

Cite this: *Green Chem.*, 2011, **13**, 1806

www.rsc.org/greenchem

PAPER

Epoxidation of methyl oleate with hydrogen peroxide. The use of Ti-containing silica solids as efficient heterogeneous catalysts†

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Received 8th February 2011, Accepted 28th March 2011

DOI: 10.1039/c1gc15151g

Titanium-silica catalysts, obtained by grafting titanocene dichloride onto mesoporous silica (MCM-41 and MCM-48) and onto nanosized pyrogenic silica, were tested in the epoxidation of methyl oleate using aqueous hydrogen peroxide. All titanium-containing materials, combined with the slow addition of hydrogen peroxide, showed good catalytic activity and comparable behaviour in terms of conversion, selectivity and yield of methyl epoxystearate, notwithstanding the morphology and the texture of the silica support. By optimizing the reaction conditions (especially, the catalyst to substrate ratio), high yields up to 91% in epoxide were obtained for Ti/MCM-41 with a high stereoselectivity (80%) for the *cis*-epoxide. The formation of the *cis/trans*-epoxide and the nature of the catalytic reaction pathway are also discussed.

Introduction

Epoxides of fatty acid methyl esters (FAMES) are a class of oleochemicals playing a pivotal role as intermediates in the production of a wide series of important industrial products and materials. Derivatives of FAMES epoxides and, especially, of methyl epoxystearate (the epoxide obtained from methyl oleate epoxidation), indeed find applications in several domains, *e.g.* in the manufacture of lubricants,^{1–5} plasticizers in polymers,^{6,7} wood impregnation,⁸ stabilizers in chlorine-containing resins,⁹ cosmetics,¹⁰ pharmaceuticals^{11,12} and, in the near future, bio-fuel additives.¹³

Nowadays, at an industrial scale, the epoxides of FAMES are generally obtained in homogeneous phase *via* the Prilezhaev reaction, using *in situ* generated peracetic or performic acids.^{14,15} However, the process presents some major drawbacks such as: 1) an uncontrolled opening of the oxirane ring, that leads to low selectivity of *cis/trans*-epoxide, and 2) a cumbersome separation of the excess organic acids from the final reaction mixture. Thus, during last decades, several studies have been performed searching for an active catalytic system for the epoxidation of vegetable oils and their derivatives, in particular FAMES, using

hydrogen peroxide in place of peroxyacids.^{16–19} In this aim, some recent papers reported interesting results using homogeneous, heterogeneous and chemoenzymatic systems. For instance, tungsten-containing heteropolyacid catalysts (“tetrakis”) were used in the presence of hydrogen peroxide and excellent epoxide yields of up to 94% under solvent-free conditions were reached.¹⁹ Similarly, the use of methyltrioxorhenium with an amine adduct led to outstanding selectivity (99%) and conversion (99%) in the epoxidation of soybean oil.²⁰ However, in these two cases, a complete separation of the homogeneous catalyst from the final mixture can pose some problems.

In the field of heterogeneous catalysis, different works over heterogeneous systems based on pure alumina in the presence of hydrogen peroxide were also described and led to high yields in methyl epoxystearate with very good selectivity (>97%), even though a large amount of oxidant with respect to the substrate (7.5 mol oxidant/mol substrate) is necessary.^{17,18} Similarly, a very high selectivity of 97% to methyl epoxystearate was obtained over a large-pore zeolite Ti-BEA and H₂O₂ in the epoxidation of methyl oleate¹⁶ with an interesting oxidant to substrate molar ratio (0.25 mol mol⁻¹). However, with this system, a maximum yield in methyl epoxystearate of only 45% was reached. Then, the epoxidation of soybean oil over the amorphous heterogeneous Ti/SiO₂ in the presence of *tert*-butanol with H₂O₂ in organic solution led to an epoxide yield of 87%.²¹ In this case, however, the separation of the high-boiling alcoholic solvent from the reaction mixture can lead to some difficulties.

Chemoenzymatic epoxidation gained much interest too, as the process typically occurs under mild conditions and with very good chemoselectivities. For instance, Novozym 435, a *Candida antarctica* lipase B immobilized on polyacrylate, is one

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† Electronic supplementary information (ESI) available: DRS-UV-Vis spectra of the calcined catalysts used in the epoxidation reaction are reported in Fig 1-SI. See DOI: 10.1039/c1gc15151g

of the most efficient and stable catalyst for the epoxidation of oleochemicals. Yields in the range of 72–91% for vegetable free fatty acids were obtained with high selectivity (>98%).²² Similarly, the use of Amano A. lipase (from *Aspergillus niger*) in hydrophobic and hydrophilic ionic liquids gave the epoxidized compound with yields in the range of 67–89% after one hour.²³ Since chemoenzymatic systems are highly chemospecific, they can unfortunately be less versatile for a wide series of oleochemical substrates.

Previously, some of us have reported that titanium-grafted silicates are efficient catalysts for the epoxidation of FAMES with *tert*-butylhydroperoxide (TBHP).^{24,25} Mesoporous materials with 3–10 nm ordered pores are suitable systems for such transformations as Ti sites are easily accessible by the bulky reactants and a peculiar cooperative interaction between the hydrophilic one-dimensional pores of the Ti-MCM-41 enhances the formation of epoxy FAME derivatives with noteworthy performance. Nevertheless, even though TBHP has the advantage of high selectivity, it is not the most sought-after oxidant from the point of view of atom economy and environmental sustainability. Hydrogen peroxide represents a more promising alternative.^{26–28} As a main drawback, the use of hydrogen peroxide usually leads to a rapid deactivation of mesoporous Ti-silica catalysts due to a clustering of surface Ti species.²⁹ By applying a slow dropwise addition of hydrogen peroxide in the reaction mixture, it has been possible to minimize the detrimental irreversible transformation of isolated Ti centers into titanium oxide-like species, in cyclohexene epoxidation.^{30,31}

In the present work, we have applied the experimental protocol of the controlled slow addition of aqueous hydrogen peroxide to the epoxidation of methyl oleate. Thanks to this procedure we expect to reduce the decomposition of the oxidant, increase the catalyst stability and reach high yields in epoxide.

Results and discussion

Titanium-grafted silica materials were used as heterogeneous catalysts in the liquid-phase epoxidation of methyl oleate with hydrogen peroxide under batch conditions.

Titanium active centres were obtained by grafting titanocene dichloride (Ti(Cp)₂Cl₂), as previously proposed by Maschmeyer *et al.*³² and then optimized by some of us for a wide series of silica supports.³³ Three silica materials with different structural and textural features (Table 1) were used as supports to evaluate the influence of the silica support on the catalytic performance.

The main advantage of such grafting methodology is that Ti(IV) sites are situated on the surface, are well dispersed and are

Table 1 Specific surface area (S_{BET}), mean pore diameter (D_p), titanium loading of Ti-containing silica catalysts after calcination

Catalyst	$S_{\text{BET}}/\text{m}^2\text{g}^{-1}$	D_p/nm	Ti content (wt%)
Ti/MCM-41	930	3.6	0.80
Ti/MCM-48	982	3.8	0.79
Ti/Aerosil	262	n.d.	0.64

n.d. = not determined

all virtually active and accessible to the reactants. In particular, Ti(Cp)₂Cl₂ was grafted over: 1) one-dimensional hexagonal ordered mesoporous material (MCM-41); 2) three-dimensional cubic ordered mesoporous material (MCM-48); and 3) nonporous pyrogenic nanosized silica particles (Aerosil).

The titanium content is comparable in all the samples and it gave rise to an even dispersion of titanium sites on the silica. Actually, the surface concentration of Ti sites was always lower than 0.3 Ti/nm² and this reduces the aggregation of catalytic centres during the epoxidation in the presence of hydrogen peroxide, as previously shown in the cyclohexene epoxidation on similar materials.³⁰

The DRS-UV-Vis spectroscopic analysis is a tool to evaluate the coordination state of Ti(IV) (species in tetrahedral coordination at 220–260 nm and species in octahedral coordination at 260–290 nm) as well as the degree of isolation of Ti(IV) in the silica matrix. Indeed, absorption bands above 290 nm indicate the aggregation of some Ti through the formation of Ti–O–Ti bonds. The DRS-UV-Vis spectra of the three samples showed mainly isolated Ti(IV) sites in Ti/MCM-41 and Ti/MCM-48 with a higher proportion of tetrahedral Ti for MCM-41. For Ti/Aerosil a broader distribution of Ti sites was evidenced by a larger band revealing not only the presence of Ti(IV) isolated sites in octahedral coordination, but also some additional aggregation of Ti centres (Figure S1 – supplementary information†).

The results obtained in the methyl oleate epoxidation with hydrogen peroxide are summarized in Table 2.

Earlier, some of us reported that Ti(IV) sites grafted onto the walls of a well-ordered one-dimensional mesoporous MCM-41 showed much better performances in the selective epoxidation of fatty acid methyl esters with TBHP than compared with Ti(IV) centres grafted onto non-ordered mesoporous or nonporous silicas.^{24,25} This particular behaviour was attributed to a synergistic interaction between the elongated shape of quasi-linear FAMES (especially the methyl elaidate²⁵) and to a favoured approach of partially oxidised FAMES (especially methyl ricinoleate³⁴ and

Table 2 Liquid-phase epoxidation of methyl oleate with aqueous hydrogen peroxide over Ti-silica catalysts after 24 h reaction

Entry	Catalyst	C (%)	S EPOX (%)	S ENON (%)	S KETO (%)	Y EPOX (%)	<i>cis/trans</i> EPOX ratio	Ox. Eff. (%)
1	Ti/MCM-41	52	83	11	6	43	80:20	39
2	Ti/MCM-48	52	78	12	10	41	72:28	39
3	Ti/Aerosil	47	83	13	10	39	78:22	38
4	MCM-41	33	50	25	22	17	38:62	25
5	No catalyst	24	40	38	22	10	26:74	18

Reaction conditions: 1.5 mmol methyl oleate, 2 mmol aq. H₂O₂ (50%), 50 mg catalyst, H₂O₂:substrate molar ratio = 1.3:1, CH₃CN, 24 h, 85 °C, dropwise oxidant addition 0.01 ml min⁻¹. C: substrate conversion; S: selectivity; Y: yield; Ox. Eff.: oxidant efficiency.

methyl vernolate²⁴) to the inner hydrophilic pore surface of MCM-41.

In contrast, in this report, all materials (Ti/MCM-41, Ti/MCM-48 and Ti/Aerosil; Table 2, entries 1 to 3) showed very similar behaviour in terms of conversion, selectivity and yield, with values of *ca.* 50%, 80% and 40%, respectively. Such results are in the same order of magnitude with those obtained over Ti-BEA.¹⁶ They are also the first ones obtained, to our best knowledge, in methyl oleate epoxidation with aqueous hydrogen peroxide over Ti-grafted silica materials. Interestingly, the presence of some Ti–O–Ti domains in Ti/Aerosil (as evidenced by DRS-UV-Vis absorption bands above 300 nm) did not affect negatively the epoxidation performance and such behaviour can be attributed to the favorable conditions due to the slow addition of oxidant.³⁵

In addition, in these examples, it is evident that the morphology and the texture of the silica support do not play a key role in terms of catalytic activity (Table 2, entries 1–3). In fact, when hydrogen peroxide is used as oxidant instead of the sterically more demanding TBHP, the steric interactions between the FAME substrate and the porous catalyst are not decisive and the morphology of the catalyst is not a critical factor.

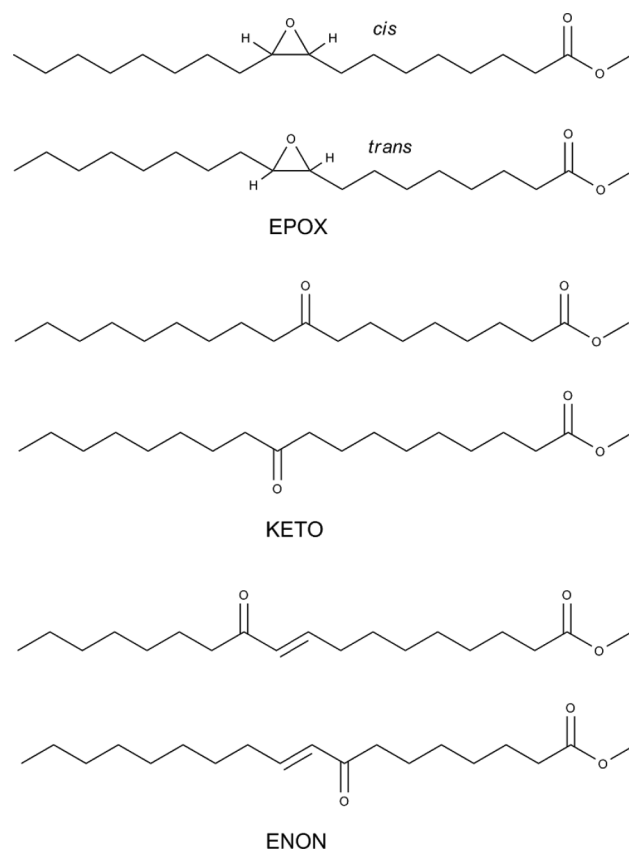
Such a result is consistent with other recent observations on different Ti-based catalytic systems, where, in the narrow interlayer space of a Ti-containing layered clay, the epoxidation reaction takes place with H₂O₂ as oxidant, but it does not with TBHP.³⁶

In terms of selectivity, methyl epoxystearate (EPOX), the epoxidised derivative, is the major product (*ca.* 80%). The most relevant side products are methyl oxooctadecanoate (ENON; a mixture of methyl 8-oxooctadec-9-enoate and methyl 11-oxooctadec-9-enoate) and methyl oxooctadecanoate (KETO; a mixture of methyl 9-oxooctadecanoate and methyl 10-oxooctadecanoate) (Scheme 1). ENON is obtained by allylic oxidation of methyl oleate, whereas KETO is formed *via* oxirane ring rearrangement from the epoxide. In both cases, no particular regioselectivity was detected and the two regioisomers for each product were obtained in practically equimolar amounts. The selectivity values to ENON and KETO are *ca.* 10% over the three catalysts. Blank reactions with pure silica MCM-41 (without Ti; Table 2, entry 4) and with no catalyst (Table 2, entry 5) led to 17% and 10% yield in methyl epoxystearate, respectively.

This behaviour shows that uncatalysed oxidation pathways have a non-negligible influence under these conditions and the presence of purely siliceous MCM-41 is not fully innocent. Actually, in the absence of Ti, most of the methyl epoxystearate observed is due to a free-radical oxidation process (*vide infra*).

In terms of stereoselectivity, the epoxidation of methyl oleate can lead to the formation of *cis* and *trans*-epoxides depending on the reaction pathway. In fact, when TBHP is used as oxidant, the epoxidation of *cis* methyl oleate proceeds *via* a heterolytic mechanism with retention of the C=C double bond configuration.^{25,37} On the contrary, if a free-radical pathway prevails over the heterolytic one, the formation of the *trans* form, the thermodynamically more stable isomer, is predominant. For this reason, in the absence of Ti (Table 2; entries 4–5) the formation of methyl *trans*-epoxystearate dominates.

In terms of oxidant efficiency (the ratio between the moles of oxidised products produced and the moles of H₂O₂ consumed),



Scheme 1 Products of the reaction: methyl epoxystearate (EPOX), methyl oxooctadecanoate (KETO) and methyl oxooctadecenoate (ENON).

the achieved results (slightly less than 40%; Table 2) are interesting and comparable with the values obtained on homogeneous and heterogeneous systems.^{16,17,38} Also for this parameter, the slow dropwise addition of the oxidant helps in reducing the disproportionation of H₂O₂ into O₂ and H₂O.^{21,31}

To improve the final epoxide yield different strategies have been contemplated and Ti/MCM-41 was used for this optimization. By increasing the oxidant/substrate molar ratio from 1.3 to 4.0, the yield to epoxide rose, but, at the same time, an increase in the formation of *trans*-epoxide was observed as well (Table 3; entries 2 and 4). Such an increase can be explained by a higher proportion of the free-radical pathway of the reaction taking place when an excess of hydrogen peroxide is present.

Conversely, by increasing the amount of catalyst, the conversion of the reaction rises from 52% to 96% and a high selectivity in epoxide (*ca.* 90%) is maintained (Table 4, entries 1–5). By augmenting the amount of Ti (substrate:Ti molar ratio from 180 to 22), it was possible to increase the yield from 43% up to 91%. In this case, no remarkable influence on stereoselectivity was noted, the formation of *cis*-epoxide being always prevalent (around 80%). Nevertheless, the combination of a higher quantity of Ti/MCM-41 (200 mg) and a large excess of H₂O₂ (6 mmol) did not lead to a sensible improvement, since the EPOX yield attained 75% with the formation of a lower fraction of *cis*-epoxide (Table 3, entry 4).

Such results in methyl epoxystearate yields (up to 91%) are the highest data obtained in literature so far over titanium-silica

Table 3 Influence of the amount of hydrogen peroxide on the catalytic performance after 24 h reaction. Tests performed over Ti/MCM-41

Entry	Catalyst (mg)	H ₂ O ₂ (mmol)	C (%)	S EPOX (%)	S ENON (%)	S KETO (%)	S others (%)	Y EPOX (%)	<i>cis/trans</i> EPOX ratio	Ox. Eff. (%)
1	50	2	52	83	11	6	5	43	80:20	39
2	50	6	83	82	12	6	0	68	61:39	20
3	200	2	73	96	1	2	1	70	92:8	55
4	200	6	82	92	5	3	0	75	74:26	20

Reaction conditions: 1.5 mmol methyl oleate, CH₃CN, 24 h, 85 °C, dropwise oxidant addition 0.01 ml min⁻¹. C: substrate conversion; S: selectivity; Y: yield; Ox. Eff.: oxidant efficiency.

Table 4 Influence of the amount of catalyst on the catalytic performance after 24 h reaction. Tests performed over Ti/MCM-41

Entry	Catalyst (mg)	C (%)	S EPOX (%)	S ENON (%)	S KETO (%)	S others (%)	Y EPOX (%)	<i>cis/trans</i> EPOX ratio	Ox. Eff. (%)
1	50	52	83	11	6	5	43	80:20	39
2	100	47	83	9	8	0	39	78:22	35
3	200	73	96	1	2	1	70	92:8	55
4	300	78	86	5	2	7	67	72:28	54
5	400	96	95	3	3	0	91	85:15	73

Reaction conditions: 1.5 mmol methyl oleate, 2 mmol aq. H₂O₂ (50%), H₂O₂: substrate molar ratio = 1.3:1, CH₃CN, 24 h, 85 °C, dropwise oxidant addition 0.01 ml min⁻¹. C: substrate conversion; S: selectivity; Y: yield; Ox. Eff.: oxidant efficiency.

molecular sieve catalysts with aqueous hydrogen peroxide. In addition, the effectiveness of oxidant use is promising also in terms of oxidant to catalyst and oxidant to substrate ratios. Under optimized conditions (Table 4; entry 5), the oxidant to catalyst ratio (mol H₂O₂/mass_{cat}) and oxidant to substrate ratio (mol mol⁻¹) are as low as 0.005 and 1.3, respectively. Actually, the value of oxidant to catalyst ratio is better than the results typically reported in literature, spanning from 0.008 in the epoxidation of methyl oleate over Ti-BEA,¹⁶ up to 0.1, in soybean oil epoxidation over Ti/SiO₂.²¹

Finally, it is important to understand the reasons leading to *trans*-epoxide formation under the tested conditions. Since in the reaction medium acetonitrile and hydrogen peroxide are simultaneously present, it can be assumed that the formation of *trans*-epoxide is due to a Payne-type free-radical reaction, where peroxyimidic acid is formed *in situ*, typically under alkaline conditions.³⁹ Actually, specific tests have confirmed that the formation of peroxyimidic acid occurs and Payne oxidation takes place.

However, some of us have recently reported that there is no influence of the Payne reaction in the epoxidation of cyclohexene over Ti(IV)-silica catalysts in acetonitrile with dropwise addition of hydrogen peroxide under fully comparable conditions.³⁰ To understand the apparent contradiction, *i.e.* Payne-type oxidation occurs only in the epoxidation of methyl oleate, it must be recalled that commercial methyl oleate samples (even reagent grade) always possess some mild alkalinity, due to residual amounts of basic transesterification catalysts during the production steps⁴⁰ and such alkalinity promotes the formation of peroxyimidic acid in the reaction mixture. In fact, if methyl oleate undergoes a repeated rinsing and washing with 0.1 M aqueous HNO₃, *trans*-epoxide formation is reduced (from 7% to 3% in *trans*-EPOX yield and *cis/trans* EPOX ratio from 26:74 to 50:50).

Epoxidation tests carried out in polar solvents other than acetonitrile showed poorer performance. Similar conversion, but lower selectivities, were obtained in ethyl acetate, while in dichloromethane comparable epoxide selectivity, but lower conversions, were found. The optimal behaviour observed with acetonitrile is consistent with previous reports in the epoxidation of other substrates. In fact, acetonitrile, thanks to its slightly basic nature, minimizes the formation of acid-catalysed secondary products.^{30,41}

The Ti-silica catalysts were easily recovered by filtration, washed, calcined and reused in a second catalytic run. In particular, after the first recycle, Ti/MCM-41 showed a loss of *ca.* 3% in both conversion and selectivity. As observed on different lighter alkenes (cyclohexene or unsaturated terpenes^{30,42}), it is worth noting that a complete removal of the organic side products adsorbed on the catalyst surface is necessary to restore the original activity of the fresh catalyst. Because of this reason, prior to recycling, the solids were carefully washed with methanol and then calcined under dry air at 500 °C.

Experimental

Preparation of ordered mesoporous silicas

MCM-41. MCM-41 was prepared with the molar ratio, 1 SiO₂:0.1 CTAB:0.27 NaOH:32 H₂O.⁴³ 19.06 g H₂O, 0.356 g NaOH and 1.204 g cetyltrimethyl ammonium bromide (CTAB, Aldrich) were mixed at 50 °C until a homogeneous solution was obtained and then 2 g of silica (Aerosil 200, Degussa) were added stepwise and stirred for 1 h. Then the mixture was put in an autoclave at 115 °C for 24 h. The resulting slurry was filtered and washed until neutral pH and dried at 80 °C overnight. The powder was then calcined at 550 °C for 8h.

MCM-48. MCM-48 was prepared with the molar ratio, 1 SiO₂ : 0.175 CTAB : 0.38 NaOH : 120 H₂O.⁴⁴ 214 g H₂O, 1.54 g NaOH and 6.22 g cetyltrimethyl ammonium bromide (CTAB, Aldrich) were mixed at 50 °C until a homogeneous solution was obtained and then 6 g of silica (Aerosil 200, Degussa) were added stepwise and stirred for 2 h. Then the mixture was put in an autoclave at 150 °C for 15 h. The resulting slurry was filtered, without washing, and dried at 80 °C overnight. The powder was poured again in an autoclave with water (7.5 g H₂O per gram of solid), the mixture was stirred for 20 min and the autoclave put at 130 °C for 6 h. This post-treatment was repeated once again. The resulting slurry was filtered and washed until neutral pH and dried at 80 °C overnight. The powder was then calcined at 550 °C for 8 h.

Preparation of Ti-silica catalysts

Catalysts were prepared by grafting titanocene dichloride (TiCp₂Cl₂; Fluka) onto different silicas (MCM-41, MCM-48, Aerosil), as previously described.^{32,42} Aerosil 380 is commercially available from Degussa. Before grafting, the supports were pretreated at 500 °C for 2 h in air and then *in vacuo* at the same temperature for 2 h. Titanocene dichloride was dissolved in anhydrous chloroform (Sigma-Aldrich) under argon and stirred for 2 h at room temperature. Triethylamine (Sigma-Aldrich) or pyridine (Fluka) was then added to the suspension and left overnight under stirring to activate the nucleophilic substitution of surface silanols onto titanocene. A weaker base, pyridine, was used in the grafting over MCM-41 and MCM-48 to protect the support. After filtering, Ti(IV) active centres were obtained after calcination under dry oxygen at 550 °C for 3h.

Textural and spectroscopic characterization

Nitrogen adsorption/desorption isotherms of materials were measured using a Micromeritics ASAP 2010 instrument. The calcined samples were outgassed at 250 °C and titanocene-containing samples at 120 °C until stable static vacuum of 3 × 10⁻³ Torr was reached. Mesopore diameters were calculated from the desorption branch of the nitrogen isotherms by the Broekhoff and de Boer (BdB) method,⁴⁵ which has been shown to provide reliable results for MCM-41 materials.⁴⁶

UV-Vis diffuse reflectance spectra were obtained in a Varian Cary 05E UV-Vis-NIR spectrophotometer using BaSO₄ as background standard. Titanium content was determined by ICP-AES on an Intrepid Iris instrument (Thermo Elemental).

Catalytic tests

All catalysts were pretreated at 500 °C in dry air for 1 h prior to use. The epoxidation tests were carried out in a glass batch reactor under inert atmosphere at 85 °C. Typically, the solution of methyl oleate (1.5 mmol; Aldrich) in 5 ml of acetonitrile was added to the catalyst (50 mg). A solution of hydrogen peroxide (50% aqueous solution) in solvent (2 mmol H₂O₂ in 2.4 mL of solution) was slowly added (0.01 ml min⁻¹ over 4 h) with an automatic dosimetric apparatus. Hot filtration tests followed by separation of the solid catalyst were performed and the resulting solution was tested in catalysis to evaluate the leaching and confirm the heterogeneous nature of the catalytic reaction.

During recycling tests, the catalyst was filtered off, washed with methanol and acetonitrile, calcined at 500 °C for 3 h under dry air, cooled *in vacuo* and reused under the same conditions.

Catalytic performance was determined on GC analysis (HP6890; HP-5 30 m – column; FID detector). Methyl palmitate was added as internal standard. All data were obtained from an average of at least three catalytic tests. Methyl oleate conversion was computed considering the substrate as the limiting agent. At the end of each reaction, minimal amounts of the oxidant were detected by potassium iodide colorimetric tests. For this reason, oxidant efficiency (Ox. Eff.) was calculated, as follows:

$$\text{Ox. Eff. (\%)} = 100\% \times (\sum \text{mol}_{\text{oxidised products}}) / (\text{mol}_{\text{H}_2\text{O}_2 \text{ consumed}})$$

considering the full consumption of the initial hydrogen peroxide after 24 h. Standard deviations on conversion and selectivity values are ± 2% and ± 4%, respectively.

Conclusions

Heterogeneous porous and non-porous grafted titanium-silica catalysts proved to be sustainable and efficient catalysts in the epoxidation of methyl oleate with aqueous hydrogen peroxide. The different textural and morphological features of the mesoporous catalysts did not noticeably affect their catalytic performance. Thanks to the applied protocol of dropwise oxidant addition, the hydrogen peroxide decomposition and local water concentration into the proximity of Ti(IV) sites were minimized. By optimizing the experimental conditions, yields as high as 91% in the desired methyl epoxy stearate were achieved. Such results are the highest data obtained in literature so far over titanium-silica molecular sieve catalysts with aqueous hydrogen peroxide.

Acknowledgements

This work was supported by the European Community's Seventh Framework Programme through the Marie Curie Initial Training Network NANO-HOST, (Grant Agreement no. 215193). M. G., R. P. and N. R. also acknowledge the Italian Ministry of Education and Scientific Research through the network "ItalNanoNet" (protocol no. RBPR05JH2P) and Regione Lombardia ("VeLiCa - From ancient crops materials and products for the future" project) for financial support.

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