Soybean oil epoxidation with hydrogen peroxide using an amorphous Ti/SiO$_2$ catalyst

A. Campanella,[a] M. A. Baltanás,[a] M. C. Capel-Sánchez,[b] J. M. Campos-Martín[b] and J. L. G. Fierro*[b]

[a] Instituto de Desarrollo Tecnológico para la Industria Química (UNL – CONICET), Güemes 3450, S3000GNL Santa Fe, Argentina

[b] Instituto de Catálisis y Petroleoquímica, CSIC, c/ Marie Curie, s/n, Cantoblanco, 28049 Madrid, Spain. E-mail: jlgfierro@icp.csic.es; Fax: +34 915854760; http://www.icp.csic.es/eac/index.htm

We report a study of the epoxidation of soybean oil and soybean methyl esters with hydrogen peroxide in dilute solution (6 wt%) using an amorphous heterogeneous Ti/SiO$_2$ catalyst in the presence of *tert*-butyl alcohol. The influence of some relevant process variables such as temperature and the hydrogen peroxide-to-double bond molar ratio on performance is examined. The highest yields of epoxidized olefins were obtained upon using a H$_2$O$_2$: substrate molar ratio of 1.1 : 1. Higher ratios than this were not effective for speeding up the reaction. Under the experimental conditions employed in this work, no degradation of the oxirane ring was observed.

Introduction

Epoxidized vegetable oils (VO) and their derivatives (*e.g.*: fatty acid methyl esters, FAME) have been used for many commercial applications, *e.g.*, as plasticisers and stabilisers in chlorine-containing resins, as additives in lubricants, as components in thermosetting plastics, in cosmetics and pharmaceutical formulations, in urethane foams and as wood impregnants.[1–5] Epoxy fatty acid compounds are obtained at industrial scale mainly by the peracid process.[6–11] The peracid oxidant is obtained *in situ* when a carboxylic acid (usually acetic acid) reacts with hydrogen peroxide in the presence of mineral acids that act as catalysts. Several drawbacks must be improved in the peracid process, including: (i) the selectivity to epoxidized products is relatively low due to acid-catalysed oxirane ring-opening; (ii) the separation of acidic by-products, whose presence may be detrimental for further applications, is not easy; (iii) the handling of highly concentrated hydrogen peroxide and strong acids is dangerous and causes corrosion problems. Thus, in recent years several papers have dealt with the setting up of catalytic processes aimed at overcoming such disadvantages, using more sustainable compounds and technologies.[11–17]

Recently, it has been shown that the incorporation of Ti on an amorphous silica support produces oxidation catalysts that are highly effective in epoxidation reactions with hydrogen peroxide.[18–20] Deployment of this mesoporous support yields active catalysts for the selective oxidation of bulky substrates that are unable to diffuse inside microporous materials, such as the (expensive) titanium silicalites.

From the structural point of view, VOs can be considered to be formed by condensation of a glycerol molecule with three moles of fatty acids (FA), resulting in the formation of a triglyceride molecule and three water molecules.[21] Refined VOs contain a triglycerides percentage of 98%, the other 2% being phosphatides, sterols, tocopherols, free fatty acids, *etc.* Soybean oil (SBO) is a highly unsaturated oil (high iodine value), whose efficient processing affords compounds with a high oxirane index, even though according to its stereochemical structure (Scheme 1) the olefinic chains in triglyceride molecules contain more than 18 carbon atoms. Because of the oxidative properties of Ti/SiO$_2$ and the advantages related to the use of solid catalysts in industrial processes, the use of these amorphous catalysts could open new possibilities in the field of the utilisation of fatty acids and esters if
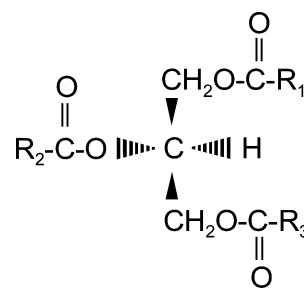
Scheme 1 Triglyceride structure (R$_1$, R$_2$, R$_3$: alkyl groups).

their double bonds could be selectively and 'deeply' epoxidized, forming stable epoxides, employing only a green oxidant such as hydrogen peroxide (*i.e.*, avoiding the use of peracids).

Results and discussion

The amount of titanium incorporated into the silica support was 0.9 wt%. The nitrogen adsorption–desorption isotherms corresponded to type 4 of the IUPAC classification, which are characteristic of mesoporous materials. They also showed a type H1 hysteresis loop located at relatively high pressures of the adsorbate. This kind of loop is usually displayed by porous materials consisting of agglomerates or a compact packing of nearly uniform, regularly ordered microspheres. The surface area was 214 m^2 g^{-1}, and the pore volume 1.5 mL g^{-1}.

The UV-Visible spectrum of the catalyst is shown in Fig. 1. This electronic spectrum consists of one peak located between 200 and 300 nm, which is characteristic of this kind of catalyst. Detailed line-profile analysis revealed the presence of a weak but sharp contribution close to 225 nm, typical of isolated titanium in tetrahedral coordination[22] and an additional, much more intense component at about 250 nm, characteristic of titanium species coordinated with water.[22] The absence of any signal somewhere around 330 nm precludes the formation of three-dimensional TiO$_2$ structures.

High-resolution photoelectron spectra of the Ti 2p core-levels of the catalyst outgassed *in situ* at 773 K were recorded. The spectra showed the characteristic spin–orbit splitting of Ti 2p levels (Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$). Since chemical information can be derived from the analysis of binding energies of each level, attention will only be paid to the most intense Ti 2p$_{3/2}$ component of the doublet. The
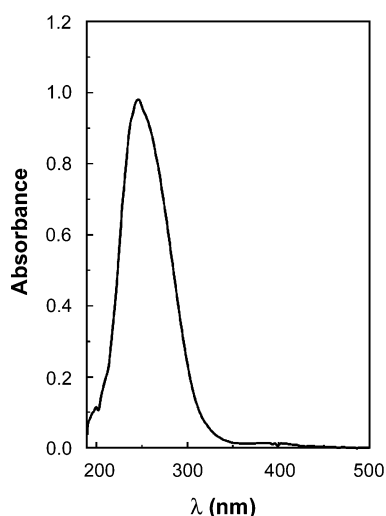
Fig. 1 UV-VIS spectra of the catalyst synthesized.

peak fitting of the experimental Ti $2p_{3/2}$ component revealed one contribution at 460.0 eV, (FWMH = 1.7 eV) typical of Ti(IV) coordinated tetrahedrally to oxide anions.[19,20]

These combined characterization results indicate that the titanium is in a tetrahedral environment, which is currently accepted to be the active site involved in these kinds of oxidation reactions of organic substrates.[22]

The Ti/SiO$_2$ catalyst was tested in the liquid phase epoxidation of SBO and soybean methyl ester substrates with dilute hydrogen peroxide solutions. Reaction conditions, double bond conversion, mass percent of epoxidized oil and percent yield are shown in Table 1.

First, the effect of temperature on the kinetics of soybean oil epoxidation was investigated. In these experiments, a H$_2$O$_2$: double bond molar ratio of 0.6 : 1 was employed. This ratio was selected to minimize by-product formation through oxirane ring-opening, consecutive reactions. An increase in the reaction temperature from 353 to 368 K led to a remarkable increase in the reaction rate at all times (Fig. 2).

In the next step, the differences in reactivity of SBO and the corresponding methyl esters were investigated. Soybean methyl esters were prepared by derivatizing SBO with sodium methoxide. Under the same reaction conditions, the conversion curves of both substrates followed the same trace (Fig. 3). This finding is in agreement with the performance described in the literature for the epoxidation of these substrates with peracids.[23]

A blank experiment was conducted to check that no decomposition of the hydrogen peroxide had occurred during the epoxidation reaction. To this end, the catalyst was added to a solution of H$_2$O$_2$ (6 wt%) in the absence of soybean oil or its methyl ester and kept in a thermostatted bath at 368 K for 48 h, after which the concentration of H$_2$O$_2$ was measured. Since the concentration of
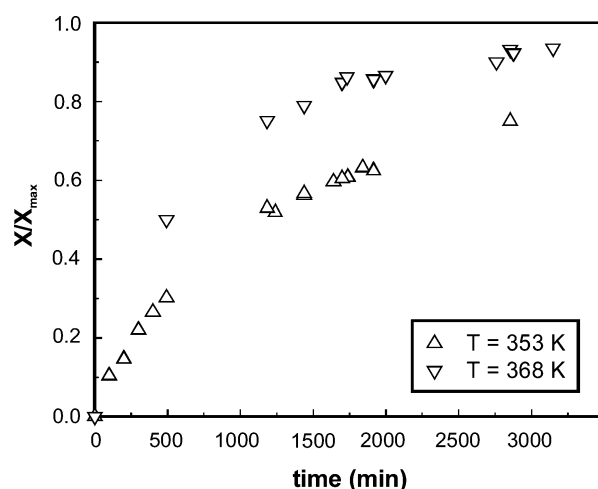

Fig. 2 Influence of temperature on double bond conversion in the epoxidation of soybean oil with hydrogen peroxide (molar ratio H$_2$O$_2$: double bonds = 0.6 : 1, X_{max} = [(IV$_{initial}$ − IV$_{min}$)/IV$_{initial}$]×100, IV$_{initial}$ = 127.67, IV$_{min}$ (theoretical, molar-ratio based, minimum iodine value) = 51.11).
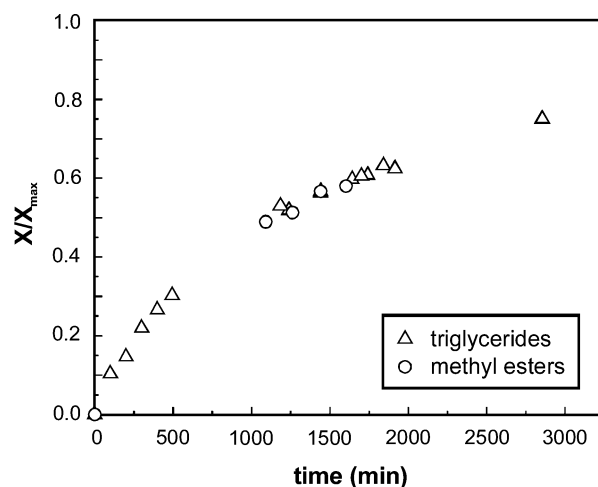

Fig. 3 Influence of the substrate nature on the conversion in the epoxidation of soybean oil with hydrogen peroxide (T = 353 K, molar ratio H$_2$O$_2$: double bonds = 0.6 : 1, IV$_{initial}$ = 127.67, IV$_{min}$ (theoretical, molar-ratio based, minimum iodine value) = 51.11). X_{max} = [(IV$_{initial}$-IV$_{min}$)/IV$_{initial}$]×100.

H$_2$O$_2$ was the same as at the beginning, its decomposition into oxygen and water can be ruled out.

In previous experiments, the molar ratio between H$_2$O$_2$ and double bonds (C=C) was kept constant and equal to 1.1 : 1 because

Table 1 Reaction conditions, double bond conversion, mass percent of epoxidized oil and epoxide yield in the study of the epoxidation of soybean oil with hydrogen peroxide in dilute solution (6 wt%) using an amorphous heterogeneous Ti/SiO$_2$ catalyst in the presence of *tert*-butyl alcohol

Protocol	T/K	H$_2$O$_2$: double bonds molar ratio	Duration/ min	Final IV[a]	Final % conversion[b]	Wt% epoxidized oil[c]	% Yield[d]
1	353	0.6 : 1	2855	70.23	44.99	40.19	43.12
2[e]	353	0.6 : 1	1602	83.27	34.78	32.43	34.80
3	368	0.6 : 1	3147	56.13	56.67	52.20	56.01
4	353	1.1 : 1	2873	37.20	72.03	66.97	71.85
5	353	5.5 : 1	1880	35.71	65.95	60.58	65.00
6	343	1.1 : 1	4320	36.54	71.38	67.09	71.98
7	363	1.1 : 1	3257	13.76	89.22	81.79	87.75

[a] IV stands for Iodine Value.[24] Initial iodine value (IV$_{initial}$) was 127.67. [b] Percent conversion of double bonds, calculated as X = [(IV$_{initial}$ − IV)/IV$_{initial}$] × 100. [c] Final weight percent of epoxidized oil (% Ep) in the organic phase. [d] Percent epoxide yield, calculated as Y = [(%Ep)/(%Ep$_t$)] × 100, where %Ep$_t$ stands for the theoretical maximum weight percent of %Ep (%Ep$_t$ = 93.16). [e] Soybean methyl esters ('methyl soyate').

this is the standard ratio used in the epoxidation of this kind of substrate with organic peracids, with only 10% H_2O_2 in excess with respect to the stoichiometric amount.[7] Thus, in order to further explore the influence of the molar ratio of H_2O_2 : C=C on the kinetics of epoxidation, two other levels of this ratio, corresponding to a large excess of the oxidant (5.5 : 1) and an excess of soybean oil (0.6 : 1), respectively, were also examined (Fig. 4). With the
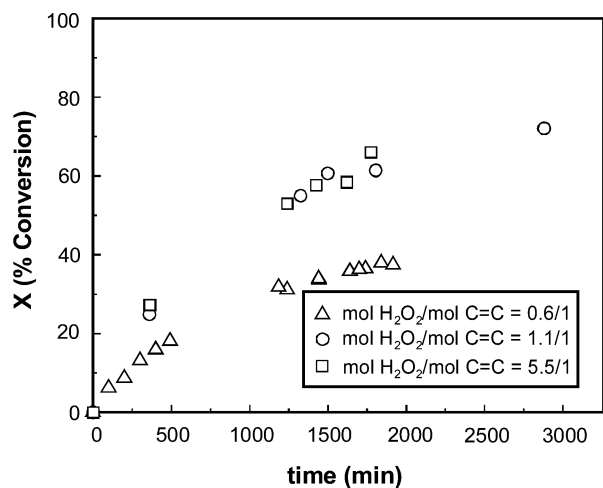

Fig. 4 Influence of the oxidant excess on the conversion in the epoxidation of soybean oil with hydrogen peroxide (T = 353 K).

excess of soybean oil (molar ratio = 0.6 : 1), the kinetics of epoxidation was slower and led to a lower concentration of epoxides at the end of the reaction than for the 1.1 : 1 ratio, as expected (In this case, a maximum epoxidation of soybean oil of 60% could be achieved. Nevertheless, the kinetics found for the 5.5 : 1 ratio almost coincided with the one obtained with the 1.1 : 1 ratio. This indicates that an optimum in reactivity is obtained for the one-to-one molar ratio of H_2O_2 : double bonds, beyond which the active sites of the catalyst cannot activate the molecules of soybean oil any further. Additionally, the increase in the reaction rate when passing from a deficit of oxidant (0.6 : 1) to nearly the stoichiometric amount (1.1 : 1) or a large excess (5.5 : 1) suggests that the presence of the epoxide product in the reaction environment does not have an inhibitory effect on the kinetics of epoxidation. Notwithstanding, at 353 K the kinetics of epoxidation were rather slow, since a sizable amount of double bonds still remained intact at reaction times as long as about 50 h.

In light of the above results, it appeared of interest to re-analyze the influence of the reaction temperature, always using the hydrogen peroxide oxidant in a slight excess (molar ratio of H_2O_2 to C=C of 1.1 : 1). As illustrated in Fig. 5, there was a remarkable impact of the reaction temperature on the epoxidation rate. At 363 K, under these experimental conditions double bond conversion levels above 90% were achieved, although such levels were obtained at still relatively long reaction times (> 54 h).

Gas-chromatography analysis is a powerful tool for identifying and quantifying reaction products, as it is able to simultaneously distinguish between the methyl esters of fatty acids and their epoxides and glycols as well.[24] Since the amounts of glycols in all GC analyses were negligible, no opening of the oxirane ring took place. Thus, it may be concluded that the epoxidation reaction using this amorphous Ti/SiO_2 is highly selective toward epoxide formation, even though long reaction times are required to achieve high conversion levels of soybean oil.

Despite this, if a comparison is made between the epoxidation reaction of SBO with the conventional peracid technology and the one described in this contribution, with a heterogeneous Ti/SiO_2 catalyst, an important advantage of the latter method is seen. The conventional peracid process is coupled with the *in situ* production of peracetic acid (usually at 333 K), by dropwise dosing H_2O_2(aq.)

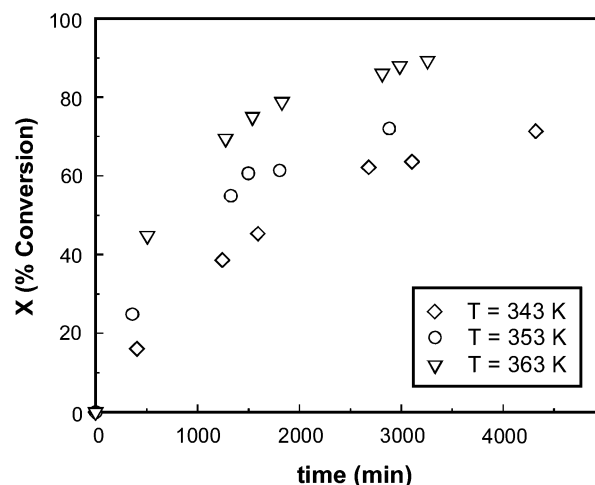**Fig. 5** Influence of temperature on the conversion in the epoxidation of soybean oil with hydrogen peroxide (molar ratio H_2O_2 : double bonds = 1.1 : 1).

at *ca.* 30 wt% concentration, employing a C=C : H_2O_2 : acetic acid molar ratio of 1 : 1.1 : 0.5.[5,7] Under these conditions, low iodine values are obtained for reaction times close to 240 min, although the epoxide yields are deficient because one fraction of the epoxide produced is degraded through ring-opening reactions of the oxirane product. However, the amorphous heterogeneous Ti/SiO_2 catalyst does not degrade the oxirane ring, even though the reaction rate is slower than in the peracid route. Thus, this new heterogeneous process for epoxidizing vegetable oils with only aqueous H_2O_2 (*viz.*, no acids) in the presence of a Ti/SiO_2 catalyst has great potential for applications at industrial scale because corrosive or dangerous reactants are no longer necessary and the complex and costly separation steps after the reactor are also avoided.

However, to be green, the process outlined in the present paper requires an easy separation of products and recycling of solvents at the end of the reaction. The strategy to be implemented once the reaction is finished is the following: at the end of each batch run, after stopping stirring, there will be a (denser) aqueous phase at the bottom of the reactor, which can be simply removed (together with the heterogeneous catalyst) by means of a bifurcation and a three-way valve placed below the vessel and—after mechanical separation of the catalyst—subjected to distillation/rectification to recover *tert*-butanol and 1-phenylethanol from this polar phase. The mixture of epoxidized oil will be fractionated because the vapor pressures of the different compounds that constitute the non-polar organic mixture are very different. The solvents employed do not form azeotropic mixtures and have very different vapour pressures with respect to vegetable oils, which are known to have boiling points well above 613 K (Table 2).

Conclusions

The epoxidation of soybean oil with dilute solutions of hydrogen peroxide in a polar organic medium in the presence of an amorphous Ti/SiO_2 catalyst and *tert*-butanol as diluent of the reactants affords high reaction yields and selectivities to epoxide. The use of a H_2O_2 : C=C molar ratio of 1.1 : 1, slightly higher than the stoichiometric one, gives the highest reaction rate; no further enhancement is obtained by using hydrogen peroxide in a large excess. Even at the highest temperature explored (353 K), which is compatible with the stability of the reactants and products, the reaction time is prolonged if a small amount of catalyst is employed. Notwithstanding, the absence of unwanted side reactions and the negligible decomposition of H_2O_2 deserve further in-depth analyses of the process variables.

Table 2 Vapor pressure of the solvents employed in the epoxidation reaction

	Vapour pressure/Pa		
T/K	1-Phenylethanol	*tert*-Butanol	Water
283	25	1946	1228
293	45	3960	2333
303	80	7533	4240
313	139	13452	7373
323	233	22838	12332
333	388	37050	19918
343	632	57714	31157
353	1015	86845	47342
363	1604	126649	70086
368	2005		84512
373	2498		101323
383	3836		
393	5813		
403	8696		
413	12852		
423	18775		
433	27125		
443	38772		
453	54859		
463	76866		
473	106700		

Experimental

Catalyst synthesis and characterization

The supported titanium catalyst was prepared according to some reports in the literature.[18–20] Titanium isopropoxide (Aldrich, reagent grade; St. Louis, MO, USA) (0.75 g) was dispersed in cyclohexanol (150 mL). The solution was heated to 423 K under stirring and then silica (5.0 g) (Grace Davison G-952, BET surface area: 310 m^2 g^{-1}, pore volume: 1.5 mL g^{-1}) was added to the solution, which was kept under vigorous stirring at 423 K for 2 h. The solid thus obtained was filtered off and washed twice with 150 mL of hot solvent, dried at 383 K, and finally calcined at 773 K for 5 h.

The titanium content of the Ti/SiO$_2$ catalyst was determined using inductively-coupled plasma absorption spectrometry, with a Perkin-Elmer Optima 3300 DV instrument (MN, USA). The BET specific surface area and pore diameters were determined by N$_2$-adsorption at 77 K using a Micromeritics Tristar 3000 apparatus (Norcross, GA, USA). Ultraviolet-visible (UV-Vis) spectra were measured on an optic fiber Advantes AVS-2048 optic fiber spectrophotometer (Advantes, The Netherlands) equipped with a total reflection probe. A BaSO$_4$ disc was used as reference. All spectra were acquired under ambient conditions.

X-Ray photoelectron spectra were recorded on a VG Escalab 200R spectrometer (VG Generators, UK) equipped with a hemispherical electron analyzer and a magnesium X-ray source (12 kV and 10 mA) (Mg Kα = 1253.6 eV). The powdered samples were packed into small aluminium cylinders and mounted on a sample rod in the pre-treatment chamber and outgassed at 773 K for 1 h. The base pressure of the ion-pumped analysis chamber was maintained below 3×10^{-9} mbar during data acquisition. Peak intensities were estimated by calculating the integral of each peak after smoothing and subtraction of the "S-shaped" background. All binding energies (BE) were referenced to the adventitious C 1s line at 284.9 eV. This reference gave BE values with an accuracy of ± 0.1 eV.

Activity measurements

Throughout this study a soybean oil (Oleaginosa Humboldt, Santa Fe, Argentina) refined in the laboratory (degummed, neutralized, bleached and deodorized) was employed. Its FA composition was determined by GLC after derivatizing the triglycerides into FAME, following a standard procedure,[24] and was as follows (wt%):

saturated FA: 6.8, oleic acid: 23.5, linoleic acid: 61.2; linolenic acid: 8.5. The iodine value (IV) was 127.67.[25]

Epoxidation reactions were carried out batch-wise in a mechanically stirred 250 mL thermostated glass-reactor equipped with a thermometer, a reflux condenser, and a septum for sample withdrawal. In a typical run, 20 g of oil (equivalent to 0.1 mol of double bond), *tert*-butanol (5.81 g) and 0.5 g of catalyst were mixed in the reactor and the suspension was heated to the reaction temperature. Then, 4 g of a 6 wt% organic solution of H$_2$O$_2$ (in 1-phenylethanol) was added dropwise to the reactor suspension while maintaining vigorous stirring over 20 min. Aliquots of 4 mL were periodically taken from the reactor. All reagents were purchased from Fisher Scientific (Pittsburg, PA, USA).

Two kind of analyses were performed with the extracted samples: (i) the iodine value, following the standard method of the American Oil Chemists' Society (AOCS)[25] to evaluate the conversion of unsaturated fatty acids; and (ii) GC analysis, to evaluate the selectivity of organic compounds. A Shimadzu GC-17ATF unit was used, furnished with a PE-5 (Perkin-Elmer, Norwalk, CT, USA) capillary column: 30 m $\times$ 0.53 mm ID $\times$ 1.5 μm film. Analytical conditions were as follows: split/splitless injector, injector port at 523 K, FID detector at 543 K, H$_2$ carrier gas (90 psig, 20 mL min^{-1}), and isothermal oven at 473 K. Response factors were obtained using capillary CG, 99% grade, heptadecanoic acid methyl ester (Sigma-Aldrich, St. Louis, MO, USA) as internal standard. Prior to injection, the dry samples were previously derivatized to fatty acid methyl esters with sodium methoxide (Sigma-Aldrich).[26]

References

1 *Handbook of Soy Oil Processing and Utilization*, ed. E. H. Pryde, O. L. Brekke, T. L. Mounts and R. A. Falb, AOCS Press, Champaign, IL, 1980, p. 462.
2 I. Frischinger and S. Dirilikov, *Toughened Plastics I: Science and Engineering*, ed. C. K. Riew and A. K. Kinloch, American Chemical Society, Washington, DC, 1993, p. 451.
3 X. Wu, X. Zhang, S. Yang, H. Chen and D. Wang, *J. Am. Oil Chem. Soc.*, 2000, **77**, 561.
4 I. Scheuffegen and A. Meffert, US Pat. 3326455, 1997.
5 F. P. Greenspan and R. J. Gall, *Ind. Eng. Chem.*, 1953, **45**, 2722.
6 B. Rangarajan, A. Havey, E. A. Grulkey and P. D. Culnan, *J. Am. Oil Chem. Soc.*, 1995, **72**, 1161.
7 R. E. Kirk and D. F. Othmer, *Encyclopedia of Chemical Technology*, 3$^{\text{th}}$ edn., Interscience Publishers, New York, NY, 1984, p. 251.
8 S. Sinadinovic-Fišer, M. Jankovic and Z. S. Petrovic, *J. Am. Oil Chem. Soc.*, 2001, **78**, 725.
9 K. Hill, *Pure Appl. Chem.*, 2000, **72**, 1255.
10 U. Biermann, W. Friedt, S. Lang, W. Lühs, G. Machmüller, J. O. Metzger, M. Rüsch gen. Klaas, H. J. Schäfer and M. Schneider, *Angew. Chem., Int. Ed.*, 2000, **39**, 2206.
11 *Recent developments in the synthesis of fatty acid derivatives*, ed. G. Knothe and J. T. P. Derksen, AOCS press, Champaign, IL, 1999.
12 Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida and M. Ogawa, *J. Org. Chem.*, 1988, **53**, 3587.
13 W. A. Herrman, R. W. Fischer and D. W. Matz, *Angew. Chem., Int. Ed.*, 1991, **30**, 1638.
14 W. A. Herrman, J. D. G. Correia, F. E. Khün, G. R. J. Artus and C. C. Rao, *Chem. Eur. J.*, 1996, **2**, 168.
15 A. Debal, G. Rafaralahitsimba and E. Ucciani, *Fat Sci. Technol.*, 1993, **95**(6), 236.
16 M. Guidotti, N. Ravasio, R. Psaro, E. Gianotti, L. Marchese and S. Coluccia, *Green Chem.*, 2003, **5**, 421.
17 M. A. Camblor, A. Corma, P. Esteve, A. Martínez and S. Valencia, *Chem. Commun.*, 1997, 795.
18 J. M. Campos Martín and M. P. de Frutos Escrig, PCT patent W9948884, 1999.

19 M. C. Capel Sánchez, J. M. Campos-Martín, J. L. G. Fierro, M. P. de Frutos and A. Padilla Polo, *Chem. Commun.*, 2000, 855.
20 M. C. Capel Sánchez, J. M. Campos-Martín and J. L. G. Fierro, *J. Catal.*, 2003, **217**, 195.
21 Y. H. Hui, *Bailey's Industrial Oil and Fat Products*, 5th edn., John Wiley and Sons, Inc., New York, 1996, p. 19.
22 V. A. de la Peña O'Shea, M. C. Capel-Sánchez, G. Blanco-Brieva, J. M. Campos-Martín and J. L. G. Fierro, *Angew. Chem., Int. Ed.*, 2003, **42**, 5851.
23 R. J. Gall and F. P. Greenspan, *Ind. Eng. Chem.*, 1955, **47**, 147.
24 *Official and Recommended Practices of the American Oil Chemists' Society*, 5th edn., AOCS Press, Champaign, IL, 1997, Method Cd 1–25.
25 *Official and Recommended Practices of the American Oil Chemists' Society*, 5th edn., AOCS Press, Champaign, IL, 1997, Method Ce 1e.
26 H. Sales, R. Cesquini, S. Sato, D. Mandelli and U. Schuchardt, *Stud. Surf. Sci. Catal.*, 2000, **130**, 1661.