Catalysis Science & Technology

Accepted Manuscript

An efficient epoxidation of terminal aliphatic alkenes over heterogeneous catalysts: when solvent matters †

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The epoxidation of unfunctionalized terminal aliphatic alkenes over heterogeneous catalysts is still a challenging task. Thanks to the tuning of a peculiar catalyst / oxidant / solvent combination, it was possible to attain good alkene conversions (73%) and excellent selectivity values (> 98%) in the desired terminal 1,2-epoxide. Over the titanium-silica catalyst and in the presence of *tert*-butylhydroperoxide, the use of the α,α,α-trifluorotoluene as an uncommon non-toxic solvent was the key factor for a marked enhancement of selectivity. The titanium-silica catalyst was efficiently recycled and reused after a gentle rinsing with fresh solvent.

Introduction

The epoxidation of olefins plays a major role in the valorisation of biomasses and fossil oil refinery by-products, since epoxides are essential and versatile intermediates building blocks for the pharmaceutical, flavour and polymer industry.[1,2] The development of sustainable oxidative procedures based on solid catalysts is therefore object of extensive research, with the aim of reducing the environmental impact of the epoxidation reaction.[3] At industry level, propene is successfully and selectively epoxidised over a mesoporous silylated titanium silicate catalyst, as in the Styrene Monomer Propylene Oxide (SMPO), or over titanium-silicalite 1 (TS-1), as in the recent Hydrogen Peroxide Propylene Oxide (HPPO) process.[4,5] Thanks to the use of a Ti(IV)-based oxide (in the former) or zeotype (in the latter) with marked hydrophobic character, in the presence of concentrated hydrogen peroxide as a source of oxygen, propylene oxide (PO) is obtained in high selectivities with minor formation of secondary products.[3,5-8] The use of hydrogen peroxide at high concentrations gives rise to major safety and transportation issues and, for this reason, the production facility of such oxidant has to be located just next to the epoxidation plant.[9,10] Unfortunately the use of TS-1, and of microporous materials in general, is not compatible with safer, more selective, but bulkier peroxides, such as *tert*-butyl hydroperoxide (TBHP) or cumyl hydroperoxide. Conversely, for bulkier and larger substrates, many progresses have been made, at least at laboratory scale, in the selective heterogeneous catalytic epoxidation of internal and cyclic alkenes.[11,12,13] In this case, mesoporous catalysts permit the successful use of bulky organic peroxides under mild conditions.[14,15] However, in the strategy of a bio-based production of intermediates for chemical industry, a growing attention has been paid to the selective epoxidation of terminal linear alkenes, since they can be conveniently obtained from unsaturated fatty acid methyl esters (FAMEs) of vegetable origin via olefin metathesis.[16,17] In spite of the performances observed on internal olefins, the selective epoxidation of 1-alkenes, still represents an ambitious challenge.[18-21] Terminal double bonds are, in fact, substantially less active towards electrophilic oxidants.[22,23,24] Long reaction times and aggressive oxidants, such as peroxoacids, are thus required. These systems imply the co-presence of free carboxylic acids in the reaction mixture, leading to rearrangement and oxirane ring-opening side products, cause corrosion problems to the production plants and often require the use of chlorinated solvents and/or hazardous solvents.[25] At laboratory scale, many efforts have been made on the sustainable epoxidation of terminal alkenes and some papers are reported in the recent literature, each of them focusing on one single aspect of the issue.[26-29] The previous experience, within our research team, on the epoxidation of various substrates, such as cyclic alkenes, unsaturated terpenes and unsaturated fatty acid derivatives, over heterogeneous single-site Ti- and Nb-containing silica solids,[30] has prompted us to pay a special attention to the epoxidation of terminal aliphatic alkenes, promoting the use of heterogeneous catalytic procedures, non-noxious solvents and selective oxidants. The investigation was performed aiming at finding the optimal combination of catalyst, oxidant and solvent for the sustainable epoxidation of 1-alkenes. In particular, 1-octene was identified as a diagnostic substrate thanks to the similarity with PO (propylene oxide) of its oxidised product.[31] Furthermore, the use of α,α,α-trifluorotoluene, which was recently proved to be an effective alternative to noxious reaction media,[32] was envisioned for the first time in the epoxidation of terminal olefins.

Experimental section

Chemicals

All substrates were used as purchased: 1-octene (98%, Aldrich), *trans*-2-octene (97%, Aldrich), *cis*-2-octene (>95%, TCI), *cis*-1,4-hexadiene (99%, Aldrich), 1,9-decadiene (98%, TCI), 1-hexene (97%, Aldrich), TBHP (5.5 M decane solution 98%, Aldrich). For all of the reactions the substrate was dissolved in purchased HPLC grade solvent (Aldrich). The solvents have been dried over 3A molecular sieves prior to

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† Electronic Supplementary Information (ESI) available: [N_2 adsorption/desorption isotherms; pore size distributions analysis of the catalysts; X-ray diffractograms; diffuse reflectance UV-vis spectroscopy; heterogeneity tests]. See DOI: 10.1039/x0xx00000x

use. All reactants were used as purchased (Aldrich). The commercially available Aeroperl granulated fumed silica (Evonik, Aeroperl 300/30, 20-40 µm particle size) and Davisil silica (Grace Davison, LC60A, 60–200 µm particle size) were used as supports.

Catalyst preparation

Three titanium-containing silicate materials have been studied as heterogeneous catalysts: Ti/SiO_2-Aero, Ti/SiO_2-Dav, Ti/MCM-41. Catalysts were prepared starting from the corresponding siliceous support, *i.e.* Aeroperl granulated fumed silica, Davisil silica or MCM-41, respectively, by the following procedure. The silicate material was pretreated in air at 573 K for 2 h and at 573 K for 2 h under dynamic vacuum (10^{-6} bar). Then it was cooled to room temperature under vacuum and it was grafted via liquid phase grafting, using a titanocene dichloride solution in chloroform and triethylamine, as previously reported.[33]

MCM-41 was synthesised with a pore wall thickness of about 2 nm according to the procedure described in the literature.[34]

Catalysts characterisation

The titanium content of the prepared samples was determined by inductively coupled plasma optical emission spectroscopy ICP-OES (ICAP 6300 Duo, Thermo Fisher Scientific) after mineralisation of the samples in a microwave digestion apparatus (Milestone MLS 1200; maximum power 500 W) with a mixture of hydrofluoric (aq. 40 wt.%) and fuming nitric acid.

N_2 physisorption measurements were carried out at 77 K in the relative pressure range from 1 x 10^{-6} to 1 P/P_0 by using a Quantachrome Autosorb 1MP/TCD instrument. Prior to analysis, the samples were outgassed at 373 K for 3 h (residual pressure lower than 10^{-6} Torr). Apparent surface areas were determined by using Brunauer–Emmett–Teller equation, in the relative pressure range from 0.01 to 0.1 P/P_0. Pore size distributions were obtained by applying the Barret–Joyer–Halenda (BJH) approach applied to the desorption branch for MCM-41 and Ti/MCM-41 samples and the NLDFT method (N_2 silica kernel based on a cylindrical pore model applied to the desorption branch) for all other samples.

XRD patterns were obtained on a ARL XTRA48 diffractometer using $Cu_{K\alpha}$ radiation (λ=1.54062 Å).

Diffuse reflectance UV–Vis (DR UV–Vis) spectra were recorded at RT using a Perkin Elmer Lambda 900 spectrometer equipped with an integrating sphere accessory, and using a custom-made quartz cell. All samples were calcined at 773 K under dry air and, prior to the DRS UV-Vis analysis, dispersed in anhydrous $BaSO_4$ (10 wt.%) and treated *in vacuo* for 1h at room temperature.

Catalytic reaction and product analysis

All catalysts were pretreated under air at 773 K and cooled at room temperature under vacuum, prior to use. The epoxidation tests were carried out under inert atmosphere, in a round-bottom glass batch reactor in a preheated oil bath with magnetic stirring (ca. 800 rpm). The substrate was dissolved in 5 mL of solvent. *Tert*-butyl hydroperoxide (TBHP; 5.5 M in decane) was used as oxidant, with an oxidant to substrate molar ratio of 1.1/1. Decane (contained in the oxidizing TBHP solution) was used as internal standard. Samples were collected at periodic intervals and the catalytic performances were computed on GC chromatograms (HP6890; HP-5 column, 30 m × 0.25 mm; FID and MS detectors) or ^{1}H-NMR. Products molecular structure was confirmed by ^{1}H-NMR spectroscopy (Bruker DRX Advance 400MHz), comparing peaks with the ones reported in literature. A standard deviation of ±2%, ±4%, ±4%, has to be considered for conversion, selectivity and yield. Promising catalytic systems were tested multiple times with different batches of catalyst, leading to comparable results.

Neither auto-oxidation nor support-catalysed epoxidation were recorded with metal-free siliceous supports (conversion about 5% with no detectable epoxide formation). After all catalytic tests, the presence of residual TBHP was checked and confirmed by iodometric assays.

Further experiments were performed in order to check the competitive kinetics of 1-octene and *trans*-2-octene, following the procedure reported above, with an oxidant/1-octene/*trans*-2-octene molar ratio of 1.1/0.5/0.5.

In order to check the leaching of titanium active species, the solid catalyst was removed from the liquid mixture by centrifugation, and the resulting solution was tested for further reaction.[35]

In the tests for the catalyst re-uses, the solid was separated by filtration, washed with fresh reaction solvent and a small amount of methanol (Fluka, HPLC grade). The filtered solid was dried at 373 K, weighed and re-used in a new test without further pre-treatment.

Results and discussion

Catalysts characterisation

First, a set of titanium-containing catalysts with different characteristics was selected (Table 1). The metal centres were added onto the silica supports following a liquid-phase grafting procedure, starting from titanocene dichloride.[11] Three different silica types with various textural features were used: (*i*) a commercial granulated Aeroperl fumed silica by Evonik (SiO_2-Aero); (*ii*) a mesoporous non-ordered commercial silica gel by Grace (SiO_2-Dav); and (*iii*) an ordered mesoporous purely siliceous MCM-41 (Table 1). The final content of titanium in the catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and fell in the range 0.6-1.1 wt.% in Ti.

All the catalysts and the silica precursors were submitted to N_2 physisorption analysis to evaluate their specific surface area and the pore size distribution. Aeroperl fumed silica and the derived Ti-containing sample showed an undefined porosity probably generated by the aggregation of the pyrogenic non-porous particles, as expected from the factory specifications (ESI; Fig. S1). Different textural characteristics were observed for Ti-based non-ordered mesoporous silica (Ti/SiO_2-Dav) and the pristine sample. Both the samples showed isotherms of IUPAC "IV" type, with "H2" hysteresis loops typical of solids with disordered structural pore size distributions (ESI; Fig. S2). The Ti deposition led to a reduction of the specific surface area, from 580 m^2 g^{-1} (for SiO_2) to 474 m^2 g^{-1}. Conversely, the pores size distribution (falling in the 4-11 nm range) was not significantly affected by the presence of the Ti(IV) centres.

Finally, the two ordered mesoporous MCM-41 solids, before and after functionalization with Ti, presented isotherms of type "IV". MCM-41 showed a surface area of 890 m^2 g^{-1} and a narrow and regular pore size distribution centred at 2.5 nm (pores volume of 0.71 cm^3 g^{-1}) (ESI; Fig. S3). The metal grafting caused a decrease of both specific surface area and pores size, reaching a surface area value of 713 m^2 g^{-1} and pores diameter of 2.2 nm, as a consequence of the partial restriction of the mesopores. The grafting methodology did not lead to significant structural modifications of the mesoporous solid (ESI; Fig. S4).

The coordination geometry and chemical environment of the metal sites dispersed on the different silica supports were evaluated by DR-UV-Vis spectroscopy (ESI; Fig. S5).

DR-UV-Vis spectrum of Ti/MCM-41 catalyst showed a main absorption centred at 235 nm with a slightly pronounced shoulder at high wavelengths (280-300 nm). The first band is attributed to the isolated tetrahedral titanium sites located on the silica surface, whereas the second UV component could be related to a small fraction of Ti(IV) sites in expanded coordination (*i.e.* oligomeric species).[36] Such shoulder absorption became progressively evident in the Ti/SiO_2-Aero and Ti/SiO_2-Dav samples. For the latest, the band centred at 280 nm dominates the spectrum. In addition, the absorption previously observed at 235 nm for Ti/MCM-41 shifted to 250 nm, as consequence of the modification of the chemical environment of the Ti sites (Fig. S5). The DR-UV-Vis spectrum of Ti/SiO_2-Dav showed a very weak shoulder at *ca.* 350 nm that could be assigned to the presence of extra-framework polycondensed TiO_2 species on the silica surface. However, these species were far less abundant than the isolated Ti sites.

The formation of oligomeric Ti species, responsible for the presence of the band centred at ca. 280 nm, especially evident for Ti/SiO_2-Aero and Ti/SiO_2-Dav catalysts, should be associated to a lower specific surface area of the two silica supports with respect to MCM-41 solid (see Tab. 1) and thus to a higher density of Ti(IV) centres on the siliceous support.[37]

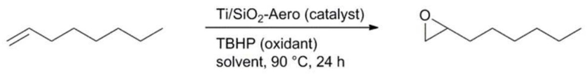
Epoxidation of 1-octene

The first set of experiments concerned the selective epoxidation of 1-octene to 1,2-epoxyoctane over Ti-grafted Aeroperl granulated fumed silica as catalysts. Such catalyst was selected first, since, as reported in widely-accepted literature, titanosilicate systems with a marked hydrophobic character are ideal catalyst for the epoxidation of simple aliphatic alkenes[38-40] and Ti/SiO_2-Aero, indeed, is the solid with a remarkably low amount of hydroxyl moieties surrounding the Ti centres (SiOH/Ti molar ratio = 0.26, as obtained by TGA analysis as described in Ref. 41). In previous works, acetonitrile proved to be an ideal solvent for liquid-phase epoxidation reactions on Ti-silica catalytic systems.[11] However, in the present case, a good conversion (66% after 1 h), but a poor selectivity to the desired epoxide, were obtained (Table 2, entry 1). The gradual loss in selectivity along the reaction is caused by the formation of a plethora of minor products (especially after 24 h) via epoxide opening, rearrangement and oligomerization reactions (heavy product with average molecular mass > 300 dalton). Among the most relevant secondary products, it is worth mentioning: 2-octanone and octanal, obtained via acid-catalysed rearrangement of the epoxide, particularly at longer reaction times; 2-octen-1-ol, that can be obtained via ring opening and rearrangement, via a non-radical pathway;[42] *tert*-butoxyoctanols, due to the reaction of epoxyoctane with *tert*-butanol (by-product from TBHP); and minor amounts of 1,2-octanediol, if traces of water are present.

The effect of the solvent was therefore studied by testing polar and non-polar aprotic solvents: ethyl acetate, toluene (Tol), α,α,α-trifluorotoluene (TFT), 1,2-dichloroethane (DCE) and 1,1,2,2-tetrachloroethane (TCE). In DCE and TCE good conversions were reached, but the selectivity was not satisfactory (entries 5,6), as chlorinated solvents usually enhance the acid character of Ti(IV)-silica catalysts and hence increase remarkably the amount of undesired side products. In toluene, no side-products were detected by spectroscopic techniques (selectivity > 98%, entry 3), but such high selectivity value was related to very low conversion values, since the catalyst was scarcely active. In ethyl acetate, that is a widely used solvent for epoxidation reaction on titanosilicate systems, a good conversion was achieved after 24 h, but only moderate selectivity was observed (entry 2).

To our delight, the use of α,α,α-trifluorotoluene led to the 1,2-epoxide in rather good conversion (63%) and very high selectivity (94%) (entry 4). Interestingly, TFT, although fluorine-containing solvent, is attracting a growing interest as a potential less hazardous alternative to dichloromethane, as it possesses solvent properties that are comparable to those of dichloromethane (DCM), but with lower volatility (b.p. 375 K for TFT vs. 313 K for DCM) and a remarkably reduced toxicity.[32,43] The solvent effect on the reaction was rationalised by means of a correlation between the solvent polarity (expressed as Reichardt E_T (30) parameter)[44] and the conversion of 1-octene. A linear relationship of the 24 h conversions *vs.* E_T (30) was found with a very good correlation parameter (Figure 1). Such result shows that the higher the polarity of the solvent, the larger was the amount of 1-octene converted over the catalyst. It also suggests that highly polar solvents are good reaction media which favour the desorption of the newly formed epoxide molecule from the catalyst surface and reduce the surface deactivation of the solids. At the same time, TFT was also the most selective solvent towards the formation of 1,2-epoxyoctane. It means that, in that medium, the further rearrangement of the epoxide to secondary products is disfavoured.

Table 2 The effect of solvent on the catalytic epoxidation of 1-octene over Ti/SiO_2-Aero with *tert*-butyl hydroperoxide.[a]



Entry	Solvent	E_T(30)[b]	C 1h [%][c]	S 1h [%][d]	C 24h [%][c]	S 24h [%][d]
1	CH_3CN	45.6	66	62	97	31
2	AcOEt[e]	38.1	12	> 98	63	73
3	Tol	33.9	8	> 98	35	> 98
4	TFT	38.5	24	98	63	94
5	DCE	41.3	18	71	72	65
6	TCE	39.4	30	31	66	< 3

[a]Reaction conditions: 100 mg catalyst; 1 mmol 1-octene; 5 mL solvent; TBHP 1.1 mmol; 363 K oil bath; 24 h; stirring ca. 800 rpm; under dry N_2. [b]Reichardt solvent parameter (in kcal mol^{-1}). [c]Alkene conversion. [d]Selectivity to 1,2-epoxide. [e]Reaction performed at 358 K.

After having chosen α,α,α-trifluorotoluene as promising solvent, the catalysts were compared in the epoxidation of 1-octene under the same conditions. The best conversion and TON values were achieved over Ti/MCM-41 (Table 3; entry 3), even though the selectivity to the desired epoxide lowered markedly along the 24 h of reaction. Such behaviour is consistent with previous observations in which Ti-grafted siliceous MCM-41 systems (even with no aluminium centres) exhibited a neat Lewis acid character, that was exploited to obtain epoxide-derived compounds via cascade reactions.[32,45-47] Ti/SiO_2-Dav led to quite good conversions (73%) and excellent selectivity (>98%), even after longer reaction times (Table 3; entry 2). However, considering that Ti/SiO_2-Dav contains a higher loading of active Ti species than the other catalysts (1.14 *vs.* 0.59 or 0.65 wt.%), a specific test has been performed with a lower mass of solid (Table 3; entry 5). A fully comparable TON value was obtained (entries 2 and 5), showing that the specific activity does not vary with the total mass of the catalyst (within this mass/substrate range). After 24 h, however, a slightly lower conversion of 1-octene was achieved.

Table 3 Performance of the titanium-silica catalysts in 1-octene epoxidation.[a]

Entry	Catalyst	C 1h[%][c]	S 1h [%][d]	TON[e]	C 24h [%][c]	S 24h [%][d]
1	Ti/SiO_2-Aero	24	98	19	63	94
2	Ti/SiO_2-Dav	33	> 98	14	73	> 98
3	Ti/MCM-41	39	96	29	94	58
4	Ti/SiO_2-Dav[b]	35	98	15	76	98
5	Ti/SiO_2-Dav[f]	20	> 98	15	60	> 98

[a]Reaction conditions: 100 mg catalyst; 1 mmol 1-octene; 5 mL TFT; 1.1 mmol TBHP; 363 K oil bath 24 h; stirring ca. 800 rpm; dry N_2.[b]Reaction performed at 383 K. [c]Alkene conversion. [d]Selectivity to 1,2-epoxide. [e] Turnover number, computed after 1 h reaction [mmol $_{\text{converted octene}}$ / mmol $_{\text{total Ti}}$]. [f]54 mg catalyst.

Ti/SiO_2-Aero showed a good performance with an intermediate TON value between Ti/MCM-41 and Ti/SiO_2-Dav, albeit slightly lower in terms both of conversion and selectivity than Ti/SiO_2-Dav, especially at longer reaction times. The attempt of increasing yields by carrying out the reaction in α,α,α-trifluorotoluene at higher temperature (383 K) did not lead to a significant improvement (Table 3; entry 4). However, the value of 75% of yield was attained more rapidly, in just 6h. Interestingly, the increase in reaction temperature did not enhance the acid-catalysed transformation of the epoxide either and the conversion values were always very good.

With regard to the oxidant, *tert*-butylhydroperoxide (TBHP) was the reactant of choice. Organic hydroperoxides indeed proved previously to be selective and stable oxidants in the presence of Ti-containing mesoporous silicates and assure very high oxidant efficiencies (*i.e.*, the amount of oxidised products obtained per amount of consumed oxidant).[3] Conversely, in the presence of aqueous hydrogen peroxide most of mesoporous titanium silica materials suffer from poor stability, active metal leaching, low oxidant efficiencies and gradual deactivation due to surface restructuring.[48-50] In the present work, iodometric assays on the final reaction mixtures revealed that TBHP had never been the limiting agent and in all cases the recorded TBHP efficiency was very high (>90%).

Under comparable conditions, in the presence of TBHP, some reference titanosilicate catalysts, such as large-pore Ti-BEA zeotype or improved nanocrystalline TS-1, have shown lower yields to 1,2-epoxyoctane (*i.e.* 5% and 40%, respectively).[51,54]

As far as the recovery and reuse of the catalyst is concerned, the solids were filtered and re-used up to four times (Figure 2). Interestingly, no re-activation by pre-treatment at high temperature was needed, whereas in previous reports in which titanosilicate systems were used, a calcination step (under air at T > 673 K) was necessary to remove properly organic deposits from the catalyst surface and recover the pristine catalytic activity.[48,52] A thorough rinsing with fresh TFT was sufficient to recover the pristine catalytic activity. Ti/SiO_2-Dav showed a good resistance to repeated recycles and the overall decrease in epoxide yield after 24 h, along four catalytic cycles, was 12%. Nevertheless, if one considers the cumulative TON values at the end each test (Fig. 2), taking into account the gradual diminution of actual catalyst mass along the four runs, this number was almost constant and, even, increased since the third run. Such behaviour shows that the catalytically active centres do not suffer from deactivation, likely thanks to the particularly mild recovery conditions.

The truly heterogeneous nature of the catalyst under these conditions has been confirmed by hot separation tests, in which the reaction mixture was centrifuged and the solid removed.[53] No sensible further reactivity was observed, thus confirming that no leaching of active species took place during the epoxidation reaction (ESI; Fig. S6). Analogously, the need of titanium as catalytically-active centre was confirmed and no relevant 1-octene epoxidation was observed in the absence of the catalyst or in the presence of the sole siliceous support, *i.e.* Ti-free SiO_2-Aero.

Epoxidation of various linear alkenes

The optimized reaction conditions determined above were employed in the epoxidation of a set of terminal and internal alkenes.

First, the internal alkene *trans*-2-octene was investigated, as a comparison with the terminal 1-octene. The use of Ti/SiO_2-Aero as catalyst, in α,α,α-trifluorotoluene and in the presence of TBHP, led to good conversion and moderate selectivity to *trans*-2,3-epoxyoctane after 1 hour reaction (Table 4; entry 1). Ti/MCM-41 showed the highest activity (61 TON) after 1 h with a complete conversion after 6 h (Table 4; entry 3).

Remarkably, under the same conditions, an interesting result was achieved over Ti/SiO_2-Dav. In fact, even though its initial activity was the lowest (in terms of TON after 1h), a complete selectivity to *trans*-2,3-epoxide was maintained along the following 24 h, leading to a quantitative conversion of the substrate alkene. Lower selectivity values were observed, instead, over Ti/SiO_2-Aero and Ti/MCM-41. In this case too, Ti/SiO_2-Dav proved to be the most selective catalyst, leading to a negligible amount of undesired secondary products.

If one compares the results obtained under the best conditions for 1-octene and *trans*-2-octene (Table 3 *vs*. 4), the trend is fully consistent with the expected behaviour of an electrophilic epoxidation of a terminal olefin with respect to an internal one: a faster reactivity for the disubstituted C=C bond than for a monosubstituted one.

A direct comparison of the reactivity of the two substrates has been performed with an epoxidation test on an equimolar mixture of 1-octene and *trans*-2-octene (Figure 3).

Table 4 Catalytic epoxidation with TBHP of *trans*-2-octene epoxidation over Ti-containing catalysts in TFT[a]

Entry	Catalyst	C [%][b]	S [%][c]	TON[d]	C [%][e]	S [%][f]
1	Ti/SiO_2-Aero	36	74	29	96	68
2	Ti/SiO_2-Dav	40	>98	17	98	>98
3	Ti/MCM-41	84	>98	61	> 98[g]	75[g]

[a] Reaction conditions: 100 mg catalyst; 1 mmol *trans*-2-octene; 5 mL TFT;1.1 mmol TBHP; 363 K oil bath 24 h; magnetic stirring (ca. 800 rpm); dry N_2. [b] Conversion after 1 h. [c] Selectivity to epoxide after 1 h. [d] Turnover number, computed after 1 h reaction [mmol $_{\text{converted octene}}$ / mmol $_{\text{total Ti}}$]. [e] Conversion after 24 h. [f] Selectivity to epoxide after 24 h. [g] Results after 6 h of reaction.

The conversion *vs.* time profiles of the intermolecular competition test (0.5 mmol 1-octene + 0.5 mmol *trans*-2-octene) were comparable to the corresponding curves of the single-substrate reaction and no particular diminution of the reactivity of 1-octene was observed. The lack of a marked competition between the terminal and internal alkenes suggests that the catalytically active Ti(IV) sites are equally accessible to both substrates. Moreover, such results confirm that the catalyst-oxidant-solvent system is suitable and applicable to both linear terminal and internal alkenes.

Encouraged by these results, a broader substrate scope was tested (Table 5) in order to explore the potential of the epoxidation method. The epoxidation of the shorter-chained 1-hexene led to a better conversion, with respect to 1-octene, at equal reaction times (5 h; Table 5; entries 1-2) and 1,2-epoxyhexane was obtained with excellent selectivities, as well. Conversely, with longer alkenes, such as 1-decene, a slower reactivity was recorded (Table 5, entry 3). Such reactivity order: 1-hexene > 1-octene > 1-decene, is fully consistent with previous literature reports on microporous titanosilicate molecular sieves.[54]

The reactivity of *cis*-2-octene was then evaluated in comparison with *trans*-2-octene. The *cis* isomer appeared to be less reactive than the *trans* isomer, with 66% conversion after 6 h vs. 88%, respectively (Table 5; entries 6, 7). Typically, for bulkier alkenes, *cis* isomers are more readily epoxidised than their *trans* analogues. This is commonly attributed to steric effects, the approach of *cis* double bonds being less hindered than *trans* ones.[55-57] In the case of linear alkenes, the formation of the *trans*-epoxide can be favoured by thermodynamic factors (on homogeneous systems too)[58-59] , by different diffusion capabilities throughout the catalyst pores for *cis*/*trans* isomers, or by a favourable cooperative interaction among substrate, catalyst and reaction medium.[60-61] In this particular case, the preferential reactivity of *trans*-2-octene can be due to a joint action of these various factors.

In terms of stereoselectivity, no isomerization at the C=C double bond has been observed for the internal olefins. In fact, *trans*-2,3-epoxyalkanes and *cis*-2,3-epoxyalkanes were exclusively detected starting from *trans*- or *cis*-alkenes, respectively. This behaviour is a clear clue that the epoxidation reaction with TBHP over these catalysts proceeds via a non-radical (heterolytic) mechanism with retention of the configuration.[56] Conversely, when the epoxidation follows a radical-based pathway, a free rotation of the intermediate radical around the C-C bond can occur and a mixture of *cis*- and *trans*-epoxides is found.

The epoxidation of 1,9-decadiene, bearing two equally substituted, terminal double bonds, led after 7 h to a mixture of the mono- and di-epoxide at a molar ratio of 70/30, even though at low conversion values (Table 5; entry 4). The observed selectivity, at such low conversion values, suggests that the epoxidation of the second C=C bond on the intermediate monoepoxyalkene occurs before the original diene is fully consumed. A similar behaviour was observed in the epoxidation of diunsaturated fatty acid methyl esters (methyl linoleate) over a fully comparable epoxidation system (Ti-silica catalyst with TBHP) and was ascribed to a balance of hydrophilic/hydrophobic character between the reactant and the catalyst surface.[36]

Finally, even though the present catalyst – oxidant – solvent combination had been optimized for the epoxidation of aliphatic terminal alkenes, *cis*-1,4-hexadiene was successfully tested under the same conditions (Table 5; entry 5), reaching a 68% conversion after 5 h, with a chemoselectivity of 98% towards the 4,5-epoxy-1-hexene and a complete regioselectivity towards the formation of the internal epoxide rather than the terminal one. Such intramolecular competition test is a further confirmation that, as expected in the case of electrophilic oxygen transfers, the internal double bond is more readily epoxidised than the terminal one.

Conclusions

A set of titanium-silica catalysts proved to be highly efficient in the selective epoxidation of terminal linear alkenes. To our best knowledge, such result is a remarkable advancement in the epoxidation of poorly activated terminal aliphatic alkenes over heterogeneous catalysts. Thanks to the careful selection of a peculiar combination of solid catalyst, oxidant and solvent, *i.e.*, Ti-grafted mesoporous non-ordered silica, *tert*-butylhydroperoxide and α,α,α-trifluorotoluene, it has been possible to obtain particularly promising yields (up to 73%) and excellent selectivities (>98%) in the epoxidation of 1-octene. Such unprecedented high selectivity to terminal linear epoxides has to be attributed to the choice of α,α,α-trifluorotoluene as an emerging interesting alternative to chlorinated solvents and is due to the negligible acid-catalysed formation of by-products from the newly obtained epoxide. The catalytic system proved to be heterogeneous in nature and fully recoverable and reusable, without the need of intermediate regeneration treatments under harsh conditions. Such catalyst - oxidant – solvent combination can be successfully applied and extended to other linear terminal alkenes (as well as to internal olefins), displaying a fully comparable marked enhancement in selectivity to the terminal epoxide desired product.

Acknowledgements

Financial support from Region Lombardy, through project “SusChemLombardia”, is gratefully acknowledged. The sample of Aeroperl silica was kindly provided by Evonik Industries AG.

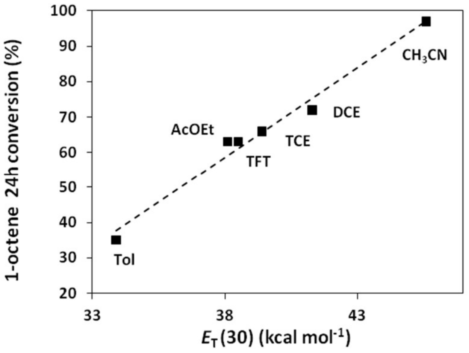


Fig. 1 Correlation between solvent polarity (expressed as Reichardt parameter E_T (30)) and alkene conversion after 24 h in the catalytic epoxidation of 1-octene.

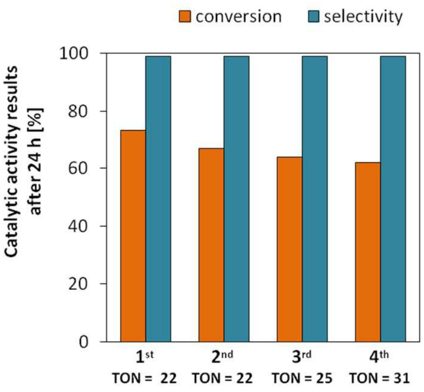


Fig. 2 Recovery and reuse of Ti/SiO$_2$-Dav (four catalytic runs). Reaction conditions for the first run: 150 mg catalyst; 1.5 mmol 1-octene; 7.5 mL TFT; 1.6 mmol TBHP; 363 K oil bath 24 h; stirring ca. 800 rpm; dry N$_2$. The catalyst was filtered after each run and reused after a simple rinsing with fresh solvent. The reagents were scaled down as well to keep the same proportions.

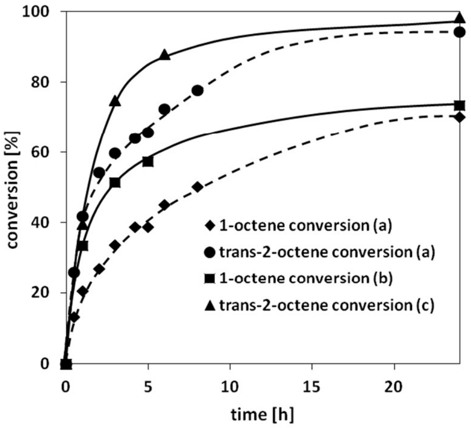


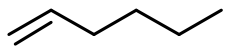
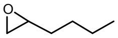
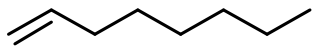
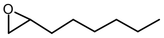
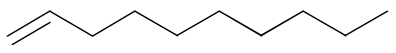
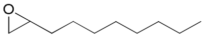
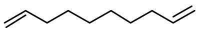
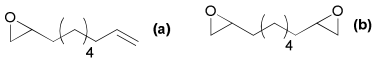
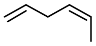
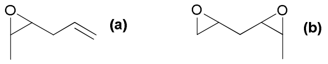
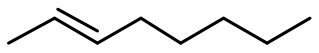
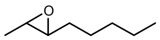
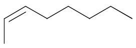
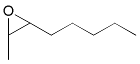
Fig. 3 Reaction **(a)** conditions: 100 mg Ti/SiO$_2$-Dav; 0.5 mmol 1-octene; 0.5 mmol *trans*-2-octene; 5 mL TFT;1.1 mmol TBHP; 363 K oil bath 24 h; magnetic stirring (ca. 800 rpm); dry N$_2$. Reaction **(b)** conditions: 100 mg Ti/SiO$_2$-Dav; 1 mmol 1-octene; 5 mL TFT;1.1 mmol TBHP; 363 K oil bath 24 h; magnetic stirring (ca. 800 rpm); dry N$_2$.Reaction **(c)** conditions: 100 mg Ti/SiO$_2$-Dav; 1 mmol *trans*-2-octene; 5 mL TFT;1.1 mmol TBHP; 363 K oil bath 24 h; magnetic stirring (ca. 800 rpm); dry N$_2$.

Table 1 Textural properties, surface properties and elemental analysis for the Ti-containing silica catalysts.

Catalyst	S_{BET}[m^2 g^{-1}] [a]	Pore diameter [nm]	Pore volume [mL g^{-1}]	Ti content [wt.%]
SiO_2-Aero	315	n.d.[b]	n.d.	-
Ti/SiO_2-Aero	295	n.d.	n.d.	0.59
SiO_2-Dav	580	4÷11	0.97	-
Ti/SiO_2-Dav	474	4÷11	0.81	1.14
MCM-41	890	2.5	0.71	-
Ti/MCM-41	713	2.2	1.05	0.65

[a] Specific surface area (from BET analysis). [b] Not determined.

Table 5 Catalytic epoxidation of linear alkenes over Ti/SiO_2-Dav with TBHP in α,α,α-trifluorotoluene[a]

Entry	Olefin	TON[b]	Time / h	Products	C [%][c]	S [%][d]
1		22	5		68	98
2		17	5		57	99
3		7	5		37	99
4		6	7		29	70**(a)** 30**(b)**
5		7	5		68	98**(a)** 2**(b)**
6		17	6		88	99
7		15	6		66	99

[a] Reaction conditions: 100 mg catalyst Ti/SiO_2-Dav; 1 mmol olefin; 5 mL α,α,α-trifluorotoluene; TBHP 1.1 mmol; 363 K oil bath; stirring ca. 800 rpm; under dry N_2. [b] Turnover number computed after 1 h reaction [mmol $_{converted\ octene}$ / mmol $_{total\ Ti}$]. [c] Alkene conversion. [d] Selectivity to epoxide.

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