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Epoxidation on titanium-containing silicates: do structural features really affect the catalytic performance?

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Abstract

Five titanium-containing silicates, with different structural features, were compared: Ti–MCM-41, ordered titanium-grafted mesoporous silica, Ti–SiO_2 Davison, nonordered titanium-grafted porous silica, Ti–SiO_2 Aerosil, nonporous pyrogenic titanium-grafted silica, MST, nonordered in-framework mesoporous material, and TiO_2–SiO_2 Grace, commercial amorphous porous mixed oxide. They were tested in the liquid-phase epoxidation reaction on six unsaturated cyclic terpenes. Good performances were obtained on the commercial mixed oxide and also on the three grafted silicates. The in-framework MST showed the worst activity results. Under these conditions, the porosity features do not affect the catalytic performances noticeably and the use of an ordered mesoporous material is not strictly required. Likewise, a very high surface area is not mandatory in order to have an efficient titanium-grafted catalyst in the epoxidation of these substrates.

Keywords: Epoxidation; Heterogeneous catalysis; Terpenes; Titanium; Mesoporous materials; MCM-41

1. Introduction

The selective epoxidation of olefins is a highly attractive topic in the synthesis of intermediates of use in fine and speciality chemistry. Under the push of environmental concerns, particular attention has been focused on the development of heterogeneous catalysts, which can be used under mild conditions with either hydrogen peroxide or organic hydroperoxides as oxidants [1,2]. Undoubtedly, the discovery of TS-1, which displays remarkable performances in the epoxidation reaction thanks to the unique structural features of the titanium centers in the microporous framework, marked a milestone in the seek for an efficient catalytic system [3,4]. Since then, titanium-based solids have been used extensively as epoxidation catalysts for both liquid- and gas-phase reactions [5], such as TS-2 [6], Ti–ZSM-48 [7], Ti–Beta [8], TAPO-5 [9], and Ti–MWW [10]. Nevertheless, most of these materials have pore diameters in the micropore range ($\phi < 2$ nm). Therefore, bulky and functionalised substrates, as fine chemicals often are, cannot be accommodated in their porous networks. In order to avoid such a limitation, a large number of wide-pore porous materials have been investigated, e.g., Ti–MCM-41 [11], Ti–HMS [12], Ti–MCM-48 [13], MST [14], or Ti–TUD-1 [15], all with pore diameters in the mesopore range (2 nm $< \phi <$ 50 nm).

The common drawback of some of these latter solids lies in their low intrinsic chemical and mechanical stability [16,17]. Actually, the solid walls between the mesopores are often too thin to withstand severe reaction conditions and an abrupt loss of order and mesoporosity is seldom observed in harsh environments [18]. On the other hand, the dimension of the pores in ordered mesoporous materials is too large to ensure a proper shape-selectivity effect, as is observed on microporous zeolitic solids. Because of these reasons, Mayoral et al. [19] recently advanced some doubts on the advantages of using M41S materials instead of other kinds of porous nonordered amorphous silica. Anyway, a systematic comparison of the catalytic performances of titanosilicates of different morphology was still lacking.

In the present study, our group began to wonder whether the highly ordered mesostructured solids of the M41S family, which often require expensive and time-consuming synthesis methods, are necessary in the epoxidation of bulky and richly functionalised fine chemicals. The aim was to compare in a systematic way the performances of five titanium-

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containing catalytic systems with different structural features. The catalysts were chosen so that among them there are ordered and nonordered materials, porous and nonporous solids, mixed oxides, and supported catalysts. Moreover, since most of the mesostructured materials have a potential application interest in the transformation of fine chemicals, the catalytic features of the catalysts were tested in the epoxidation of terpenic substrates of interest in the flavour and fragrance industry. To take easily into account possible deactivation and/or by-product formation phenomena, which frequently appear after long reaction times and affect the productivity of fine chemicals unfavourably, the performance data were compared at the end of the catalytic run.

2. Experimental

2.1. Catalyst preparation

Five titanium-containing silicate materials were used as heterogeneous catalysts: namely, Ti–MCM-41 (**A**), Ti–SiO_2 Davison (**B**), Ti–SiO_2 Aerosil (**C**), MST (**D**), and TiO_2–SiO_2 Grace (**E**).

Ti–MCM-41 (**A**) was prepared following the methodology described in [20]. MCM-41 was synthesised according to procedures developed by Mobil researchers [21,22]. Some simplifications of the procedures were employed following suggestions reported by Di Renzo and co-workers [23]. The molar ratios of the components were the following: SiO_2 : hexadecyltrimethylammonium chloride (CTA-Cl) : NH_3 : H_2O = 180 : 95 : 3397 : 6515. Following Corma and co-workers [24] we avoided any alkali metal cations in the reaction mixture. Ti–MCM-41 was prepared starting from MCM-41 according to the grafting technique proposed by Thomas and co-workers [25], using a solution of titanocene dichloride (Aldrich) in chloroform (Carlo Erba, RPE) and triethylamine (Aldrich) [20].

Ti–SiO_2 (**B**) was prepared, as previously reported [26], by applying the grafting procedure to the commercially available SiO_2 Grace Davison 62.

Ti–SiO_2 (**C**) was prepared according to the same grafting methodology described above for **B**. SiO_2 Aerosil 380, obtained from Degussa, was used instead of SiO_2 Grace Davison 62.

MST (**D**; mesoporous silica–titania) was prepared as previously reported [14].

TiO_2–SiO_2 (**E**) was obtained from Grace and used without further modification.

The titanium content of the prepared samples was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) according to the methodology described in [20], on a Perkin–Elmer 5000 spectrophotometer. The titanium loadings of the samples were 1.88 wt% for **A** (Si/Ti = 41), 1.75 wt% for **B** (Si/Ti = 44), 1.78 wt% for **C** (Si/Ti = 43), 1.84 wt% for **D** (Si/Ti = 42), and 1.40 wt% for **E** (Si/Ti = 55).

2.2. Catalyst characterisation

The powder X-ray diffraction (XRD) patterns were obtained with a Philips automated PW 1729 diffractometer. Scans were taken at a 2θ step of 0.02° (2.5 s per step) in the range 1.5°–50° using Cu-K_α radiation (Ni-filtered).

BET specific surface area, BJH pore size distribution (from the desorption branch of the isotherm), and total pore volume (by Gurvitsch rule) were obtained by nitrogen adsorption–desorption at 77 K, using a Micromeritics ASAP 2010 analyser. Before the adsorption, the solids were preheated under high vacuum in three steps: 1 h at 423 K, 1 h at 513 K, and finally 4 h at 623 K.

Diffuse reflectance UV–vis spectra were recorded using a Perkin–Elmer Lambda 19 spectrometer equipped with an integrating sphere attachment in the wavelength range 200–500 nm. The spectra were recorded on the samples after calcination at 823 K in dry nitrogen. The measurements were conducted at room temperature under strict exclusion of air.

Fourier transform infrared (FT-IR) spectra were recorded on a BIORAD Digilab FTS-40 spectrometer equipped with a KBr beamsplitter and a DTGS detector. The previously dried solid samples were analysed as KBr pellets at a resolution of 4 cm^{-1}.

2.3. Catalytic tests

Five terpenic substrates were used as purchased: α-terpineol (**1**; 96% Aldrich mixture of enantiomers), (+)-terpinen-4-ol (**2**; 96% Aldrich), (−)-isopulegol (**4**; puriss. Fluka), (−)-carveol (**5**; 97% Aldrich; *cis*/*trans* ratio = 40 : 60), and (R)-(+)-limonene (**6**; 97% Aldrich; 98% ee). Carvotanacetol **3** (*cis*/*trans* ratio = 40 : 60) was prepared from carveol **5** by catalytic hydrogenation with $Rh[(PPh_3)_3]Cl$, modifying the methodology described in [27].

All of the catalysts **A**–**E** were pretreated in air at 773 K (10 K min^{-1} temperature programme from room temperature to 773 K) for 1 h and cooled to reaction temperature in vacuo. The epoxidation tests on the terpenes were carried out in a round-bottom glass batch reactor (V_{MAX} = 20 ml) at 363 K (oil-bath heater) with magnetic stirring (ca. 800 rpm). Acetonitrile (Aldrich, HPLC grade) was used as solvent, previously dried on molecular sieves (Siliporite 3A), anhydrous *tert*-butylhydroperoxide (TBHP; Aldrich, 5 M solution in decane) as oxidant (oxidant : substrate molar ratio = 1 : 1), and the catalyst to substrate ratio was 30 wt%. The total volume of the mixture was 10 ml. Samples were taken after reaction times of 1 and 24 h and the catalytic performances were computed on GC chromatograms (HP5890; DB-225 column, 30 m × 0.25 mm; FID and MS detectors). Mesitylene (Fluka, purum) was used as internal standard. The reaction products were also determined by ^{1}H-NMR analysis (Bruker DRX 300) of the crude reaction mixture after 24 h, after solvent removal in vacuo. The need for titanium as the effective active site on which epoxidation takes place was first checked. Neither significant autooxidation nor support-catalysed contributions to epoxidation were recorded in epoxidation tests on α-terpineol 1 with titanium-free siliceous supports, namely, MCM-41, SiO_2 Davison, and SiO_2 Aerosil. The terpene conversion was about 9–10% and the epoxide amount was under the chromatographic detection limit. Similar results were obtained in epoxidation tests without catalyst at all.

The presence of the oxidant at the end of each reaction was systematically checked by means of either GC analysis or iodometric titration and a sensible amount of unreacted TBHP was always found after every catalytic run. Therefore, in none of the tests the organic hydroperoxide had been the limiting agent of the reaction.

Some tests were also performed on all of the five catalysts **A**–**E** with a different amount of catalyst, in order to ascertain whether mass transfer limitations could affect the catalytic performances remarkably. Under these conditions, no remarkable liquid–solid mass transport limitations were detected.

In the tests for the recovery of the catalyst, the solid was separated by filtration on a Büchner funnel and thoroughly washed with fresh acetonitrile and then with methanol (Fluka, HPLC grade). The filtered solid was dried gently at 423 K, weighed, activated again at 773 K in air, and then reused in a new test as described above. It is noteworthy that careful removal of the organic compounds adsorbed onto the siliceous surface is necessary to restore the original activity of the fresh catalyst. For this reason, prior to recycling, the solids were washed with a highly polar solvent, such as methanol.

Some tests were also performed to check the leaching of titanium species which may act as homogeneous catalysts: in these experiments the solid catalyst was removed from the liquid mixture by centrifugation and the resulting solution was tested for further reaction, as previously described [26]. No further oxidation activity was observed on any of these five catalysts.

3. Results and discussion

3.1. Catalyst characterisation

XRD analysis was performed on the five titanium-containing silicates **A**–**E** and on the silicate supports, i.e., MCM-41, SiO_2 Davison, and SiO_2 Aerosil. Only MCM-41 and Ti–MCM-41 **A** displayed XRD patterns in the range $1.5° < 2\theta < 10°$, which can be indexed in a hexagonal unit cell. The interplanar distances (d_{100}) and the hexagonal unit cell parameter ($a = 2d_{100}/\sqrt{3}$) of the two samples resulted: 3.56 and 4.11 nm, for MCM-41, and 3.93 and 4.54 nm, for Ti–MCM-41 **A**, respectively. These results confirm that only **A** and MCM-41, the support from which **A** was obtained, have an ordered network of parallel mesopores with hexagonal symmetry. In contrast, **B**, **C**, **D**, and **E** all have an amorphous nonordered structure. For these latter materials only a broad peak is present at ca. 23°, due to Si(Ti)/Si(Ti) pair correlation.

The N_2 adsorption–desorption isotherms of the five titanium-containing samples (**A**–**E**) are shown in Fig. 1 (a–e) and the textural features of the five titanosilicates **A**–**E**, together with those of the three siliceous supports (MCM-41, SiO_2 Davison, and SiO_2 Aerosil), are listed in Table 1.

First, it is worth emphasizing that the isotherms of the titanium-grafted samples are identical to those of the related purely siliceous supports (here not shown), namely, SiO_2 Davison, SiO_2 Aerosil, and MCM-41. Such behaviour suggests that the grafting of the titanium precursor onto the silicate surface did not remarkably affect the textural features of the materials. Indeed, only a small diminution of specific surface area and total pore volume was observed after the grafting, due to the deposition of titanium species onto the internal surface of the porous solids (as in samples **A** and **B**). This result is consistent with the data obtained from XRD analysis, according to which, after the titanium-grafting, there was a slight change in the structural parameters (d_{100} and a), but the order and the hexagonal symmetry were maintained.

SiO_2 Davison, Ti–SiO_2 Davison **B**, and TiO_2–SiO_2 Grace **E** presented type-IV nitrogen physisorption isotherms with H1 hysteresis (IUPAC classification) and well-defined final plateau, typical of an adsorbent with a narrow distribution of mesopores of fairly uniform size. On the other hand, the two solids derived from pyrogenic silica, namely, SiO_2 Aerosil and Ti–SiO_2 Aerosil **C**, showed type-IV isotherms with H3 hysteresis without final plateau, indicative that the adsorbent does not possess a well-defined mesopore structure. In this case it is not advisable to attempt to derive either the pore size distribution or the total pore volume from physisorption methods. Actually, for our purposes pyrogenic silica is used as a nonporous material.

Differently from other samples, MCM-41 and Ti–MCM-41 **A** showed type-IV completely reversible isotherms, with the mesopore-filling step in the range P/P_0 0.20–0.35, a peculiar feature of this ordered mesoporous material [3,4,14].

According to the shape of the hysteresis, for all samples except SiO_2 Aerosil and Ti–SiO_2 Aerosil **C**, BJH mesopore size analysis yielded narrow distributions around the average values reported in Table 1.

In summary, textural analysis data confirmed that each of the five titanium-containing silicates has a different structural peculiarity: i.e., Ti–MCM-41 **A** is a grafted and ordered mesoporous material; Ti–SiO_2 Davison **B** is grafted and mesoporous, but is not ordered; Ti–SiO_2 Aerosil **C** is grafted, but is not porous; MST **D** is mesoporous, but is neither grafted nor ordered; TiO_2–SiO_2 Grace **E** is a porous nonordered mixed oxide.

The diffuse reflectance UV–vis spectra of the calcined samples **A**–**E** are reported in Fig. 2. All the samples have in common an intense UV absorption band with a maximum in the range 220–280 nm due to a charge transfer between framework oxygen to titanium(IV) [14,20,28].

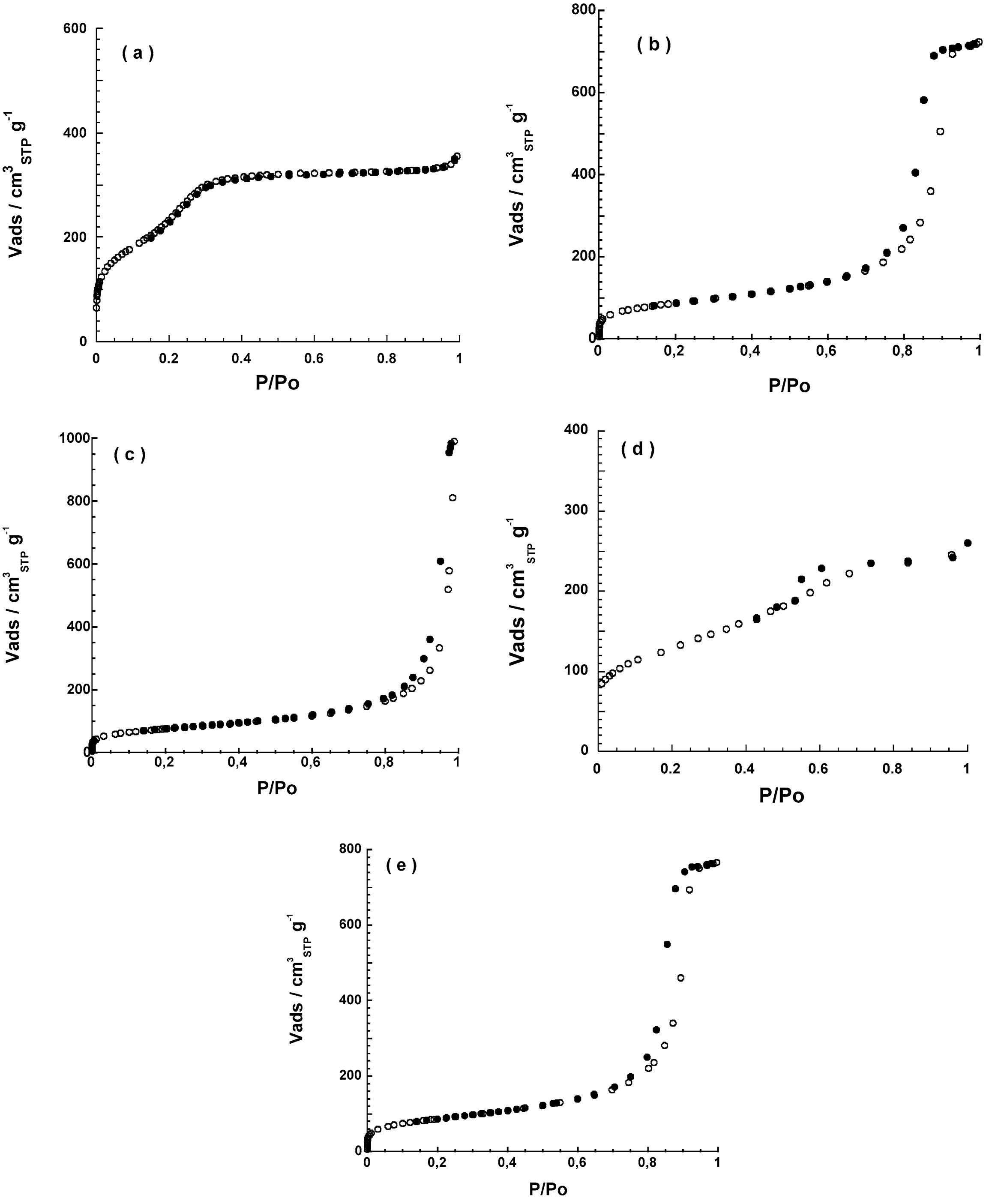


Fig. 1. Nitrogen physisorption isotherms for Ti–MCM-41 **A** (a), Ti–SiO$_2$ Davison **B** (b), Ti–SiO$_2$ Aerosil **C** (c), MST **D** (d), and TiO$_2$–SiO$_2$ Grace **E** (e) samples. Open symbols, adsorption; full symbols, desorption.

The position of this band is affected by the coordination geometry around the titanium atom and by the presence of adsorbates. More precisely, the bands in the region 210–240 nm are attributed to oxygen to tetrahedral Ti(IV) ligand to metal charge transfer [28,29], whereas the bands at higher wavelength ($\lambda > 240$ nm) are explained as due to tetrahedral Ti(IV) sites which undergo a change to octahedral coordination [30]. In particular, the presence of strong absorption in the range 280–300 nm is due to octahedral titanium species in highly dispersed TiO$_2$ particles with a particle size smaller than 5 nm [31,32]. In the spectra reported in Fig. 2, the position of the maximum shifts towards higher wavelengths in the order **A** $<$ **C** $<$ **B** $<$ **D** $<$ **E**. Such behaviour means that in Ti–MCM-41 **A** the tetrahedral component of Ti(IV) was prevalent, whereas in the mixed oxide TiO$_2$–SiO$_2$ **E** a remarkable amount of the titanium

Table 1
Specific surface area (S_{BET}), total pore volume (V_p), mean pore diameter (D_p), and titanium loadings of the solid samples after calcination

Sample	S_{BET} ($m^2\,g^{-1}$)	V_p ($ml\,g^{-1}$)	D_p (nm)	Ti loading (wt%)
MCM-41	972	0.65	2.6	–
Ti–MCM-41 **A**	861	0.53	2.4	1.88
SiO_2 Davison	330	1.16	12.8	–
Ti–SiO_2 Davison **B**	303	1.10	12.8	1.75
SiO_2 Aerosil	333	n.d.[a]	n.d.[a]	–
Ti–SiO_2 Aerosil **C**	268	n.d.	n.d.	1.78
MST **D**	454	0.38	4.6	1.84
TiO_2–SiO_2 Grace **E**	303	1.16	12.7	1.40

[a] Not determined.

sites was in the octahedral coordination. Actually, the grafting of a titanium precursor onto a high surface-area siliceous support leads to the formation of highly dispersed tetrahedral Ti sites (Fig. 1, sample **A**) [28,30]. On the other hand, the occurrence of TiO_2 nanodomains is more likely in solids with a lower specific surface area and/or when the hydrolysis and condensation reactions during sol–gel synthesis help the formation of octahedral Ti–O–Ti oligomers [33]. However, it is important to note that any separate TiO_2 phase (in particular anatase) with a particle size larger than 5 nm can be ruled out by the absence of bands in the range 350–400 nm for all samples, no matter their textural properties [34].

The FT-IR spectra of the calcined samples **A**–**E** are reported in Fig. 3. In all of the five catalysts a band centred mainly at 960 cm^{-1} was constantly found. A similar absorption is commonly accepted as the characteristic vibration of Ti–O–Si bonds in titanium-containing silicate materials [33,35]. It therefore confirms the presence of titanium species grafted onto or dispersed into the silica matrix [30].

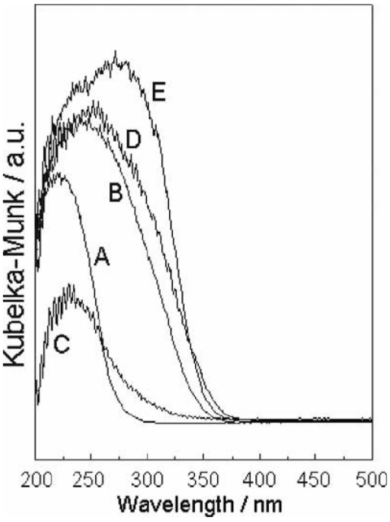


Fig. 2. Diffuse reflectance UV–vis spectra of Ti–MCM-41 (**A**), Ti–SiO_2 Davison (**B**), Ti–SiO_2 Aerosil (**C**), MST (**D**), and TiO_2–SiO_2 Grace (**E**) samples.

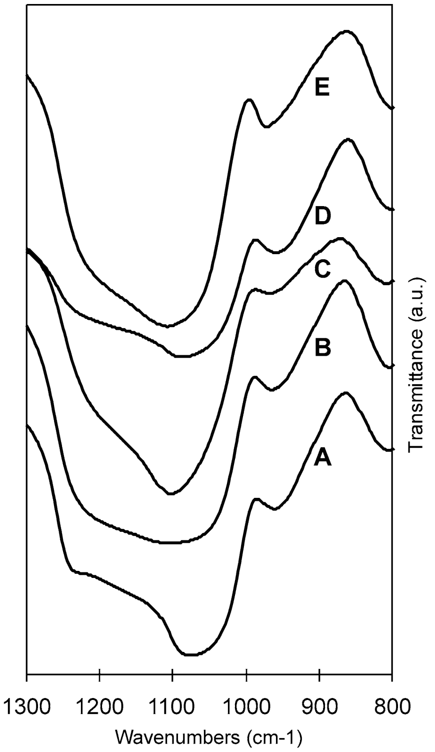


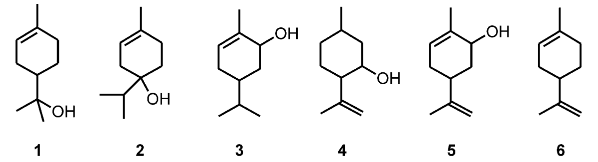
Fig. 3. FT-IR spectra of the calcined samples: Ti–MCM-41 (**A**), Ti–SiO_2 Davison (**B**), Ti–SiO_2 Aerosil (**C**), MST (**D**), and TiO_2–SiO_2 Grace (**E**).

Since this band is due to the overlapping of two contributions (namely, the Ti–O–Si connectivity at 935 cm^{-1} and the Si–OH stretching at 980 cm^{-1}), small differences in its position are attributable to the presence of different ligands surrounding the tetrahedral titanium sites when it is either placed in the matrix or grafted onto the surface of the silica [29,33]. Nevertheless, this absorption is not suitable for discriminating isolated titanium sites from more complex oligomeric species [30]. Merging the results from the UV–vis DRS and FT-IR analysis, it is possible to conclude that the titanium-grafting technique leads to evenly dispersed and isolated catalytic sites only when supports with very high surface area are used (sample **A**). The sol–gel synthesis method, instead, may give rise, even at low titanium content, to the growth of considerable amounts of TiO_2 nanodomains (sample **D**) [33]. Whenever the specific surface area of the siliceous supports is not extremely high, the solid displays intermediate features: both isolated tetrahedral and oligomeric octahedral titanium sites are simultaneously present (samples **B** and **C**) [30].

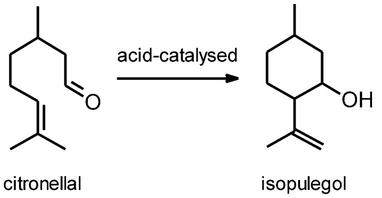
3.2. Catalytic results

The catalytic performances of the five titanium silicates were compared in the epoxidation, under the same conditions, of the six unsaturated alcohols **1**–**6** (see Scheme 1).

The results are reported in Table 2. Since no leaching of homogeneously active titanium compounds was detected, all of the catalysts worked as effective heterogeneous catalyst



Scheme 1.



Scheme 2.

(cf. Experimental section). In this study, another well-studied in-framework titanium substituted silicate, as [Ti]–MCM-41, could be taken into account. Nevertheless, this ordered mesoporous material had already shown, under the same reaction conditions, a specific activity not only lower than the related extraframework Ti–MCM-41 **A** [20,36], but also lower than the nonordered in-framework mesoporous silica–titania MST **D** [14]. So, because of these poor performances, [Ti]–MCM-41 was left out of the comparison.

3.2.1. Catalytic performances

With regard to the specific activity, the mixed oxide catalyst **E** showed the best performance of all, with two remarkable exceptions on substrates **1** and **6**. In these two cases, the highest activity values were obtained with the titanium-grafted materials Ti–MCM-41 **A** and Ti–SiO_2 Davison **B**, respectively. These results are in agreement with the observation that the epoxidation of olefinic substrates is faster on titanium-grafted silicates (such as **A**, **B**, and **C**) than on in-framework titanosilicates (such as **D**, **E**, and [Ti]–MCM-41) [36]. In fact, on extra-framework titanium-grafted silicates the catalytically active sites have been grafted and are virtually all exposed and accessible, whereas on in-framework materials some of them may be buried within the silicate walls and thus unapproachable to reactant molecules. In this case, α-terpineol **1** and limonene **6** can be considered as purely olefinic substrates, because the alcoholic group is either absent or very far from the unsaturation and, on such molecules, titanium-grafted materials displayed the best activity values. On the other hand, when the OH-group is in proximity of the C=C double bond, the promotion effect of the alcoholic group (vide infra) prevails and there is not a remarkable difference between the epoxidation rates of either grafted or in-framework materials [20]. In this case, whenever the OH-group was in allylic (**3** and **5**) or homoallylic (**2** and **4**) position, the differences among the specific activities of the various titanosilicates became smaller and the mixed oxide **E** turned out to be the most active catalyst.

Table 2
Turnover numbers and selectivity (in parentheses) of the catalysts after 24 h reaction

Terpenes	Catalyst[a]				
	A	B	C	D	E
1	44[b] (51)[c]	37 (60)	29 (57)	22 (58)	28 (53)
2	38 (61)	37 (80)	31 (88)	23 (65)	44 (90)
3	43 (64)	44 (84)	40 (81)	40 (74)	59 (71)
4	36 (80)	38 (82)	32 (88)	19 (84)	45 (89)
5	40 (73)[d]	45 (84)	43 (83)	30 (83)	52 (75)
6	30 (90)[d]	33 (89)	32 (92)	19 (85)	25 (75)

[a] Reaction conditions: $m_{\text{catalyst}} = 50$ mg; 1 mmol substrate; TBHP : terpene molar ratio = 1 : 1; CH_3CN; 363 K; 24 h; V_{TOT} mix = 10 ml; magnetic stirring (ca. 800 rpm).

[b] TON: Turnover number after 24 h ([mol converted terpene]/[mol Ti]).

[c] Selectivity to monoepoxide after 24 h (%).

[d] Selectivity to endocyclic monoepoxide after 24 h (%).

With regard to the selectivity to epoxidised compounds, the values followed the aptitude of each catalyst for generating by-products. Using unsaturated alcoholic terpenes as substrates (terpenes **1**–**5**), some of the by-products were due to the inter- or intramolecular attack of the OH-group on the already formed epoxy ring. In particular, 2-hydroxy-1,8-cineol and 2-hydroxy-1,4-cineol were obtained as main by-products in the epoxidation of α-terpineol **1** and terpinen-4-ol **2**, respectively [20]. On the secondary alcohols carvotanacetol **3** and isopulegol **4**, most of the by-product formation was due to the oxidation of the alcoholic function into the related ketone: carvotanacetone and isopulegone, respectively. When two double bonds are present, as in terpenes **5** and **6**, the selectivity values in Table 2 are related to the formation of the endocyclic 1,2-monoepoxide only. In such cases, the preferential attack of oxygen to the endocyclic C=C bond rather than the terminal exocyclic one was noted (typical *endo* : *exo* ratio is in the range 80 : 20–90 : 10 for both **5** and **6**). Such a regioselectivity is likely due to the more highly electron-rich character of the trisubstituted unsaturation with respect to the exocyclic one [20,37]. Therefore, in the epoxidation of both **5** and **6**, most of the by-product formation was due to the exocyclic monoepoxide production (7–10% selectivity). Small amounts of the ketone compounds, i.e., carvone and menthenones, were also detected. Under these conditions, because of the scarce excess of TBHP oxidant, the production of the diepoxide was negligible in all the tests.

The formation of many by-products was catalysed by the acidic character of the titanosilicate. A qualitative evaluation of the acidic character of the five solids can be obtained from the comparison of the conversion rates in the acid-catalysed conversion of citronellal into isopulegol [38] (see Scheme 2).

By carrying out this reaction in toluene at 363 K in the presence of the five catalysts under investigation, we drew the following order of acidic character: **A** > **C** > **D** > **B** ≈ **E**. This prompted us to exploit the remarkable acidic character of **A** in the one-pot conversion of citronellal to isopulegol epoxide [39]. According to this order, in the present work, on substrates **1**–**5** the lowest selectivity values were obtained on Ti–MCM-41 **A**, whereas the best selectivity performances were recorded on Ti–SiO_2 **B** (terpenes **1**, **3**, and **5**) and on TiO_2–SiO_2 **E** (terpenes **2** and **4**). On limonene **6**, thanks to the absence of the OH-function, which could otherwise lead to the formation of a wider number of acid-catalysed by-products, the selectivity values obtained with all of the catalysts averaged high.

It is also worth observing that the selectivity values did not depend noticeably on the structural features of the catalyst. For instance, the selectivity in the epoxidation of **4** is ca. 85% on all the solids. Such behaviour suggests that, on all the five titanium-containing silicates, the catalytic active site works virtually in the same way, notwithstanding the geometric structural surroundings.

From the comparison of the conversion profiles vs time of the five different catalysts, it is possible to have a deeper insight into the catalytic activity at the beginning of the reaction and into a possible deactivation near the end of the 24-h time. As an example, the conversion profiles of isopulegol **4** on solids **A**–**E** are reported in Fig. 4. It is noteworthy that in all cases the conversion values after 1 h parallel quite accurately the ones recorded after 24 h. Such behaviour implies that, under these particular conditions, the most active catalysts after 1 h reaction (namely, **A**, **B**, and **E**) were the most active systems after 24 h as well.

With regard to the trend of the conversion profile, all of the catalysts were active mostly in the first 3 h. Then there was a sensible deactivation in the following time and the conversion values reached a sort of asymptotic limit in 24 h, as already observed on the same kinds of catalysts [20]. Such deactivation seems to be particularly relevant with MST **D** and is likely due to the adsorption of products and, most of all, of by-products onto the catalyst surface. Indeed, these organic adsorbates are to be removed with a careful washing and calcination in the recycling tests to restore the original activity of the catalyst (*vide supra* Experimental section).

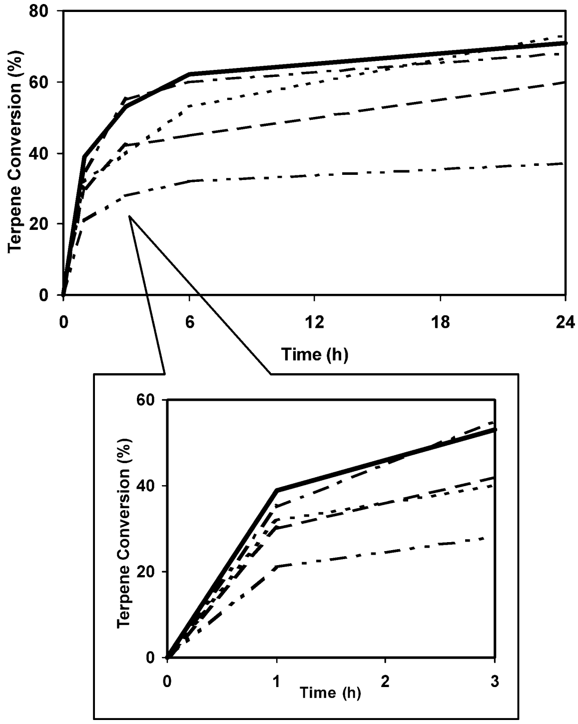


Fig. 4. Isopulegol **4** conversion (%) vs time on catalyst **A** (···), **B** (—), **C** (- - -), **D** (-·-·), and **E** (-··-). Reaction conditions: $m_{catalyst} = 50$ mg; 1 mmol substrate; TBHP : terpene molar ratio = 1 : 1; CH_3CN; 363 K; 24 h; V_{TOT} mix = 10 ml; magnetic stirring (ca. 800 rpm).

3.2.2. *Effect of the OH-group*

On all of the catalysts, the allylic substrates, i.e., carvotanacetol **3** and carveol **5**, are more readily epoxidised than limonene **6**, on which no alcoholic function is present. The dependence of the catalyst activity on the distance between the OH-group and the double bond had been deeply examined in previous works on both ordered and nonordered mesoporous materials [14,20]. According to a widely accepted model, the presence of the OH-group on the substrate affects the overall rate of the reaction by means of the binding of the OH-moiety to the titanium site [40,41]. Such a binding enhances the transfer rate of the oxygen atom from the peroxidic reagent to the olefinic substrate. In this study, the positive effect of the OH-group on the reaction rate has been observed with no remarkable differences on both porous or nonporous catalysts, as well as on both ordered and nonordered materials. This trend is a clue that, under these conditions, the OH-group promotion mechanism is not sensitive to the morphology of the bulk of the catalyst.

Moreover, as already noted in a previous paper [26], the OH-group also plays a key role in directing the diastereospecific epoxidation of the unsaturated cyclic terpenes, since the oxygen transfer from TBHP to double bond occurs on the same side of the rigid six-membered ring where the hydroxy-group is placed. Indeed, in the case of substrates **1**, **2**, **3**, and **5**, the formation of the stereoisomers bearing the epoxy ring in *syn* position with respect to the OH-moiety was selectively observed on all of the catalysts, with no detectable differences among the five materials **A**–**E** (the diastereoisomeric excess value is > 95% in all cases) [26]. Whenever the OH-group is not present, as in **6**, no remarkable diastereoisomeric induction was detected and the formation of both *cis*- and *trans*-limonene oxide was recorded (d.e. value ca. 12% on all the catalysts **A**–**E**) [26]. Thus, the diastereoselectivity features too seem to be insensitive to the morphology and porosity of the different materials.

3.2.3. *Effect of the catalyst porosity features*

Taking into comparison the three titanium-grafted materials (**A**, **B**, and **C**), they showed, in almost all cases, very similar activity and selectivity performance (Table 2). They all belong to the family of extra-framework titanium-containing materials, but the main differences among them are the structural features. In fact, both **A** and **B** are porous materials with a narrow pore size distribution placed at 2.4 and 12.8 nm, respectively (Table 1). On the other hand, catalyst **C**, like the pyrogenic silica from which it was obtained, does not possess any porosity either in the micropore or in the mesopore range. Such similarity in the catalytic results confirms that the catalyst porosity features do not have a significant influence on the epoxidation activity. Actually, under these conditions and on these substrates, the pore diameters of the materials are too large to affect the production of the epoxidised compounds noticeably. So, even though mesoporous sieves with narrow pore size distributions are employed, they cannot act as shape-selective catalysts, as microporous materials do.

Because of these results, the question whether nonordered or, even, commercial titanosilicates could be used instead of ordered mesoporous ones arises strongly. Recently, in the comparison between two epoxidation catalysts, obtained by grafting Ti(*iso*-PrO)$_4$ onto MCM-41 and onto a silica gel, respectively, the ordered catalyst showed a lower activity than the nonordered one by using both H_2O_2 and TBHP as an oxidant [19]. Similarly, titania–silica catalysts prepared through aerogel [42], xerogel [43], and flame aerosol technology [44] (all amorphous nonordered solids) were shown to be effective epoxidation catalysts. With regard to the systematic comparison here reported, no advantages resulted from the use of an ordered mesoporous material, such as Ti–MCM-41 **A**, with respect to other either grafted or in-framework titanium-containing silicates. Moreover, the best performances, under these conditions and on these substrates, were achieved on a commercially available silica–titania mixed oxide (catalyst **E**).

3.2.4. Effect of specific surface area

Another interesting point about the titanium-grafted materials is worth emphasizing. Both **B** and **C** have a far lower surface area than **A** (303 and 268 $m^2\,g^{-1}$ vs 861 $m^2\,g^{-1}$, respectively). Nevertheless, these two catalysts showed activity values comparable to or better than (as in the epoxidation of **5** and **6**) those obtained on **A**. These results mean that a very high surface area is not mandatory for a titanium-grafted epoxidation catalyst. Furthermore, the grafting of titanocene precursors onto a low-surface-area siliceous solid leads to the formation of oligomeric titanium oxide aggregates on the surface [25,30] and on samples **B** and **C** the number of Ti–O–Ti oligomeric sites in octahedral coordination is not negligible at all, as evidenced in Fig. 2. Thus, the good catalytic data obtained on solids **B** and **C** confirm the hypothesis according to which small aggregates of TiO_2 not only are not detrimental in the epoxidation process, but also take part in the reaction. In this case also, complete site isolation is not mandatory in order to have active and selective titania–silica epoxidation catalysts [33]. On this subject, it has been recently shown that the dinuclear silica-supported $(\equiv SiO)_2TiOTi(OO^tBu)_4$ species, prepared by the grafting route, is an efficient catalyst, which is 100% selective in cyclohexene gas-phase epoxidation at room temperature [45].

3.2.5. Recycling tests

The five catalysts underwent three catalytic cycles overall, in order to evaluate the propensity to be recovered and recycled. After the third run the loss of activity was 20% for **A**, 10% for **B**, 4% for **C**, 27% for **D**, and 42% for **E**, with respect to the activity of the fresh catalyst. Moreover, the values of selectivity to 1,2-monoepoxide did not change remarkably on passing from the first to the third catalytic run. Such behaviour suggests that there is not a valuable modification or rearrangement of the catalytic active site during the recycling steps.

These data indicate that these titanosilicate solids withstood up to three catalytic runs with negligible changes in their selectivity and with a loss in their specific activity, which is small in the case of grafted solids (**A**, **B**, and **C**) and sensible in the case of the other two materials (**D** and **E**).

4. Conclusions

The main conclusion coming from the comparison of the data obtained in the epoxidation of this series of six unsaturated cyclic terpenes is that the use of materials with an ordered array of mesopores is not strictly necessary in order to have an efficient heterogeneous epoxidation catalyst. Provided that the pore diameter of the solid is large enough to accommodate the substrate molecules and that the titanium active sites are evenly dispersed and available on the silica support surface, the morphology of the surroundings of the titanium atoms does not considerably affect the catalytic performances. Likewise, a very high surface area is not mandatory in order to have an efficient titanium-grafted catalyst and the presence of TiO_2 nanodomains, which may form either during or after the grafting of the titanium precursors onto the SiO_2 surface, is not detrimental, whenever TBHP is used as oxidant.

Because of these remarks, in this kind of epoxidation reaction and under these conditions, catalysts with nonordered morphology and/or obtained by the titanium grafting technique could be preferentially employed. In fact, they are prepared by means of easier and less time-consuming synthesis methodologies with respect to other ordered mesoporous materials. Moreover, they offer catalytic performances which are better than those of in-framework titanium-containing solids and, at least, comparable to those obtained with highly ordered mesoporous materials.

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