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Titanium–Silica Catalysts for the Production of Fully Epoxidised Fatty Acid Methyl Esters

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Abstract Grafted titanium-containing mesoporous silica catalysts were used in the selective epoxidation of C-18 unsaturated fatty acid methyl esters (FAMEs). High yields in mono- and diepoxide derivatives were obtained under acid-free reaction conditions with TBHP as oxidant. Ti-MCM-41 showed the best performance in terms of activity over the three FAMEs. Easy separation of the desired products and recycling of the catalyst were demonstrated.

Keywords Fatty acid methyl ester · Epoxidation · Titanium catalyst · Renewables · Oleochemicals

1 Introduction

Epoxidised fatty acid derivatives from vegetable sources are used not only in several domains for large-scale applications (e.g. plasticizers in polymers, additives in lubricants or components in plastics) [1–3], but also as precursors of a wide series of high added-value compounds (such as in specific formulations for lubricants, cosmetics or biochemical applications) [4–7]. More environmentally friendly and 'cleaner' synthetic routes than the nasty conventional process based on peroxoacids are thus desirable. Methyltrioxorhenium [8, 9], immobilized chemoenzymatic systems [10, 11] and titanium-containing silicas [12–15] seem to be currently the most promising alternatives as catalysts for the epoxidation of unsaturated fatty derivatives. Actually, the difficult catalyst separation and metal recovery are major disadvantages for the homogeneous systems to an easy exploitation of the process. On the other hand, immobilized enzymes display good performances and are easily recyclable, but they are very sensitive to the kind of substrate employed and they are often not suitable for obtaining high yields in polyepoxidised products. In the field of the selective oxidation of oleochemicals, titanium–silica catalysts showed good stability, versatility and recoverability with respect to conventional systems [2]. The use of titanium-containing heterogeneous systems provides a suitable and practical methodology for the production of mono- and di-unsaturated fatty acid methyl esters (FAMEs) with high purity and under acid-free conditions to be used as intermediates in the production of high added-value fatty derivatives.

In the present work, particular attention was paid to the extensive epoxidation of C-18 FAMEs and to obtaining satisfactory yields of epoxy derivatives after a simple work-up of the reaction mixture.

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2 Experimental Details

Ti-MCM-41 (1.8 wt.% Ti; 950 $m^2\ g^{-1}$ surface area; 2.5 nm mean pore diameter) and Ti–SiO_2 (1.9 wt.% Ti; 285 $m^2\ g^{-1}$ surface area; 16 nm mean pore diameter) were prepared by grafting titanocene dichloride, $Ti(Cp)_2Cl_2$ (Fluka, purum >95%) onto either a purely siliceous mesoporous MCM-41 or a commercial silica (obtained from

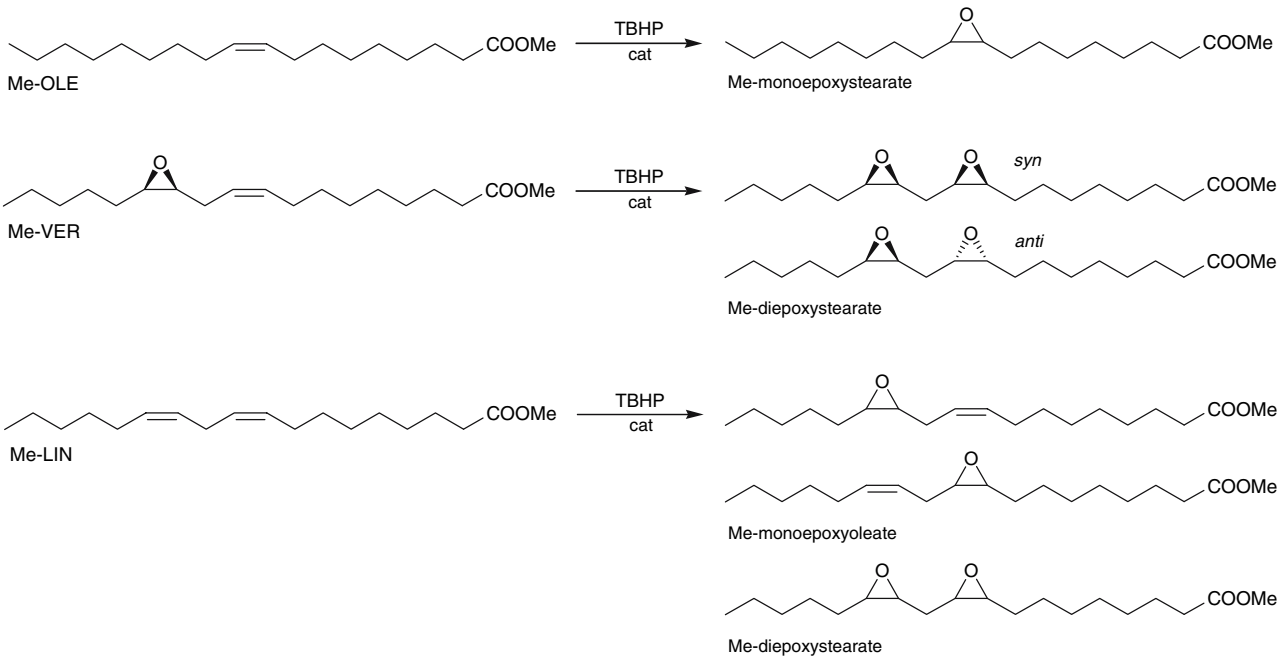
Grace) [14, 16]. Methyl oleate (Aldrich, 99%) and methyl linoleate (Aldrich, ≥99%) were used as received. Vernonia oil (70% vernolic acid, as determined by GC analysis; 2.1 epoxy functionalities per molecule) was obtained from Ver-Tech, Inc. (Bethesda, USA). Methyl vernolate was obtained by transesterification of vernonia oil with methanol in the presence of sodium methoxide, followed by purification by chromatography on a silica gel 60 column, with a mixture of hexane:ether (10:1) as the eluent. The catalysts were calcinated at 773 K under dry air before use. The epoxidation tests were carried out in a glass batch reactor (stirring rate 500 rpm) at 363 K using ethyl acetate (AcOEt, Carlo Erba), as solvent (2.5 mL), previously dried on molecular sieves (3A) and methyl palmitate (Fluka) as internal standard. Anhydrous *tert*-butylhydroperoxide (TBHP; Aldrich, 5 M solution in decane) was used as oxidant (TBHP/FAME molar ratio = 1.4 and 2.2). The Ti to substrate molar ratio was 1:80. The presence of the oxidant at the end of each reaction was systematically confirmed by means of GC analysis or iodometric titration. Samples were analysed by GC analysis (HP5890; HP-5 column, 30 m × 0.25 mm; FID or MS detectors, head pressure 150 kPa). Standard deviation is ±2% and ±3% in conversion and selectivity values, respectively.

The desired epoxidised FAMEs were isolated from the final mixture, after filtration of the catalyst, by treatment with sodium thiosulfate and concentration under vacuum. Eventually, longer times under high vacuum (with liquid nitrogen trap) were needed to minimize the residual amounts of *tert*-butanol left. The recovered catalyst was washed with methanol, calcined at 773 K under dry air and then used again.

3 Results and Discussion

Grafted titanium-containing catalysts, Ti-MCM-41 and Ti–SiO_2, were used as heterogeneous catalysts and compared in the epoxidation of methyl oleate (Me-OLE), methyl vernolate (Me-VER) and methyl linoleate (Me-LIN) (Scheme 1). In general, Ti-MCM-41 showed the best performance in terms of activity over the three FAMEs (Table 1). In all cases the substrate was completely (or almost completely) consumed after 24 h and the highest initial activity (at 1 h) was recorded in the epoxidation of Me-OLE. Such outstanding results are explained by the peculiar chemical environment surrounding the isolated Ti(IV) sites [14]. Conversely, over Ti–SiO_2 lower conversion and initial activity values were observed, even though it was possible to achieve, after 24 h, high yields in monoepoxide from Me-OLE (92%).

Me-OLE was the most reactive substrate over both catalysts (Fig. 1a, b). No epoxide-ring opening or rearrangement by-products were detected and methyl monoepoxystearate was selectively obtained in both cases. This is due to the remarkable selectivity of *tert*-butyl hydroperoxide (TBHP) as oxidant and to the fact that the reaction is carried out under acid-free conditions. The configuration at the unsaturation was retained and from *Z* double bonds *cis* epoxides were systematically prepared.



Scheme 1

Table 1 Epoxidation of unsaturated FAMEs over titanium-grafted catalyst

Catalyst	FAME	C (%)[a]	SA (h^{-1})[b]	S_{MO} (%)[c]	S_{DO} (%)[d]
Ti-MCM-41	Me-OLE	100	54	>98[e]	–
Ti-MCM-41	Me-VER	92	34	–	>98
Ti-MCM-41	Me-LIN	94	38	28[f]	72
Ti-MCM-41	Me-LIN[g]	100	35	4[f]	96
Ti–SiO_2	Me-OLE	92	16	>98[e]	–
Ti–SiO_2	Me-VER	88	15	–	>98
Ti–SiO_2	Me-LIN	61	14	61[f]	39

Conditions: batch reactor; AcOEt solvent; 363 K; TBHP/FAME molar ratio = 1.4

[a] Conversion after 24 h, [b] Specific activity after 1 h, [c] Selectivity to monoepoxide after 24 h, [d] Selectivity to diepoxide after 24 h, [e] Monoepoxystearate, [f] Monoepoxyoleate, [g] TBHP/FAME molar ratio = 2.2

Me-VER was similarly easily epoxidised, but the conversion values of the substrate, although high, in neither case reached 100%. The related diepoxide (diepoxystearate) was the only detected product and the chemoselectivity to the desired compound was thus excellent with both catalysts. In addition, since the starting Me-VER is optically active (the FAME, derived from *Vernonia galamensis* vegetable oil, is methyl (*9Z*)-(*12S,13R*)-12,13-epoxy-octadecenoate), the formation of the two possible diastereoisomers, namely *anti* (*9S,10R,12S,13R*) and *syn* (*9R,10S,12S,13R*) was quantified (Scheme 1). The diastereoselectivity was however very modest and in both cases an *anti*/*syn* ratio of ca. 60:40 was found.

Me-LIN was rapidly converted by Ti-MCM-41 and it showed an initial conversion profile lower than Me-OLE and rather similar to Me-VER (Fig. 1a). With a larger excess of oxidant (TBHP/FAME ratio = 2.2, which corresponds to a TBHP/C=C bond ratio = 1.1) it was even possible to achieve a complete conversion of Me-LIN over Ti-MCM-41 (Table 1). Conversely, over Ti–SiO_2 the initial reactivity of Me-LIN was comparable to the other substrates, but a marked decrease in epoxidation rate was observed after the second hour of reaction, suggesting a more notable deactivation of the catalyst with Me-LIN than with the other FAMEs (Fig. 1b). With regard to selectivity, large amounts of diepoxide were obtained over Ti-MCM-41 (96% yield with TBHP/FAME ratio = 2.2). Such interesting result is explained by the high hydrophilic character of the Ti-MCM-41 surface that favours the adsorption of the monoepoxide, increases the residence time of this intermediate in the surroundings of the catalytically active site and therefore enhances the production of the doubly epoxidised product [15]. With regard to regioselectivity, over both catalysts, the two isomeric monoepoxides (at 9,10 and 12,13 positions) formed in similar amounts, even if a moderate preferential formation of methyl 9,10-epoxyoctadec-12-enoate over methyl 12,13-epoxyoctadec-9-enoate was detected over Ti-MCM-41 (with a ratio of 64:36, respectively). With regard to stereoselectivity, the two couples of *anti* and *syn* diastereoisomeric diepoxides were obtained with a ratio of ca. 60:40, respectively, over both catalysts, as well as observed with Me-VER.

At the end of the reaction, the solid catalyst was easily removed by filtration (or centrifugation) and reused in a new catalytic test, after a calcination treatment to remove the organic side products. The original selectivity of the catalyst was restored with a loss in conversion within 5%. The truly heterogeneous nature of both grafted titanium–silica catalysts was confirmed by hot filtration of the catalyst after ca. 40% conversion (2 h) and by checking the filtrate solution for further reactivity (only 2% of further conversion was recorded).

This epoxidation method can be easily applied to the preparation of grams of pure fully epoxidised FAMEs

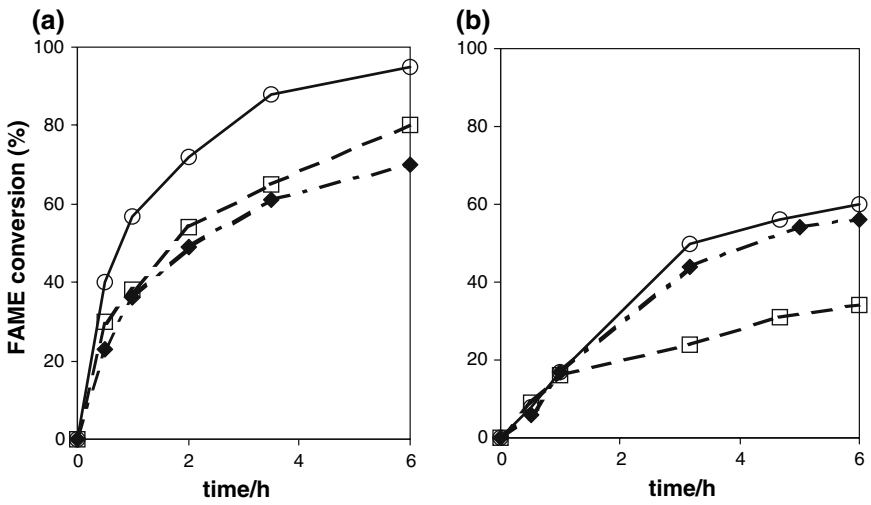


Fig. 1 Conversion profile of Me-OLE (○), Me-VER (◆) and Me-LIN (□) over (**a**) Ti-MCM-41 and (**b**) Ti-SiO_2. Conditions: AcOEt; 363 K; TBHP/FAME ratio = 1.4

without any acidic contaminant by a simple work-up of the final reaction mixture and, for instance, isolated yields as high as 92% in methyl epoxystearate (over batches of 5 g of starting unsaturated FAME) were achieved.

4 Conclusions

Grafted titanium-containing silica materials proved to be suitable catalysts for the extensive and selective epoxidation of unsaturated FAMEs. Thanks to their high versatility they can be employed in the conversion of monounsaturated, diunsaturated and also partially epoxidised substrates. In particular, very high yields (up to 95%) of fully epoxidised methyl linoleate can be obtained over Ti-MCM-41 with a relatively small excess of TBHP oxidant (only 10% more than the stoichiometric amount needed). Furthermore, the ease in catalyst recovery, the use of acid-free reaction conditions and hence the minor presence of secondary products (often incompatible with the following use of the epoxy derivatives) make these catalytic systems promising alternatives to the widely used processes for the epoxidation of oleochemicals and of substrates derived from renewable sources.

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