

Epoxidation of unsaturated FAMES obtained from vegetable source over Ti(IV)-grafted silica catalysts: A comparison between ordered and non-ordered mesoporous materials

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Abstract

The liquid-phase epoxidation of mixtures of fatty acid methyl esters (FAMES) over titanium-containing silica materials, using *tert*-butylhydroperoxide (TBHP) as oxidant, is here reported. The mixtures were obtained from vegetable renewable source, i.e. from high-oleic sunflower oil, coriander oil, castor oil and soya-bean oil. The influence of the nature and the position of functional groups on the C-18 chain of the FAMES was studied. Very high activity and selectivity were obtained in the epoxidation of castor and soya-bean oil methyl esters in a reaction medium free from organic acids. Ti-MCM-41 (an ordered mesoporous titanium-grafted silica) displayed in this case, for the first time, superior performances, from a synthetic point of view, with respect to non-ordered mesoporous titanosilicates.

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1. Introduction

In last few years the use of renewable feedstock has been often proposed as a feasible and sustainable approach to the production of chemicals, due to both economic and environmental reasons [1,2]. Among them, fatty acids and their derivatives are relatively underused as synthetic starting materials, in spite of their natural abundance. Nevertheless, the exploitation of fats from vegetable sources implies many advantages: not only they are eco-compatible, renewable and non-noxious compounds towards greenhouse effect, but, above all, they can be converted into several multi-functionalised molecules through a relatively small number of synthetic transformations. In fact, the range of compounds obtainable from oils and fats can be extended, by varying the nature and/or the position of the substituents on the fatty acid hydrocarbon chain [3–5]. In particular,

epoxidised fatty acid derivatives from vegetable sources can be used in various domains, e.g. as stabilisers and plasticizers in polymers, as additives in lubricants, as components in plastics and in urethane foams and, in general, as intermediates for a large number of commodities [6–10]. Unfortunately, the severe acidic conditions, under which the conventional performic acid process is commonly carried out, give rise to several drawbacks in industrial plants, mainly due to large amounts of undesired by-products and the manipulation of highly-reactive hazardous chemicals. So, in order not to lose the benefit represented by the exploitation of a renewable raw material, it is worth looking for an alternative epoxidation path [11–13].

In this goal, titanium-containing heterogeneous catalysts have already shown attractive performances in the transformation of mono-unsaturated fatty acid methyl esters (FAMES) [14–16]. Hereafter, four titanium-based catalysts were tested in the heterogeneous epoxidation with *tert*-butylhydroperoxide (TBHP) of four mixtures of FAMES obtained from vegetable oils, whose fatty acid composition is widely different from one another. Since each of the four oils is naturally rich in one pecu-

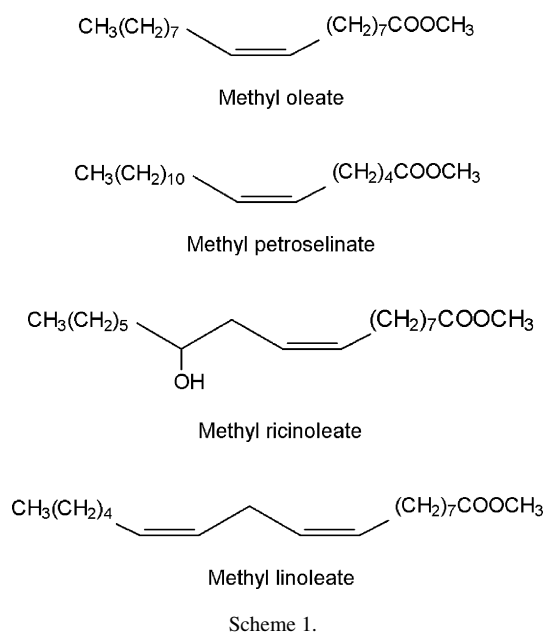
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Table 1
Composition of the fatty acid methyl ester (FAME) mixtures

		Composition (wt.%)			
		HO ^a sunflower	Coriander	Castor	Soya-bean
Palmitate	C16:0 ^b	2	3	2	13
Stearate	C18:0	3	–	1	4
Oleate	C18:1	84	31	6	19
Linoleate	C18:2	10	13	3	56
Linolenate	C18:3	–	–	–	5
Behenate	C22:0	1	–	–	1
Ricinoleate	C18:1–OH	–	–	87	–
Petroselinate	C18:1 Δ ⁶	–	52	–	–
Others		–	1	1	2

^a HO: high-oleic.

^b C *xx*:*y*, where *xx* is the number of carbon atoms of the fatty acid and *y* is the number of unsaturations. Δ^{*n*}, where *n* is the position of the unsaturation.



liar C-18 fatty acid (namely, high-oleic sunflower oil in oleic acid, coriander oil in petroselinic acid, castor oil in ricinoleic acid and soya-bean oil in linoleic acid; Table 1 and Scheme 1), FAME mixtures were taken as models to study how the position of the unsaturations and the substituents on the hydrocarbon chain affect the catalytic features.

Furthermore, to avoid the formation of secondary products due to the opening of the epoxide ring, *tert*-butylhydroperoxide was chosen as the oxidising agent, as it does not give rise to undesired acidic by-products. The catalysts of choice have different textural features and they were selected so that porous and non-porous solids as well as materials with ordered and non-ordered pore structure are all represented in the selected systems.

2. Experimental

Four titanium-containing silicate materials were used as heterogeneous catalyst: namely, Ti–MCM-41 (A), Ti–SiO₂ Davison (B), Ti–SiO₂ Aerosil (C) and TiO₂–SiO₂ Grace (D).

A, B and C were obtained respectively from siliceous MCM-41 [17], from SiO₂ Davison 62 and from SiO₂ Aerosil 380 by grafting titanium sites, using a solution of titanocene dichloride (Ti(Cp)₂Cl₂; Fluka) in chloroform (CarloErba, RPE) and triethylamine (Aldrich) [18,19]. TiO₂–SiO₂ D was obtained from Grace and used without further modification. Each catalyst was calcined at 823 K in flowing oxygen (80 mL min^{−1}) for 6 h before use.

The catalytic performance of the materials was tested in the epoxidation reaction of four FAME mixtures. Each FAME mixture was obtained from vegetable oils (high-oleic sunflower oil, coriander oil, castor oil and soya-bean oil, respectively) by esterification with NaOCH₃ and following distillation. The composition of each FAME mixture was determined by gas-chromatography (Agilent 6890) over a 100 m SP-2330 column (Table 1).

The epoxidation tests were carried out under inert atmosphere in a glass batch reactor (stirring rate 1000 rpm) at 363 K using ethyl acetate as solvent (4 mL; Riedel de Haen; solvent:substrate volume ratio = 8), anhydrous *tert*-butylhydroperoxide (TBHP; Aldrich, solution in decane) as oxidant (oxidant:substrate molar ratio = 1.33), ca. 0.50 mL of FAME mixture and 25 mg of solid catalyst (substrate:catalyst molar ratio = 230). Samples were taken after a reaction time of 1, 3, 6 and 24 h and the products were analysed by GC–MS (HP-5890 equipped with HP 5971 MSD; 30 m HP-5 column; on-column injector; methyl palmitate as internal standard). In none of these tests TBHP has been the limiting reagent and a residual amount of unreacted TBHP has been always observed by gas-chromatographic analysis after a reaction time of 24 h. The exact amount of TBHP left was also determined periodically by conventional thiosulfate/iodide titration. In all cases the recorded TBHP selectivity (i.e. the amount of oxidised products versus the amount of converted TBHP) was very high (>95%).

Specific activity is defined as the amount of converted C=C double bond per total amount of titanium in the unit of time ([mol_{C=C}] [mol_{Ti} h]^{−1}). Selectivity is defined as [mol_{desired product}] / Σ [mol_{all products}]. After each test, the mass balance was always computed and checked (i.e. the amount of consumed products must be equal to the mass of the formed products detected), to avoid the omission of heavy by-products.

Over the four catalysts the leaching of active titanium species in homogeneous phase has been checked by hot separation of the solid catalyst from the reaction mixture (according to [20]). In none of the cases, residual catalytic activity has been detected in the liquid mixture. No transesterification derivatives and no products obtained by positional or stereochemical isomerisation of the double bonds have ever been detected, because of the weak acidity of the titanosilicates here employed.

X-ray diffraction (XRD) patterns of MCM-41 and Ti–MCM-41 (before and after catalytic tests) were obtained on a ARL X'TRA operating with Cu Kα radiation, generated at 30 mA and 40 kV at 2° 2θ min^{−1}, using slits of 0.9°, 0.9° and 0.3 mm for scattering, divergence and receiving, respectively, with graphite monochromator and a Peltier detector.

The amount of ≡SiOH groups on the catalysts was evaluated by thermogravimetric analysis (TA Instruments SDT2960

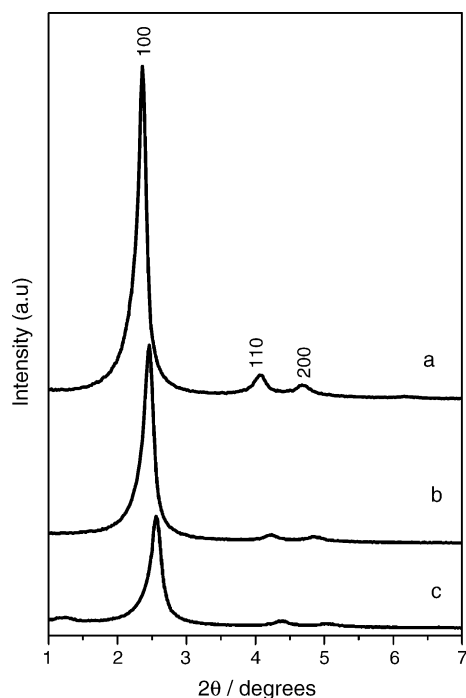


Fig. 1. XRD patterns of (a) calcined MCM-41, (b) $\text{Ti}(\text{Cp})_2\text{Cl}_2$ grafted on MCM-41 and (c) calcined Ti-MCM-41 A.

model) from the water weight loss in the temperature range 473–1073 K.

Diffuse reflectance UV–vis spectra were recorded in situ after outgassing the samples at 823 K for 5 h (Perkin-Elmer Lambda 900 spectrometer with an integrating sphere attachment).

3. Results and discussion

3.1. Catalyst characterisation

Fig. 1 shows XRD profiles of calcined MCM-41 (curve a), MCM-41 after grafting of $\text{Ti}(\text{Cp})_2\text{Cl}_2$ (curve b) and Ti-MCM-41 (curve c) obtained after calcination at 823 K under oxygen, which was performed to remove the organic moieties of the grafted organometallic complex and activate the catalyst. The XRD analysis allowed to monitor the structural modification of the MCM-41 after the introduction of Ti(IV) centres and activation of the catalyst. MCM-41 (curve a) shows the typical X-ray diffraction pattern of an ordered hexagonal network

of mesopores with (100), (110) and (200) reflections [17]. The appearance of well resolved (110) and (200) peaks is an indication that the MCM-41 used for the preparation of the titanium-containing catalyst has a well ordered mesopore network.

By grafting titanocene onto the walls of MCM-41 (curve b), and by subsequent calcination (curve c), the (100) decreased in intensity of around 40%. However, the hexagonal XRD pattern was still clearly observed, as all the three main reflections were found. It was therefore inferred that Ti-MCM-41 catalyst has just a more disordered arrangement of mesopores than the parent MCM-41. The structural rearrangements on passing from MCM-41 (without titanium) to the calcined Ti-MCM-41 were also monitored by a slight shift of the (100) reflection to higher 2θ ; values from 2.36° ($d_{100} = 3.7$ nm) to 2.56° ($d_{100} = 3.4$ nm).

The textural features of the materials, along with the titanium content and the surface silanol concentration, are summarised in Table 2. Catalysts A, B and D displayed a porous structure in the mesopore range, whereas catalyst C, derived from pyrogenic silica, is a non-porous material. Ti-MCM-41 A is an ordered mesoporous material, Ti-SiO₂ B a non-ordered mesoporous material, Ti-SiO₂ C a non-porous material and TiO₂-SiO₂ D a commercial mesoporous mixed oxide.

Diffuse reflectance UV–vis spectra of the calcined catalysts A–D are reported in Fig. 2. A (curve a) shows a sharp UV band at 210 nm, due ligand to metal charge transfer (LMCT) from oxygen to tetrahedral Ti(IV), indicating that a high concentration of isolated Ti(IV) sites in tetrahedral coordination is present on this catalyst [21,22]. Bands at $\lambda \geq 230$ nm are consistent with an incipient oligomerisation of Ti(IV) species. B (curve b) shows a broad band with maximum at 240 nm, which can be assigned to the presence of Ti–O–Ti dimeric species [23]. The broad absorption centred at 250 nm, extending up to 370 nm, showed by C (curve c) and the one at ca. 280 nm of D (curve d) evidence the presence of TiO₂-like clusters [21,23]. Isolated and dimeric Ti(IV) species may also be present in these catalysts, however the very broad main absorption does not allow to recognise clearly any possible band at lower wavelength. Nevertheless, especially in the spectrum of catalyst D, the absorption at 280 nm showed broad shoulders at 210 and 240 nm, which may be attributed to isolated and dimeric species, respectively.

The presence of highly isolated tetrahedral Ti(IV) sites plays a role in favouring both the formation of Ti(IV)-peroxo complexes intermediates [24,25] and the interaction between these oxidis-

Table 2
Textural features, titanium content and surface silanol concentration of the titanium-containing catalysts

Catalyst	$S_{\text{BET}}^{\text{a}}$ ($\text{m}^2 \text{g}^{-1}$)	D_{p}^{b} (nm)	Ti content (wt.%)	Δ wt. ^c (%)	SPC ^d (mmolSiOH g^{-1})
Ti-MCM-41 A	955	2.5	1.88	2.6	2.9
Ti-SiO ₂ B	303	12.7	1.75	1.0	1.1
Ti-SiO ₂ C	268	n.d. ^e	1.78	1.3	1.4
TiO ₂ -SiO ₂ D	303	12.8	1.40	0.9	1.0

^a Specific surface area (from BET analysis).

^b Mean pore diameter.

^c Water weight loss during TG analysis in the temperature range 473–1073 K.

^d Specific polar character: amount of SiOH groups per gram of catalyst.

^e Not determined.

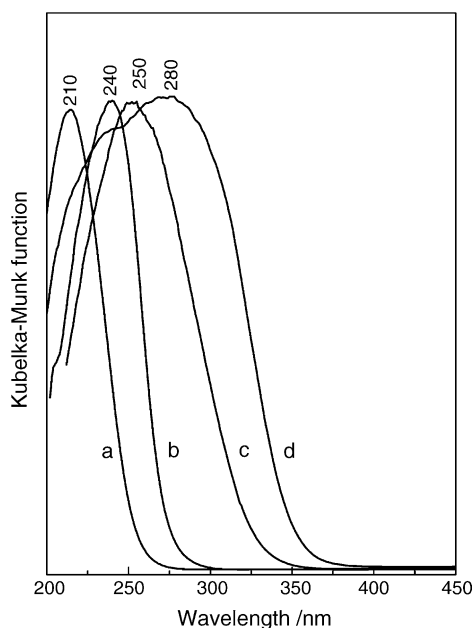


Fig. 2. DR UV-vis spectra of Ti-MCM-41 **A** (curve a), Ti-SiO₂ **B** (curve b), Ti-SiO₂ **C** (curve c) and TiO₂-SiO₂ **D** (curve d) after calcination at 823 K and evacuation at the same temperature.

ing species and organic substrates. Moreover, it is extremely important to evaluate the amount of Ti(IV) sites effectively exposed on the catalyst surface and able to play a role in the epoxidation reaction. CD₃CN adsorption at room temperature on titanium-grafted silicas, followed by FT-IR spectroscopy, was used to measure the fraction of available and exposed Ti(IV) sites. The integrated area of the 2303 cm⁻¹ band, associated with the direct interaction of CD₃CN on Ti(IV) sites [26–28], normalised to the thickness of the pellets, was used to calculate the amount of CD₃CN adsorbed on Ti(IV) sites and therefore to obtain a relative order of the fraction of exposed and accessible catalytic sites for the materials. These data are reported in Table 3.

Since the DR UV-vis characterisation has evidenced that no Ti-O-Ti oligomers are detectable in Ti-MCM-41 **A**, it is possible to assume that this catalyst has the highest number of available sites (i.e. virtually 100% exposure). Consequently, both Ti-SiO₂ **B** and TiO₂-SiO₂ **D** have a 28% exposure and in Ti-SiO₂ **C** only 25% of the Ti(IV) sites is exposed. Such order in the fraction of effectively exposed Ti(IV) sites has to be considered whenever the activity of the different catalysts is compared and the role of the accessible catalytic centres has to be evaluated.

Table 3
Fraction of exposed and accessible titanium(IV) sites

Catalyst	Adsorbed CD ₃ CN (cm ⁻¹ /mg cm ⁻²)	Relative exposition of Ti(IV) active sites (%)
Ti-MCM-41 A	0.6	100
Ti-SiO ₂ B	0.17	28
Ti-SiO ₂ C	0.15	25
TiO ₂ -SiO ₂ D	0.17	28

Furthermore, in order to have a measure of the polar character of the catalyst surface and of the surroundings of the titanium active sites and to predict roughly the ability to interact with lipophilic substrates, the specific amount of surface ≡SiOH group was determined in each sample by thermogravimetric analysis from the water weight loss in the temperature range 473–1073 K. The amount of ≡SiOH per gram was computed assuming that each H₂O molecule derives from the condensation of two ≡SiOH surface groups (Table 2). According to this parameter, Ti-MCM-41 **A** possesses the highest polar character, as it has a concentration of surface silanol groups more than twice with respect to that of the other three catalysts **B-D**.

3.2. Catalytic tests

3.2.1. High-oleic sunflower oil FAME

The activity of the catalysts was first compared in the epoxidation of the high-oleic (HO) sunflower FAME mixture, whose major component is methyl oleate (Table 1). Over this substrate, the ordered mesoporous material Ti-MCM-41 **A** showed to be the most active system (Table 4). Indeed, after a reaction time of 1 h, over catalyst **A** the reaction was 1.6–1.3 times faster than over the other three systems. After 24 h, the unsaturated FAMES of the mixture were practically completely epoxidised over **A** and over **C**, whereas the conversion was lower over catalysts **B** and **D**. The superior behaviour of **A** could be explained not only by the presence of well-spaced and structurally well-defined Ti(IV) tetrahedral centres, but also by the excellent availability and exposure of the catalytically active sites. In fact, both the formation of Ti(IV)-peroxo complexes intermediates [24–25] and the interaction between the oxidising species and the substrates are favoured in **A**. Similarly, as shown in the previous Section 3.1, in **A** virtually all of the titanium sites are exposed and accessible, hence they can all take part in the epoxidation reaction. Thus, the favourable concurrence of these two factors could account for the very good performance of **A**. On the contrary, the smaller amount of available and accessible titanium sites in the proper coordination in catalysts **B-D** is responsible for the poorer results observed in terms of initial catalytic activity.

With regard to selectivity, all the four catalysts led selectively to the formation of methyl epoxy-stearate (the monoepoxy-derivative of methyl oleate). However, the relatively poor selectivity value recorded over **A** (85%) is only apparent, as this value accounts for the selectivity to monoepoxy-derivatives only.

Table 4
Catalytic performances in the epoxidation of the FAME mixture obtained from high-oleic sunflower oil

Catalyst	C (%) ^a	S (%) ^b	A ([mol _{C=C}] [mol _{Ti} h] ⁻¹) ^c
Ti-MCM-41 A	98	85	71
Ti-SiO ₂ B	76	94	44
Ti-SiO ₂ C	95	96	47
TiO ₂ -SiO ₂ D	66	90	55

^a Conversion of unsaturated FAMES after 24 h.

^b Selectivity to monoepoxides after 24 h.

^c Specific activity after 1 h.

Table 5

Catalytic performances in the epoxidation of the FAME mixture obtained from coriander oil

Catalyst	C (%) ^a	S (%) ^b	A ([mol _{C=C}] [mol _{Ti} h] ⁻¹) ^c
Ti–MCM-41 A	94	91	26
Ti–SiO ₂ B	62	94	12
Ti–SiO ₂ C	59	87	25
TiO ₂ –SiO ₂ D	42	80	37

^a Conversion of unsaturated FAMES after 24 h.^b Selectivity to monoepoxides after 24 h.^c Specific activity after 1 h.

Actually, since in high-oleic sunflower FAME a 10 wt.% of di-unsaturated methyl ester is present in the starting mixture (methyl linoleate; Table 1), this component was completely epoxidised over the very active catalyst **A** and, after 24 h, a remarkable amount (ca. 8%) of diepoxy-stearate was detected in addition to monoepoxy-stearate. In contrast, in the tests over **B**, **C** and **D** the doubly-epoxidised component was barely detected.

3.2.2. Coriander oil FAME

When the epoxidation was carried out on the FAME mixture obtained from coriander oil, a different behaviour was observed. The major component of such mixture is methyl petroselinolate (52%), whose C=C unsaturation is located at C-6 position.

In general, all catalysts (**A–D**) were less active in the epoxidation of the mixture obtained from coriander oil than that from HO-sunflower oil (Table 5 versus Table 4). In particular, if the specific activity after 1 h is considered, the mixed oxide **D** resulted to be the most active catalyst. Conversely, if the data after a reaction time of 24 h are considered, Ti–MCM-41 **A** was by far the most active catalyst with respect to the other three ones. The catalyst **D** indeed, in spite of its high initial conversion rate, lost rapidly its activity and after 24 h a conversion of 42% only is reached. Nevertheless, it is worth noting the small initial activity of catalyst **A**, taking into account that the ordered Ti–MCM-41 material showed previously to be a very active catalyst in the epoxidation of pure monounsaturated FAMES, such as methyl oleate or methyl elaidate [15].

The low activity observed over all systems in the epoxidation of the petroselinolate-rich FAME mixture is consistent with the behaviour observed in previous reports over a conventional oxidant reagent (*m*-chloroperbenzoic acid) [29] or an alumina-supported molybdenum oxide catalyst [30]. Indeed, Gunstone and co-workers noted that epoxidation rate is slower the closer the C=C bond to the terminal carbon atoms (i.e. either to the carbomethoxy group or to the ω-carbon). Accordingly, methyl petroselinolate was 2.6 times less reactive than methyl oleate over the heterogeneous MoO₃ system.

3.2.3. Castor oil FAME

When castor oil FAME mixture, whose major component is methyl ricinoleate (87%), was used as substrate, Ti–MCM-41 **A** displayed a striking initial activity with respect to the other catalytic systems **B–D** (Table 6). In fact, only over catalyst **A** the substrate was epoxidised in large amount as soon as after 1 h and it was completely and selectively converted after

Table 6

Catalytic performances in the epoxidation of the FAME mixture obtained from castor oil

Catalyst	C (%) ^a	S (%) ^b	A ([mol _{C=C}] [mol _{Ti} h] ⁻¹) ^c
Ti–MCM-41 A	97	>98	130
Ti–SiO ₂ B	76	97	30
Ti–SiO ₂ C	53	98	16
TiO ₂ –SiO ₂ D	80	>98	56

^a Conversion of unsaturated FAMES after 24 h.^b Selectivity to monoepoxides after 24 h.^c Specific activity after 1 h.

24 h. In contrast, the other three catalysts showed an activity similar (**D**) or even poorer (**B** and **C**) than that observed for HO-sunflower oil mixture. In all cases, methyl 12-hydroxy-9,10-epoxyoctadecanoate was selectively obtained and very small amounts of 12-oxo-octadec-9-enoate were detected (<2%).

So, only Ti–MCM-41 **A** displayed a marked enhancement of the epoxidation rate due to the presence of the OH-group in homoallylic position. Such favourable effect is well known on homogeneous catalysts [31] and has been deeply studied by some of us in the epoxidation of unsaturated terpenes over heterogeneous titanium-containing silicate systems [19,32]. It is therefore likely that the peculiar morphology of the Ti–MCM-41 (with mono-dimensional and relatively ‘narrow’ mesopores) improves the interaction between the OH-moiety of the bulky methyl ricinoleate molecule and the catalyst surface, hence helping the formation of the substrate-peroxide adduct and enhancing the oxygen transfer from the oxidant to the alkene.

3.2.4. Soya-bean oil FAME

When the reaction was carried out on the FAME mixture derived from soya-bean oil, the influence of the presence of a di-unsaturated methyl ester as major compound (methyl linoleate; 56%) was studied. In this case, once again, Ti–MCM-41 **A** showed a higher activity with respect to the other three systems (Table 7). That is to say, the remarkable activity of **A**, already observed in the epoxidation of the HO-sunflower and castor oil FAME mixtures, is even more pronounced in the epoxidation of the methyl esters derived from soya-bean oil. In fact, **A** is 2.2–2.8 times more active than **B**, **C** or **D**, as it is evident from the activity values after 1 h.

In addition, the very high amount of diepoxidised species obtained after 24 h over **A** is another feature worth highlighting. This behaviour can be explained by studying the selectivity pro-

Table 7

Catalytic performances in the epoxidation of the FAME mixture obtained from soya-bean oil

Catalyst	C (%) ^a	S (%) ^b	A ([mol _{C=C}] [mol _{Ti} h] ⁻¹) ^c
Ti–MCM-41 A	90	56	96
Ti–SiO ₂ B	54	21	37
Ti–SiO ₂ C	66	36	44
TiO ₂ –SiO ₂ D	36	19	35

^a Conversion of unsaturated FAMES after 24 h.^b Selectivity to diepoxides after 24 h.^c Specific activity after 1 h.

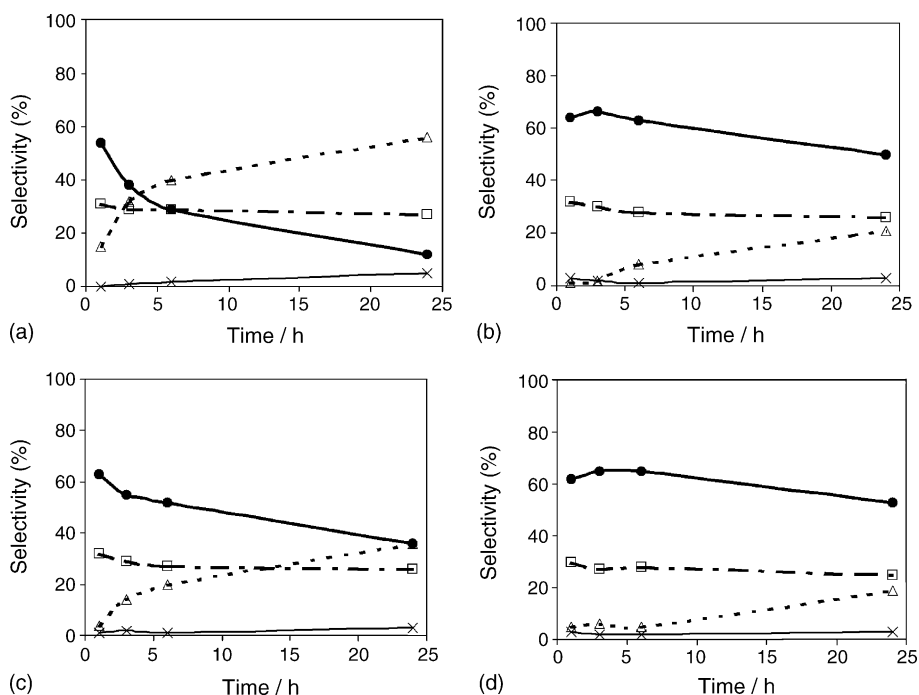


Fig. 3. Selectivity to epoxidised compounds vs. time in the epoxidation of soya-bean oil FAME mixture over Ti-MCM-41 **A** (a), Ti-SiO₂ **B** (b), Ti-SiO₂ **C** (c) and TiO₂-SiO₂ **D** (d). Methyl monoepoxyoctadecenoate (MEEN, ●), methyl 9,10,12,13-diepoxyoctadecanoate (DEAN, △), methyl monoepoxyoctadecanoate (MEAN, □), others (×).

file versus time recorded over the four catalysts (Fig. 3a–d): the amount of the doubly epoxidised compound, i.e. methyl 9,10,12,13-diepoxyoctadecanoate (DEAN), obtained after 1 h on **A** is significantly higher in comparison to the other two catalysts, due to the very high activity of the former. Such a difference accounts for the quantitative transformation of the diene into DEAN after 24 h and Ti-MCM-41 **A** only is able to give rise to DEAN as the major component of the reaction mixture. On the contrary, over **B**, **C** and **D**, the fraction of methyl monoepoxyoctadecenoate (MEEN; the two isomeric compounds derived from the epoxidation of only one unsaturation of methyl linoleate) is more relevant than on **A** after the same reaction time, because of their lower activity. The remaining epoxidised products are due to the epoxidation of methyl oleate and methyl linolenate, already present in the starting soya-bean oil FAME mixture. So, monoepoxides, which are predominantly formed at the beginning of the reaction, are rapidly converted into diepoxides over **A**, whereas over **B**, **C** and **D** the formation of doubly-epoxidised derivatives is more difficult.

This result deserves special attention, as methyl linoleate is usually reported to be less easily epoxidised than methyl oleate [13,33]. The excellent activity of **A** in the conversion of methyl linoleate is likely due to the presence of a high surface concentration of well-defined and highly accessible Ti(IV) tetrahedral sites, as explained above. Nevertheless, it is widely accepted that the titanium site dispersion on the siliceous support and the titanium coordination state are not the only factors affecting the epoxidation activity [34–37]. The hydrophilic interaction between the substrate and the surroundings of the titanium species may also influence the catalytic performances and address the formation of DEAN. In the two-step epoxida-

tion of methyl linoleate, any specific interaction between the intermediate MEEN and the surface of the catalyst may play a significant role in influencing the epoxidation of the second C=C bond.

More precisely, the polar character of the surface and the typical morphology of Ti-MCM-41 with cylindrical channels could favour the approach of the epoxy-group of MEEN to the catalyst surface and the oxygen transfer from Ti(IV)-peroxo complexes to the monoepoxy-monounsaturated substrate. Therefore, the presence of the first epoxy-group on the FAME chain could affect the epoxidation step by a mechanism similar to that observed on unsaturated alcohols and on the castor oil FAME mixture here reported. Indeed, considering the specific polar character of the four materials (Table 2), it is evident that the trend of ≡SiOH availability surrounding the catalytic centres matches very well with the order of selectivity to diepoxides after 24 h (Fig. 4). It is therefore proposed that, after the formation of the first epoxyring on the chain of methyl linoleate, the formation of the second one becomes easier, whenever the surroundings of the titanium centre are rich in silanols.

It is therefore evident that Ti-MCM-41 **A** showed performances that are clearly different from those of other titanosilicate materials (**B–D**). Actually, every change in the nature or position of the functions on the FAME substrate gives rise to remarkable differences in reactivity when **A** is used as catalyst (e.g. the epoxidation rate is enhanced when a hydroxy-group is present and, conversely, is depressed when the C=C bond is shifted from C-9 to C-6 position), whereas such differences are by far less striking over the other catalytic systems.

This unique behaviour is likely due to two concurrent reasons: the peculiar morphology of **A** (an ordered hexagonal network

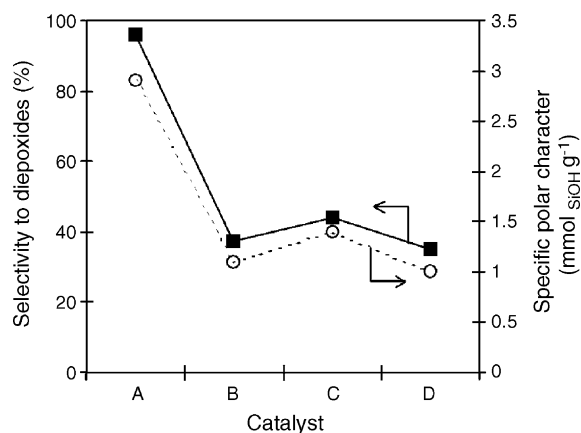


Fig. 4. Comparison between the specific polar character of catalysts A–D and their selectivity to diepoxides after 24 h in the epoxidation of soya-bean oil FAME mixture.

of mesopores) and the particular distribution of the polar and apolar moieties along the fatty C-18 chains.

This is the first time, to our best knowledge, that an ordered mesoporous titanium-containing silicate shows distinctly better performances than other non-ordered ones in the catalytic epoxidation of alkenes. In fact, previous works, carried out in a systematic way under the same conditions, evidenced that the use of ordered mesostructured materials is not strictly necessary when small- or medium-sized substrates have to be epoxidised [34]. On the other hand, in this report, we enlighten the advantages of using Ti–MCM-41 rather than other non-ordered titanosilicates, especially in the epoxidation of castor oil or soya-bean oil FAME mixtures.

Nevertheless, by combining the specific activity values in Tables 4–7 and the data of relative exposition of Ti(IV) active sites (Table 3), it is also evident that the few exposed titanium centres in non-ordered solids B, C and D are by far more active, taken singularly, than those present on Ti–MCM-41 A. In fact,

by normalising, for instance, the specific activity values of HO-sunflower oil FAME epoxidation (Table 4) with respect to the exposed titanium sites, the following turn-over frequency values (defined as amount of converted C=C double bond per amount of exposed titanium in the unit of time) are obtained: 71, 157, 188 and 196 h⁻¹, for A, B, C and D respectively. Such example of good intrinsic activity of titanium sites in grafted low surface-area silicas is a further evidence that the presence of oligomers and/or nanodomains of octahedral Ti(IV), formed during or after the grafting of titanium precursors on the SiO₂ surface (confirmed by UV–vis DRS), is not detrimental when TBHP is used as oxidant [34]. However, in the present work, the four catalysts were considered in their entirety and, in this case, Ti–MCM-41 displayed attractive performances in terms of conversion, selectivity and short reaction times for a potential future application, thanks to the large availability of titanium sites, even if they are not as active, considered singularly, as the sites found over catalysts B, C and D.

3.3. Recycling tests

To better fulfil the green chemistry guidelines and to assess the propensity of the materials to be recovered and reused, the A–D catalysts were recycled in a second catalytic run for the epoxidation of the HO-sunflower FAME mixture. The solid catalyst was filtered, washed with fresh solvent and then re-activated in air at 823 K. Such calcination step proved to be essential to restore the previous catalytic activity and to remove the sticky organic deposits (mainly high molecular mass compounds derived from the oligomerisation and condensation of fatty epoxides), which are strongly adsorbed on the solids during the 24 h reaction and which lead to an irreversible deactivation of the catalyst. In fact, some tests in which fresh reagent (HO-sunflower FAME mixture) and fresh oxidant (TBHP) were added into the reaction mixture after a time of 20 h showed that practically no further reaction occurred in the following 6 h.

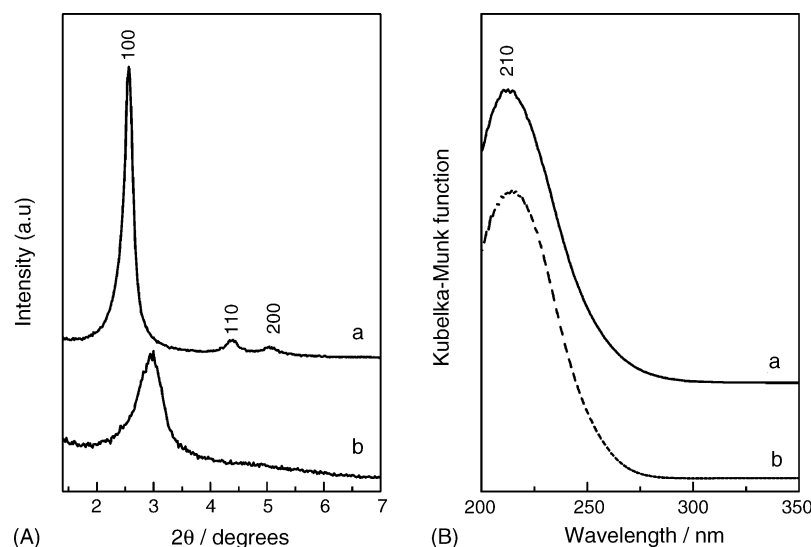


Fig. 5. XRD pattern (section A) and DR UV–vis spectra (section B) of freshly calcined Ti–MCM-41 (curve a) and Ti–MCM-41 re-activated after one catalytic test (curve b).

After the re-activation, in the second run, the diminution in initial activity was moderate in the case of the grafted systems A–C (ca. 10% less than the activity of the fresh catalyst) and a bit larger (16%) in the case of the commercial solid D. The selectivity values were in all tests as good as those obtained on the fresh catalysts. Such behaviour suggests that there is not a noteworthy modification or rearrangement of the catalytic active site during the re-activation and the recycling steps.

This is confirmed also by XRD and DR UV–vis analyses of Ti–MCM-41 A catalyst after its use in catalytic tests (Fig. 5). XRD pattern diffraction (section A, curve b) showed that the (1 0 0) peak shifted to higher 2θ values, broadened and decreased in intensity respect to the (1 0 0) peak of the fresh sample (curve a), indicating a shrinkage of the hexagonal unit cell and a decrease of pore organization. Nevertheless, the presence of the (1 0 0) peak indicates that the hexagonal organization of the MCM-41 mesopores is not completely lost. DR UV–vis spectra (section B) shows a narrow band at ca. 210 nm both on fresh and used Ti–MCM-41, indicating that Ti(IV) catalytic centres have retained their tetrahedral coordination and have not been significantly modified upon catalytic tests.

4. Conclusions

Titanium-grafted mesoporous silica materials showed to be suitable catalysts for the epoxidation of unsaturated FAME mixtures in a reaction medium that is completely free from organic acids. They are also versatile, as they have been used over a series of four FAME mixtures obtained from different vegetable sources exhibiting interesting performances.

In particular, very high conversion and selectivity values were obtained with Ti–MCM-41 in the epoxidation of castor oil or soya-bean oil FAME mixtures.

In such cases, the superior catalytic performances displayed by this ordered mesoporous titanosilicate with respect to the other non-ordered materials can be explained by the concurrence of various favourable factors, such as the presence of large amounts of highly accessible and well defined Ti(IV) tetrahedral active sites and the peculiar environment around the Ti(IV) sites (i.e. the high density of silanols surrounding the Ti(IV) sites), which accounts for the enhanced formation of epoxidised species when highly polar moieties (for instance, hydroxy-group in methyl ricinoleate or an epoxy-ring in methyl monoepoxyoctadecenoate) are already present on the substrate molecules.

However, interesting performances were also recorded over grafted non-ordered silicas and, over these materials, the titanium sites (considered singularly) showed remarkable turnover frequency values, even higher than those obtained over Ti–MCM-41.

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