectra

On the other hand, UV spectroscopy has been widely used in the characterization of heterogeneous titanium catalysts. The spectra of the titanium–silsesquioxane complexes were taken from solutions of different concentrations in a nonpolar solvent such as hexane. As can be seen, at low concentration (10^{-6} M) the absorption maximum is observed at 205 nm (Fig. 3), a value consistent with titanium in a tetrahedral environment and close to the values reported in the literature for titanium–silsesquioxanes [11–13,30]. This band is not completely symmetric, and it presents a shoulder at about 225 nm that is more intense for the less rigid monopodal species **1**-Ti(O^iPr)$_3$. The shift of the band to higher wavelengths has been attributed to an increase in the coordination of the titanium [4,23]. This higher coordination might be due to intermolecular interactions between silsesquioxanes, even at very low concentrations, and their importance should be greater at higher concentrations. In fact, the spectra at the higher concentration (10^{-5} M) show a dramatic shift of the maximum absorption to higher wavelengths, with significant differences depending on the titanium species (Fig. 4). The most flexible system, **1**-Ti(O^iPr)$_3$, shows a broader band with the maximum at 247 nm, whereas the bands for the more rigid and hindered species are sharper, and the maximum appears at lower wavelength: 237 nm in the case of **2**-Ti(O^iPr)$_2$ and 230 nm for **3**-Ti(O^iPr). The broadening is consistent with a less rigid species, in which a higher number of vibrational levels are superimposed on the electronic transitions. To maximize the intermolecular interactions, the higher silsesquioxane concentration would be in the solid phase without solvent.

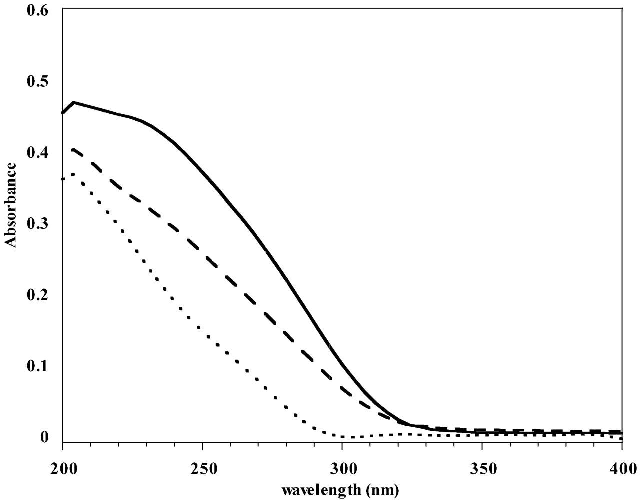


Fig. 3. UV spectra (10^{-6} M) of the titanium–silsesquioxane complexes: **1**-Ti(O^iPr)$_3$ (solid line), **2**-Ti(O^iPr)$_2$ (dashed line) and **3**-Ti(O^iPr) (dotted line).

Diffuse-reflectance UV spectra of the titanium–silsesquioxane complexes were also recorded (Fig. 5). As can be seen, the shapes of the spectra are completely different from those obtained in solution. Two bands are clearly present, a narrow one centered at 229 nm and another, broader band whose shape and maximum depend on the titanium species. As with the solution spectra, the broadest and most strongly shifted band (286 nm) corresponds to the flexible species

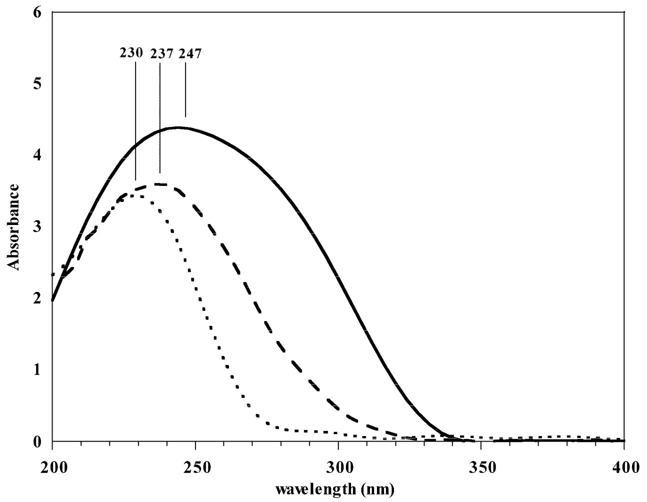


Fig. 4. UV spectra (10^{-5} M) of the titanium–silsesquioxane complexes: **1**-Ti(O^iPr)$_3$ (solid line), **2**-Ti(O^iPr)$_2$ (dashed line) and **3**-Ti(O^iPr) (dotted line).

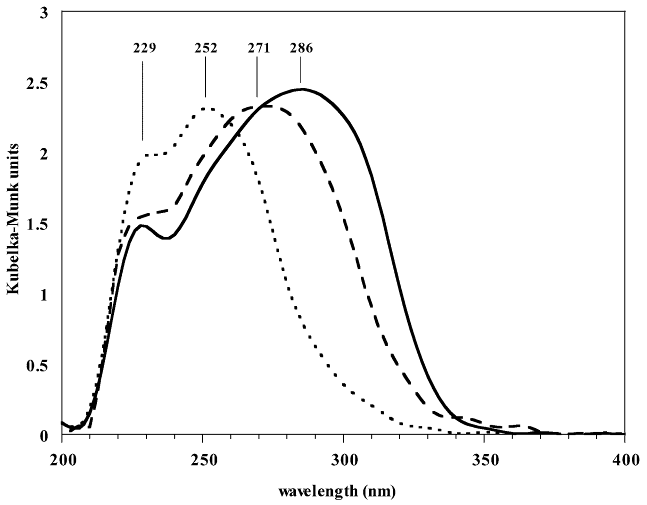


Fig. 5. DRUV spectra of the titanium–silsesquioxane complexes: **1**-Ti(O^iPr)$_3$ (solid line), **2**-Ti(O^iPr)$_2$ (dashed line) and **3**-Ti(O^iPr) (dotted line).

1-Ti(O^iPr)$_3$. The bipodal species **2**-Ti(O^iPr)$_2$ presents a narrower band centered at 271 nm, and, finally, the tripodal system **3**-Ti(O^iPr) gives rise to the narrowest spectrum, and this has a maximum at 252 nm. It is important to note that the broad bands are nearly perfect gaussian curves, with only minor contributions of very weak bands when deconvoluted. These results demonstrate that the UV spectrum is not only influenced by the structure of the titanium site, but also the acquisition method used to obtain the spectrum. Although the contribution of water to the titanium coordination cannot be completely excluded, the use of dried samples and the total absence of OH band in the IR spectra (3000–4000 cm^{-1}) seem to indicate that the modification of the titanium coordination from tetrahedral to pyramidal or octahedral is due to the oxygen atoms of the silsesquioxane molecules that act as coordinating moieties, a situation favored by the higher concentration in solution or the close proximity in solid phase.

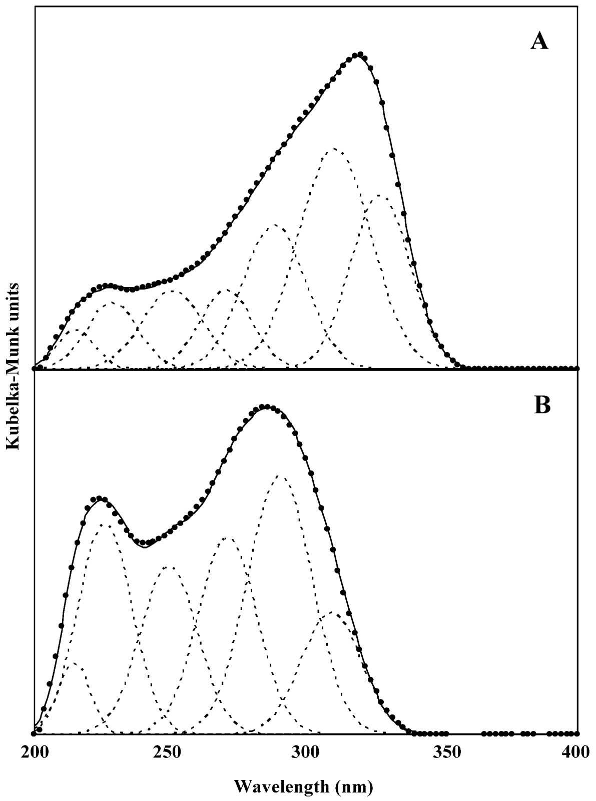


Fig. 6. Deconvolution of the DRUV spectra of Merck60 supported catalysts: (A) 1.07 and (B) 0.24 mmol-Ti g^{-1}.

As a tentative assignment, we believe that the purely tetrahedral species always show a band at 225 nm, regardless of the number of Si–O–Ti bonds, whereas the pentacoordinated titanium band appears at around 250, 270, and 290 nm for tripodal, bipodal, and monopodal species, respectively.

3.2. Comparison of titanium centers on silsesquioxanes and silica supports

3.2.1. Conventional silica supports

On the basis of the findings described above, a comparison between these well-characterized titanium species and the silica-supported catalysts seemed worthwhile. Titanium catalysts on Merck60 silica with different titanium loadings (1.07 and 0.24 mmol-Ti g^{-1}) were prepared from Ti(O^iPr)$_4$. DRUV spectra for the dried samples (140 °C under vacuum) were recorded (Fig. 6). In both cases, wide nonsymmetrical spectra were obtained, and these were deconvoluted with no restrictions in order to compare them with the spectra of the model titanium–silsesquioxane complexes.

As can be seen, the same fit of the spectra requires several bands that can be grouped into three zones. Two bands are apparent below 250 nm, at around 215 and 225 nm, and these can be assigned to tetrahedral titanium centers, without any indication of the number of Si–O–Ti bonds. With regard to pentacoordinated species, the three expected bands at 250, 270, and 290 nm are observed, which seems to indicate the presence of all types of titanium species on the silica surface. One or two additional bands appear at higher wavelengths: at 310 nm in both solids and at 325 nm only in the catalyst with high titanium loading. These bands can be assigned to octahedral titanium, either isolated (probably monopodal) or in the form of small TiO_x aggregates. The band at 325 nm is most likely due to these titania particles, which cannot be detected by XRD and are not present in the solid with a higher titanium dispersion. The presence of species with coordination higher than 4 is not strange, if we take into account that the silica-supported catalysts were not calcined at high temperature.

In the cases of samples exposed to ambient moisture (Fig. 7), the bands assigned to tetrahedral species practically disappear because of the coordination of water. This change is accompanied by an increase in the bands at higher wavelengths, mainly at 290 and 310 nm. This result is in agreement with the tentative assignment of these bands to pentacoordinated and octahedral species. Moreover, the coordination that is higher than 4 in the dried samples seems to be due to coordinating groups in the solid (Fig. 1). According to this hypothesis the remaining tetrahedral species would be situated in surface sites with hindered accessibility, whereas water has free access to those sites and tetrahedral sites are not present in nondried samples.

Further evidence to support the band assignment may come from the relative intensities of the bands in catalysts prepared on a silica support with a different density of silanol groups, which in turn leads to different populations of titanium species.

When a highly ordered mesoporous silica, such as MCM-41, is used as a support, the deconvolution of the DRUV spectrum (Fig. 8) shows a much lower contribution of the octahedral species in spite of the even higher titanium loading. This phenomenon is probably a consequence of the higher dispersion, which is due to the larger surface area. In this way, titania aggregates are more difficult to form, as indicated by the absence of a band at 325 nm. Although all three bands attributed to pentacoordinated species are present, a slight but significant increase in the contribution of that assigned to the tripodal species (250 nm) is seen (Table 1). This observation is in agreement with the tripodal

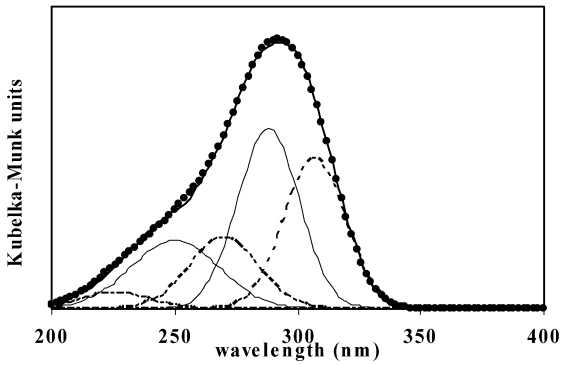


Fig. 7. Deconvolution of the DRUV spectra of Merck60 supported Ti catalysts (0.24 mmol-Ti g^{-1}) without drying under vacuum.

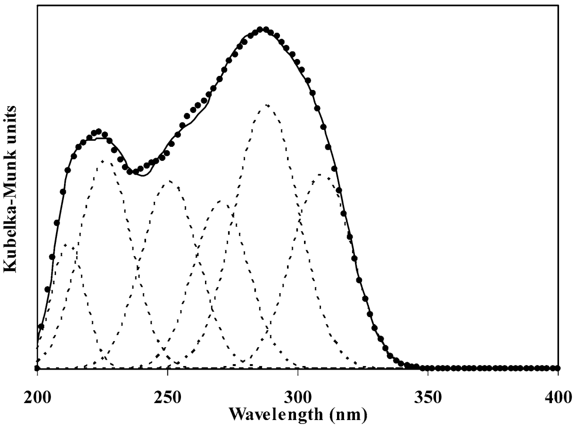


Fig. 8. Deconvolution of the DRUV spectrum of MCM41-Ti(O^{i}Pr).

Table 1
Relative contributions to the UV spectrum of silica-supported titanium catalysts and relationship with catalytic results

Support	Ti loading (mmol g^{-1})	Ti dispersion[a] (atoms nm^{-2})	Contribution (%) of the different bands (in nm) to the UV spectrum[b]							Contribution of direct epoxidation[c]
			210	225	250	270	290	310	325	
Merck60	1.07	1.53	0.8	9.2	9.7	4.6	29.6	18.7	27.3	45
	0.24	0.29	3.9	19.1	16.4	19.7	28.4	12.5	0	56
MCM-41	1.25	1.18	6.4	17.3	16.7	14.5	26.5	18.5	0.1	60
Aerosil200	0.80	2.78	4.3	9.7	15.4	13.3	25.1	25.1	7.2	43
	0.10	0.31	1.3	4.8	19.1	13.7	48.5	12.6	0	71
M60(TMS)	0.24	0.36	5.4	15.8	16.5	26.8	25.6	9.8	0	71
$M60(C_{18})$	0.23	0.46	0	3.1	17.4	41.3	24.7	13.6	0	87
M60(HCl)	0.25	0.29	5.6	13.7	21.5	25.2	20.4	13.6	0	63
C	0.26	0.28	9.1	5.5	20.1	27.4	34.0	3.9	0	84
M60(EtCOCl)[d]	0.23		3.0	6.2	22.7	27.2	18.5	14.9	7.4	71

[a] Nominal dispersion calculated from the titanium loading and the surface area of the support.

[b] Integration of the deconvoluted peak in Kubelka–Munk units.

[c] Percentage of H_2O_2 conversion in the cyclohexene epoxidation reaction through the direct epoxidation mechanism. Calculated as $100 \times (\text{epoxide} + \text{diol} - \text{cyclohexenol})/(\text{epoxide} + \text{diol} + \text{cyclohexenol} + 2 \times (\text{cyclohexenyl hydroperoxide}))$.

[d] Catalyst used three times.

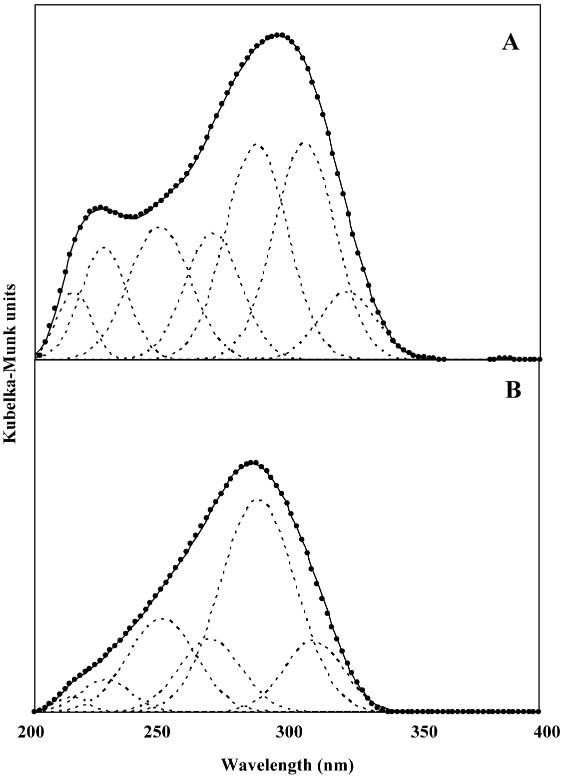


Fig. 9. Deconvolution of the DRUV spectrum of Aerosil200 supported catalysts: (A) 0.80 and (B) 0.10 mmol-Ti g^{-1}.

Table 2
Yields of the different products in the cyclohexene epoxidation with H_2O_2

Support	Ti loading (mmol g^{-1})	Yield (%) of the different products[a]			
		Epoxide	Diol	Cyclohexenol	Chhp
Merck60	1.07	22.7	23.3	10.8	10.8
	0.24	21.8	29.3	7.8	9.2
MCM-41	1.25	20.4	31.1	10.1	3.6
Aerosil200	0.80	20.5	17.0	9.8	8.3
	0.10	36.1	38.8	8.3	5.0
M60(TMS)	0.24	34.5	44.4	8.1	6.4
M60(C_{18})	0.23	23.2	39.4	2.7	1.6
M60(HCl)	0.25	29.5	37.5	9.3	7.7
M60(EtCOCl)	0.26	18.8	50.7	4.0	2.4
M60(EtCOCl)[b]	0.23	18.2	51.8	7.4	5.4

[a] Referred to H_2O_2.
[b] Catalyst used three times.

species described for other titanium catalysts on MCM-41, where calcination leads to this being practically the only species present in the solid [31]. The higher contribution of the tetrahedral species is again in agreement with the hypothesis of support coordination. The high degree of order in the walls of MCM-41 to a large extent precludes the coordination of titanium with the neighboring silanol and/or siloxane observed for the rougher silica surface.

In the case of the nonporous silica Aerosil200, monopodal pentacoordinated dimeric species have been proposed on the basis of the stoichiometry of the reaction between silanols and $Ti(O^iPr)_4$ [32]. The lower silanol density would make the formation of dipodal species difficult and thus favor the higher population of monopodal species. The possibility of dimers is in agreement with the high surface concentration in the solid with maximum loading (Table 1). Octahedral species are present in the high-loading catalyst, as shown by the DRUV spectrum (Fig. 9A), although in a lower amount than in the case of Merck60. However, the low-loaded solid presents the same Ti dispersion as found with Merck60, but the UV spectra are completely different. As far as the possible pentacoordinated species are concerned, the most prominent band in the Aerosil-based solid (Fig. 9B) corresponds to that assigned to monopodal species (290 nm), a situation that is consistent with the lower silanol density.

Regarding to the results in alkene epoxidation with dilute H_2O_2 (yields of all of the reaction products are gathered in Table 2), the solids with larger numbers of octahedral titanium centers also present the lower selectivity for the direct epoxidation mechanism (Table 1), 45% versus 56% in the case of Merck60 and 43% versus 71% for Aerosil200. This is in agreement with the higher activity of the octahedral titanium for H_2O_2 decomposition through a radical mechanism, leading either to decomposition of the oxidant or to the formation of allylic oxidation products. The difference between the two silica supports at low loading is more difficult to explain. In fact, from the activity of titanium–silsesquioxanes in solution [11–13], a higher activity of the solid with higher contribution of tripodal sites (250 nm), reflected in a higher selectivity for the direct mechanism, would be expected. However, the reverse is true, and several factors make the direct translation from solution to heterogeneous reactions difficult. First of all, the use of a different oxidant, H_2O_2 instead of *tert*-butyl hydroperoxide, in a different reaction medium may modify the relative catalytic activities of the different sites. Moreover, the use of a solid introduces other factors, such as diffusion and accessibility, that may alter the performance of the sites and hence the relative rates of the competitive reactions. In this regard the nonporous support with particles of small size, Aerosil200, would be favored, in agreement with the results.

3.2.2. *Hydrophobic silica supports*

In a subsequent set of experiments, we tried to modify the silanol density of Merck60 in a controlled manner in order to vary the population of surface titanium species. Since silanization is reported as a method to eliminate the isolated silanols [33,34], the use of a silanized support would result in a reduction in the amount of monopodal species. Merck60 silica was silanized with trimethylsilyl groups, to give M60(TMS), and dimethyloctadecylsilyl groups, to give M60(C_{18}). A dramatic reduction in the band at 290 nm is evident in the deconvoluted DRUV spectrum of M60(C_{18})-$Ti(O^iPr)$ (Fig. 10), and the band at 270 nm is now the most prominent. The same trend is observed in the case of the M60(TMS) support (Table 1). This result is in agreement with a higher proportion of bipodal species. It is also worth noting the significant decrease in the bands at low wave-

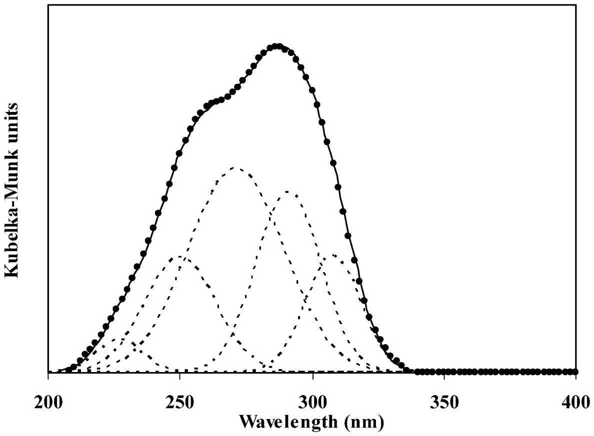


Fig. 10. Deconvolution of the DRUV spectrum of Merck60(C_{18})-Ti(O^iPr).

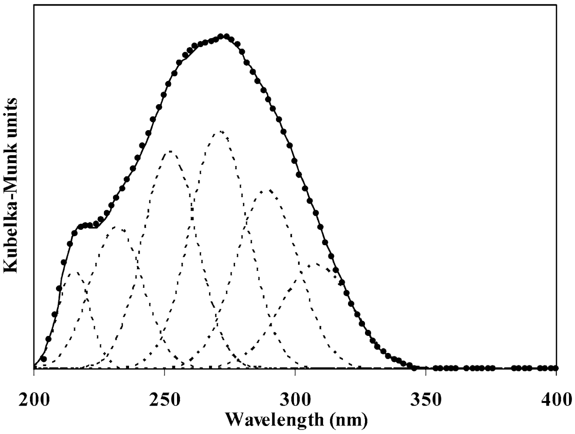


Fig. 11. Deconvolution of the DRUV spectrum of Merk60(HCl)-Ti(O^iPr).

length (Fig. 10). If one considers these bands as corresponding to truly tetrahedral sites, these centers must be located in surface sites that are not easily accessible, which would explain the impossibility of higher coordination. The silanization of the silica surface before titanium grafting may create additional hindrance to those sites, making it impossible to form titanium centers at all. The reduction in these bands is not as pronounced in the case of the less bulky trimethylsilyl group, and this is consistent with the idea outlined above.

In the cyclohexene epoxidation reaction, the catalysts prepared from hydrophobic silicas led to improved contributions of the direct mechanism (Table 1), 71% for M60(TMS) and 87% for M60(C_{18}). The significant reduction of the octahedral contribution (>300 nm) observed in the UV spectrum of M60(TMS)-Ti(O^iPr) (Table 1, spectrum not shown) may account for this improvement, as a consequence of the decrease in the H_2O_2 decomposition by radical mechanism. However, the contribution of octahedral sites in M60(C_{18})-Ti(O^iPr) is even slightly higher than that in M60-Ti(O^iPr), and the explanation for the excellent selectivity must lie elsewhere. In this case the reduction in the contribution of the tetrahedral sites is very significant (<250 nm), which in the literature are described as the main reason for the epoxidation. However, as pointed out before, they may be envisaged as Ti sites in places with hindered accessibility, mainly for bulky molecules. Therefore, they may also be responsible for H_2O_2 decomposition, inasmuch as the alkene cannot enter those sites. The effect would be then the same as for the elimination of octahedral sites, showing that the sites assigned as pentacoordinated Ti are those truly responsible for epoxidation in silica-supported catalysts.

3.2.3. Hydrophilic silica supports

Further confirmation of the tentative assignation of the UV bands could be the use of supports with higher silanol density, in an attempt to increase the number of tripodal species on the surface. The increase in silanol density would be possible through hydrolysis of the surface siloxane bonds in silica to form vicinal silanols. Such a hydrolysis reaction can take place by treatment of silica with hydrochloric acid in the aqueous phase or by reaction with an acyl chloride under anhydrous conditions, followed by hydrolysis [25]. This treatment on Merck60 silica, followed by grafting of $Ti(O^iPr)_4$, led to solids whose DRUV spectra are represented in Figs. 11 and 12. As can be seen, the relative contribution of the band assigned to monopodal species (290 nm) is sig-

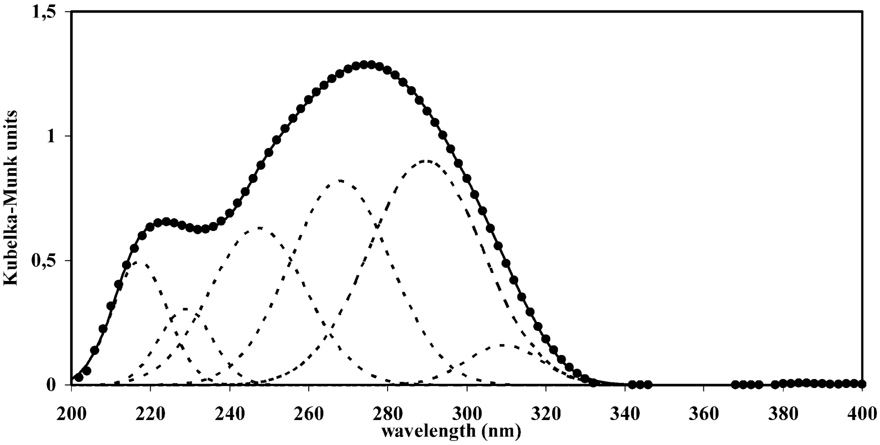


Fig. 12. Deconvolution of the DRUV spectrum of Merck60(EtCOCl)-Ti(O^iPr).

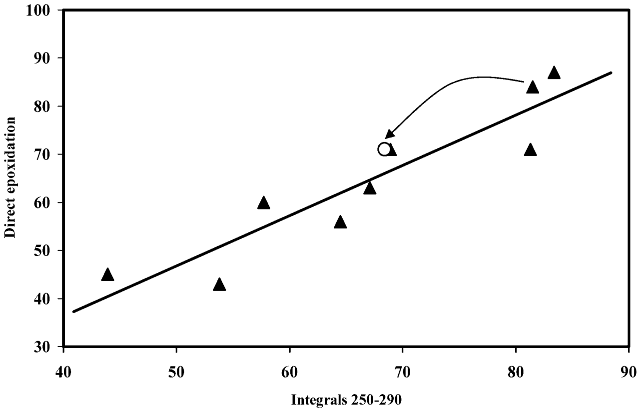


Fig. 13. Correlation between the contribution of the UV bands in the range 250–300 nm and the contribution of the cyclohexene epoxidation through the direct mechanism to the productive conversion of H_2O_2: freshly prepared (▲) and used (○) catalysts.

nificantly reduced in M60(HCl)-Ti(O^{i}Pr) (Fig. 11), and this is associated with an increase in the bands for the tripodal and bipodal species. However, the contributions of octahedral and tetrahedral species present only minor modifications. This result is in agreement with the slight improvement of the selectivity toward the direct epoxidation (Table 1).

In contrast, treatment with an acyl chloride keeps the ratio between the three types of pentacoordinated species almost unchanged, whereas it sharply decreases the content of octahedral and tetrahedral species (Fig. 12). As a consequence, this solid leads to almost the highest selectivity for the direct epoxidation. For a further confirmation of the hypothesis about the significance of the species responsible for the UV bands in the 250–300-nm range, a correlation between the selectivity for the direct mechanism and the total contribution of those bands to the full spectrum is shown in Fig. 13. As can be seen, there is a correlation between the two parameters, with a slope close to 1. Similar correlations were tried with all of the UV contributions, but none of them was significant. This result seems to indicate that the species responsible for those bands (250, 270, and 290 nm), assigned as isolated, pentacoordinated, accessible Ti centers, are also the reason for the direct epoxidation of cyclohexene, whereas octahedral centers (>300 nm) and nonaccessible tetrahedral ones (<250 nm) are mainly responsible for the radical mechanism.

3.2.4. Changes in the titanium species upon recycling

One important point is the modifications induced in the structure of the catalytic sites due to the interaction with the reaction medium. The presence of a large amount of water should produce an increase in the titanium coordination number and, consequently, a modification in the DR-UV spectrum (comparison between Figs. 6B and 7), although this change is reversible after drying. Thus, in situ characterization of the titanium centers under reaction conditions would not be very illustrative in this case.

Furthermore, we have reported some titanium leaching from the silica-supported catalysts, although as inactive species [26], due to the cleavage of some Si–O–Ti bonds. This phenomenon even happens with Ti zeolites [35], where four Si–O–Ti bonds are always present. In view of the possible modifications of the catalytic sites, it seemed interesting to study the recycled catalysts by DR-UV. The general observed trend is a reduction in the contribution of the bands assigned to pentacoordinated species (250–300 nm) and an increasing contribution of the octahedral ones (>300 nm). As an example, the catalyst prepared on the hydrophilic support M60(EtCOCl) shows a decrease of that contribution from 81.5% in the freshly prepared catalyst to 68.4% after three runs (Table 1). Moreover, this decrease is more pronounced for the band at 290 nm, assigned to the monopodal species and, presumably, more sensitive to hydrolysis. Parallel to these decreases, the contribution of the direct epoxidation is reduced from 84% in the first run to 71% in the third one (Table 2), fitting well in the correlation shown in Fig. 13.

Thus we can say that, under the epoxidation conditions, part of the active sites are transformed into octahedral ones, which are active only for the radical mechanism. This may be one of the reasons for the progressive deactivation of the catalyst with reuse.

4. Conclusions

The DRUV spectra of the model titanium–silsesquioxane complexes make it possible to tentatively assign UV bands to the different surface species on silica-supported titanium catalysts. Isolated tetrahedral titanium sites are not very common, probably because of coordination of neighboring groups such as silanol and/or siloxane. This result is in a sharp contrast with the spectra recorded for zeolites and other crystalline materials, which include high-temperature calcination as the last synthesis step. All of these types of coordination should produce mainly pentacoordinated species that seem to be clearly differentiated in the range of 250–300 nm. A clear correlation can be established between the contribution of those bands to the total UV spectrum and the importance of the direct epoxidation mechanism for H_2O_2 conversion in the case of cyclohexene. Thus, the development of more efficient silica-supported titanium catalysts for alkene epoxidation with H_2O_2 should be directed to the increase in the contribution of the pentacoordinated species, in order to prevent the radical mechanism.

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