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Industrial resin "INDION 130" modified with vanadyl cations as highly efficient heterogeneous catalyst for epoxidation of fatty compounds with TBHP as oxidant†

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Industrial grade cation-exchange resin "INDION 130" was modified with vanadyl cations by an ion-exchange method and then used for the epoxidation of unsaturated fatty materials including acids, esters and vegetable oils using *tert*-butyl hydroperoxide (TBHP) in decane as oxidant. The effect of oxidant/double bond ratio, catalyst concentration, recycling of the catalyst and temperature on the conversion to epoxides was studied. After the epoxidation, the catalyst could easily be recovered by filtration and successfully reused for at least seven runs without any loss in catalytic activity.

Introduction

Renewable raw materials are known to be environmentally friendly, biodegradable, of low cost and readily available, and they have received considerable interest in recent decades due to their potential to serve as feedstock to substitute petroleum-derived materials.[1] Fats and oils are the most widely used renewable raw materials in the chemical industry as they provide widespread possibilities of different applications. They are the cheapest and most abundant biological feedstocks which are available in large quantities and can be used as starting materials for various transformations.[2] Epoxidation of vegetable oils, *i.e.* of their unsaturated triglycerides, is a commercially important reaction as these epoxides can be used as precursors for synthesizing numerous value-added chemicals including alcohols (polyols), glycols, olefin compounds and polymers.[3–5] Furthermore, they can directly be used as plasticizers and polymer stabilizers, as paint and coating components and as lubricants.[6,7] The Prileshajev reaction, *i.e.* the epoxidation of alkenes with peracids usually obtained *in situ* through the acid-catalyzed peroxidation of the corresponding organic acid with hydrogen peroxide, is the most applied method in industry for the epoxidation of unsaturated fatty acids and triacylglycerols.[8–9] Soluble mineral acids, most commonly sulfuric acid, are used as catalysts for this reaction. However, there are some disadvantages to be dealt with, such as equipment corrosion, more byproducts and environmental problems. The introduction of acidic ionic exchange resins as heterogeneous catalysts is an important technical improvement in the production of epoxidized oils, which improves the yield and/or selectivity.[10–13] Nevertheless, there are some disadvantages such as lower thermal stability, long reaction time and in some instances higher cost, limiting their applications in large-scale commodity manufacture. Immobilization of metal ions to the ion exchange resins is a promising and cost-effective approach to transform homogeneous metal catalysts to heterogeneous forms with the added benefits of facile recovery/recycling and higher stability of the catalyst. In this context, ion exchange resins such as perfluorinated sulfonic acid polymer (*i.e.* Nafion-H and Nafion SAC-13) have been modified with metal ions and successfully used as superior heterogeneous catalysts for a wide range of applications in organic transformations. For example, Nafion-immobilized molybdenum oxychloride ($MoOCl_4$) has been used for the synthesis of nitrones *via* oxidation/condensation of aldehydes with primary amines[14] and oxo-vanadium-modified Nafion[15] has been used for the hydrophosphonylation of aldehydes. However, the expensive nature, super-acidic character and less functional group compatibility of Nafion resins make their synthetic utility limited for practical applications.

INDION 130 is an inexpensive, easily available, macroporous, strongly acidic, industrial grade, sulfonic acid-containing cation exchange resin with an exchange capacity of 4.9 meq g^{-1}. Owing to its high thermal stability and superior catalytic activity, it has been successfully used as an acid catalyst for numerous organic transformations including multicomponent coupling,[16–18] esterification[19,20] and alkylation reactions.[21,22] However, to the best of our knowledge, it has never been modified with metal ions to be used as a heterogeneous catalyst for organic transformations.

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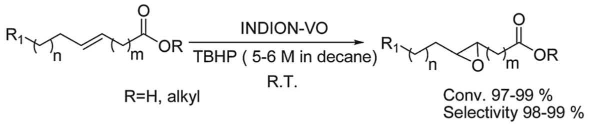
† Electronic supplementary information (ESI) available: EDX spectra of INDION-VO catalyst and FTIR and ^1H NMR of epoxidized oil. See DOI: 10.1039/c5nj00744e



Scheme 1 Epoxidation of fatty acids, esters and acid oils.

Vanadium compounds such as oxides, alkoxides, acetylacetonate and other coordination compounds containing oxo-vanadium(IV) ions are well known to react with alkylperoxides, *e.g. tert*-butyl hydroperoxide (TBHP), to give reactive oxo-peroxo-vanadium(V) species and have widely been used as effective catalysts for oxidation reactions including epoxidation of olefins.[23] In this regard Sen *et al.*[24] reported the use of oxo-vanadium(IV) dihydrogen phosphate as a heterogeneous catalyst for olefin epoxidation using TBHP as oxidant. Hsiao *et al.*[25] reported polymer-supported vanadium complexes as catalysts for the oxidation of alkenes with TBHP in water. Grivani and coworkers[26] demonstrated novel oxo-vanadium Schiff base complexes as homogeneous catalysts for epoxidation of cyclooctene in different solvents using TBHP as oxidant. Nunes *et al.*[27] reported mononuclear oxo-vanadium(IV) complexes for olefin epoxidation using TBHP as well as hydrogen peroxide (H_2O_2) as oxidants. Belaidi *et al.*[28] reported vanadium-chromium-bentonite as a green heterogeneous catalyst for epoxidation of cyclohexene with TBHP as an oxidant. Very recently we have described an oxo-vanadium Schiff base covalently immobilized to chemically functionalized graphene oxide (GO) as an efficient heterogeneous catalyst for the epoxidation of fatty acids and esters using TBHP as oxidant.[29] However, a multistep synthetic procedure involving modification of GO surface by 3-aminopropyltrimethoxysilane and then immobilization of oxo-vanadium complex makes the developed procedure tedious and expensive.

Cordelle and coworkers[30] demonstrated dinuclear vanadium complexes with tridentate Schiff base ligand for epoxidation of cyclooctene using aqueous TBHP as oxidant under solvent-less conditions with moderate selectivity. However, these methods have certain drawbacks such as multi-step tedious synthetic procedures for oxo-vanadium catalysts, use of additional organic solvents such as acetonitrile for the epoxidation reactions and moderate product yields.

Herein, we report for the first time an easily accessible, cost-effective and highly efficient heterogeneous vanadyl cation-modified industrial grade INDION 130 resin (INDION-VO) as heterogeneous catalyst for the epoxidation of fatty compounds such as acids, esters and vegetable oils with TBHP as oxidant under mild reaction conditions (Scheme 1). The developed heterogeneous oxo-vanadium catalyst exhibited higher catalytic activity than the homogeneous catalyst with the added benefits of facile recovery and recycling of the catalyst.

Results and discussion

Synthesis and characterization of the INDION-VO catalyst

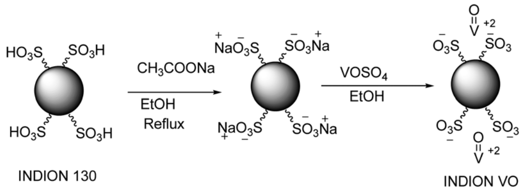
INDION 130 acidic ion exchange resin was modified with vanadyl cations (V(IV)=O) by using the ion exchange method with vanadyl sulfate ($VOSO_4 \cdot 5H_2O$) in refluxing ethanol for 12 h (Scheme 2).

The functionalization of INDION resin with oxo-vanadium (VO^{2+}) ions was confirmed by XPS, FTIR and ICP-AES analyses. The XPS spectra (Fig. 1) of INDION-VO exhibited a characteristic band at 523 eV (V $2p_{3/2}$), which confirmed the presence of vanadyl cation in the synthesized material.

In addition, the FTIR spectrum of the INDION-VO catalyst (Fig. 2) exhibited absorption bands at 994 and 998 cm^{-1}, which are assigned to the ν(V=O) vibration.[15] The presence of sulfonate (SO_3^-) group in the synthesized catalyst was confirmed by the appearance of two bands: one at around 1126 cm^{-1} and another at 1176 cm^{-1} due to asymmetric and symmetric stretching of S=O vibrations, respectively.[31]

The thermal stability of the synthesized catalyst was determined by thermogravimetric analysis (TGA) in the presence of nitrogen. As shown in Fig. 3(a and b), the vanadyl-modified resin catalyst exhibited higher thermal stability as compared to INDION resin (Fig. 3(a)).

Furthermore, the vanadium content in the synthesized catalyst was determined by ICP-AES analysis and it was found



Scheme 2 Synthesis of INDION-VO catalyst.

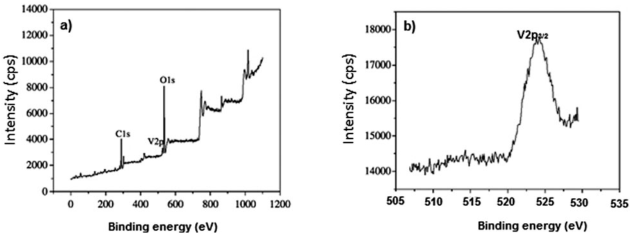


Fig. 1 XPS spectra of INDION-VO: (a) survey scan; (b) vanadium ion.

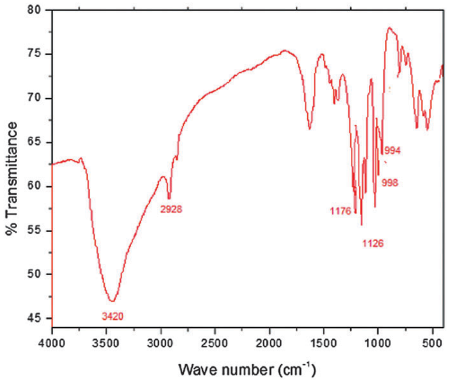


Fig. 2 FTIR spectrum of INDION-VO.

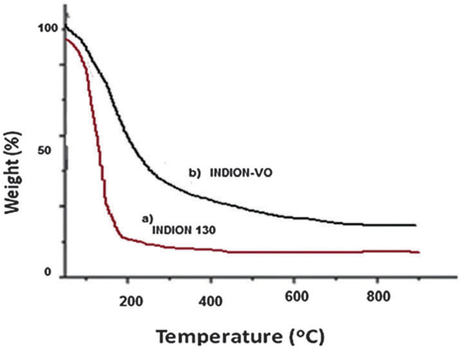
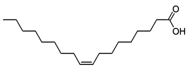
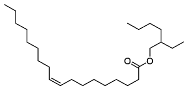
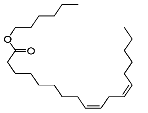
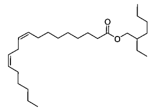
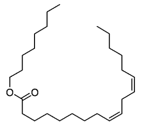
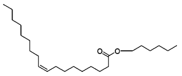
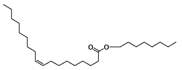
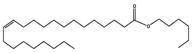


Fig. 3 TGA of INDION-VO (b) and INDION 130 (a).

Table 1 Epoxidation of fatty acids, esters and oils using INDION-VO catalyst[a]

Entry	Reactant	Retention time[b] (min)	Conv.[b] (%)	Selec.[b] (%)	Yield[c] (%)
1		18.47	99.2 90.4[d] —[e,f] 80.2[g]	99.1 97.2[d] —[e,f] 62.8[g]	98.6 86.5 — 76
2	Acid oil ($C_{18:1}$,$C_{18:2}$,$C_{18:3}$)	26.52	99.0	99.4	98
3		27.11	98.4	99.1	97
4	Methyl ester of acid oil	26.89	98	99.1	97.7
5‡		28.65	98	99.2	97.6
6‡		29.42	98.8	99.2	98
7‡		29.26	99.1	99.2	98.4
8		30.10	98.6	99.0	98.2
9		30.85	96.4	99.0	95.8
10		29.71	94.1	99.1	93.5

[a] Reaction conditions: fatty material (1 mmol), TBHP (1.5 mmol; ‡3.0 mmol), catalyst (5 wt%; ‡10 wt%), room temperature, reaction time 7 h. [b] Conversion and selectivity for epoxide were determined by GC (Varian CP-3800, column: CP Sil 24, oven temp. program: 2 min at 80 °C, 10 min to 250 °C at 25 °C min^{-1}, 10 min to 300 °C at 5 °C min^{-1}, carrier gas N_2). [c] Isolated yield. [d] Using homogeneous oxo-vanadium benzene sulfonate as catalyst. [e] Using INDION 130. [f] Blank experiment without catalyst. [g] Using VO-Amberlyst-15 resin catalyst.

to be 0.8 mmol per gram. Elemental analysis data based on EDAX indicated 1.3 wt% of elemental vanadium on the surface of the catalyst (see Fig. S1, ESI†) confirming the successful modification of the ion exchange resin with vanadyl cations.

Catalytic activity

With the vanadyl-modified INDION (INDION-VO) catalyst in hand, we aimed to explore its catalytic activity for the epoxidation of oleic acid with TBHP in 1 : 1.5 molar ratio at room temperature in the presence of 5 wt% catalyst. Homogeneous oxo-vanadium benzene sulfonate and unmodified INDION 130 resin were also tested for comparison (Table 1, entry 1). The results as shown in Table 1 revealed that the oxo-vanadium-modified resin catalyst exhibited higher activity than homogeneous vanadium catalyst. The superior catalytic activity of the heterogeneous catalyst can be attributed to the promoting effect of the polymeric backbone of the ion exchange resin which may interact with substrate and TBHP on the surface. However, unmodified INDION 130 ion exchange resin did not exhibit any catalytic activity under the described reaction conditions (Table 1, entry 1). Blank experiments, in the absence of catalyst, did not produce the epoxidized product even after a prolonged reaction time (12 h). Furthermore, to establish the superiority of the INDION-VO catalyst, we synthesized VO-Amberlyst-15 resin catalyst by following a similar strategy and used it for the epoxidation of oleic acid under identical experimental conditions (Table 1, entry 1). The poor product yield in the case of VO-Amberlyst-15 established the superiority of the INDION-VO catalyst over the other sulfonic polystyrene resin-based catalysts.

Further, to obtain the optimum reaction conditions, various parameters (reaction time, molar ratio of TBHP to substrate and catalyst concentration) were studied using oleic acid as the representative substrate. As shown in Fig. 4, the reaction conversion was found to increase with time and gave maximum conversion of oleic acid to corresponding epoxide (99.2%) in 7 h.

The effect of molar ratio of ethylene unsaturation/TBHP on the conversion to epoxide was studied by varying the ratio from 1 : 1 to 1 : 2.5 (Fig. 5). The conversion of oleic acid to corresponding epoxide was found to increase with the concentration of the oxidant and the maximum conversion was achieved when the molar ratio of oleic acid and TBHP was 1 : 1.5. A further increase in TBHP concentration did not affect the conversion and selectivity for epoxide formation to any significant extent. These findings established that the developed method is highly selective for epoxide formation over C=C bond cleavage.

Further we studied the effect of catalyst amount on the reaction. Initially the reaction conversion was found to increase with increasing catalyst amount from 1 to 5 wt% with respect to oleic acid (Fig. 6). A further increase in the catalyst amount did not influence the reaction and the epoxide yield remained almost the same. Hence, 5 wt% catalyst was considered as the optimum amount for further studies.

After having optimized the reaction conditions, we explored the potential of the developed system for the epoxidation of various fatty compounds including acids, esters and acid oil, which is a waste product from the vegetable oil industry, under optimized reaction conditions. The results of these

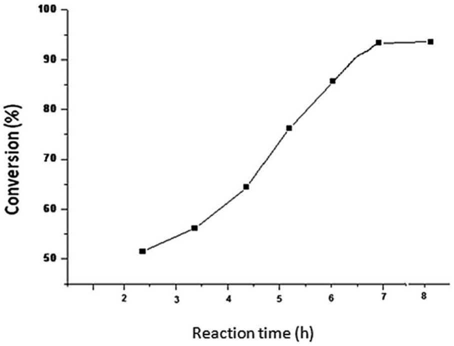


Fig. 4 Effect of reaction time on the epoxidation of oleic acid [oleic acid : TBHP (1 : 1.5), room temperature, catalyst 5 wt%].

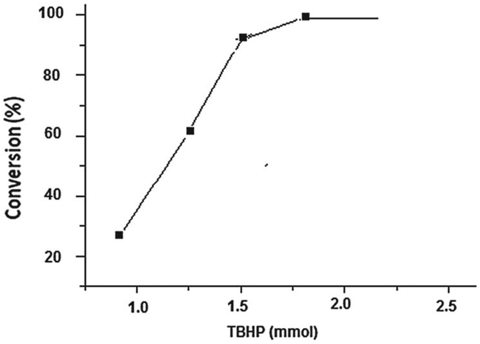


Fig. 5 Effect of TBHP concentration on the epoxidation of oleic acid [oleic acid (1 mmol), room temperature, catalyst 5 wt%, time 7 h].

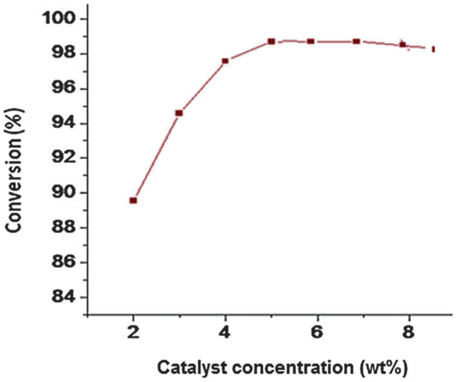


Fig. 6 Effect of catalyst concentration on the epoxidation of oleic acid [oleic acid : TBHP (1 : 1.5), room temperature, time 7 h].

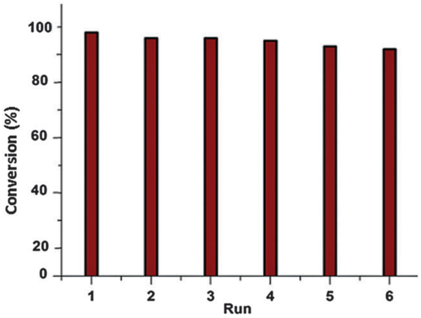


Fig. 7 Results of recycling experiments.

experiments are summarized in Table 1. All the substrates were efficiently converted to corresponding epoxides with excellent selectivity under the described experimental conditions. The formation of the epoxide product was initially characterized by the FTIR technique (Fig. S2, ESI†). The disappearance of the band at 3005 cm^{-1}, attributed to the –C═C– double bond, in the FTIR spectra of epoxidized products supports the consumption of double bonds and formation of epoxides during the reaction.

Further, in ^{1}H NMR spectra of the epoxidized oil (Fig. S3, ESI†), the peaks between 5.3 and 5.5 ppm due to the protons attached to –C═C– are absent, confirming the successful formation of epoxides. In addition, the appearance of a multiplet in the range of 3.1–3.2 ppm, assigned to epoxide protons, confirmed the formation of respective epoxidized products (Fig. S3, ESI†).

Furthermore, we performed recyclability experiments to check the recycling of the developed heterogeneous catalyst by considering the oxidation of oleic acid as a representative example. After the reaction, the catalyst was recovered from the reaction mixture by filtration, washed with methanol and dried at 110 °C before reuse. The recovered catalyst was used for six consecutive runs by using the same experimental conditions (Fig. 7). The reused catalyst exhibited almost similar activity and afforded almost similar conversion and selectivity of the epoxide.

To check the leaching of active vanadium species, we stopped the reaction after one hour and isolated the catalyst by filtration from the hot reaction mixture. After isolating the catalyst, the reaction was continued for subsequent 6 h under the described reaction conditions. The conversion of oleic acid remained very similar to that obtained after 1 h. This study suggested that there was no leaching and the reaction did not proceed in the absence of the catalyst. Furthermore, the vanadium content as determined by ICP-AES analysis in the recovered catalyst after six runs was found to be very similar (0.78 mmol g^{-1}) to that of the fresh one (0.8 mmol g^{-1}). These results confirmed that the developed catalyst was highly stable and truly heterogeneous in nature and exhibited consistent catalytic activity for several runs.

The developed INDION-VO catalyst is more advantageous than the reported heterogeneous oxo-vanadium catalyst[28] in terms of its facile synthetic methodology, easy accessibility of INDION resin and comparable activity.

Conclusions

We have demonstrated an easily accessible, cost-effective and highly efficient vanadyl-modified industrial grade ion exchange resin, INDION 130, as a heterogeneous catalyst for epoxidation of fatty materials including fatty acids, esters and vegetable oils using TBHP as oxidant under mild reaction conditions. The heterogeneous catalyst exhibited higher catalytic activity than the homogeneous oxo-vanadium catalyst with the added benefits of facile recovery and recycling of the catalyst.

Furthermore, low cost, high activity/selectivity and efficient recycling make the developed system more attractive for practical applications.

Experimental

Material

Industrial grade INDION 130 (styrene-divinylbenzene copolymer) was purchased from Ion Exchange India Limited in the form of light-colored spherical beads and dried at 110 °C before use. This is a macroporous strongly acidic material having sulfonic acid functional groups with acid site concentration of 4.8 meq g^{-1}. These functional groups throughout the entire structure are readily accessible and provide efficient performance. The commercially available INDION 130 ion exchange resin was found to be stable up to 150 °C. Fatty acids and sodium acetate were purchased from Alfa Aesar and used as received. Vanadyl sulfate and TBHP solution, 5.0–6.0 M in decane, were procured from Sigma-Aldrich and used without further purification. Acid oil used was the refinery waste which was used as received.

Techniques used

Fourier transform infrared spectroscopy (FTIR) was conducted with a Perkin Elmer Spectrum RX-1 IR spectrophotometer. XPS measurements were obtained using a KRATOS-AXIS 165 instrument equipped with dual aluminum–magnesium anodes using Mg Kα radiation ($h\nu$ = 1253.6 eV) operated at 5 kV and 15 mA with pass energy of 80 eV and an increment of 0.1 eV. The conversions and selectivity of the products were determined by high resolution GC-FID (Varian CP-3800). ^{1}H-NMR spectra of the products were obtained at 500 MHz by using a Bruker Avance-II 500 MHz instrument. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was carried out with an ICP-AES spectrometer (DRE, PS-3000UV, Leeman Labs Inc., USA). Samples for ICP-AES were prepared by leaching out 0.01 g of sample with conc. HNO_3, and then heated for 30 min and the volume made up to 10 ml. TGA of the samples was carried out using a thermal analyzer (TA-SDT Q-600). All samples were analyzed in the temperature range of 40 to 900 °C at a heating rate of 10 °C min^{-1} under nitrogen flow.

Synthesis of INDION-VO

The required INDION-VO catalyst was synthesized by refluxing a mixture of INDION 130 ion exchange resin (styrene-divinylbenzene copolymer) (1 g), sodium acetate (0.398 g, 4.85 mmol) and vanadyl sulfate pentahydrate (0.6 g, 2.37 mmol) in 50 ml of ethanol for 12 h under nitrogen atmosphere. The light blue colored heterogeneous INDION-VO was separated by filtration and washed with plenty of distilled water and methanol in order to remove the unreacted or excess amount of vanadyl sulfate. Filtered catalyst was dried under vacuum at 60 °C for 5 h. The successful synthesis of the catalyst was confirmed by comparing the XPS and FTIR analysis with an existing report.[15] XPS (V_{2p}): 523 eV; FTIR (cm^{-1}): 3420 (s, broad, OH), 1628 (s, H_2O), 1176, 1126 (s, O=S=O; SO_3), 998 (s, V=O). Metal loading was determined by ICP-AES analysis and was found to be 0.8 mmol g^{-1} catalyst.

Typical experimental procedure for epoxidation

The epoxidation experiments were carried out in a 25 ml round-bottomed flask equipped with a magnetic stirrer and a reflux condenser. The flask was charged sequentially with oleic acid (1 mmol), TBHP (5–6 M in decane, 1.5 mmol) and INDION-VO catalyst (5 wt% with respect to oleic acid). The resulting mixture was stirred at room temperature for 7 h. The progress of the reaction was monitored by thin-layer chromatography (silica gel) at regular intervals of time. After completion of reaction, the catalyst was separated by filtration, washed with methanol and dried for reuse for recycling experiments. The filtrate thus obtained was diluted with dichloromethane and washed with lukewarm water and ethanol successively to remove free acid. The resulting organic layer was concentrated under reduced pressure and dried over anhydrous Na_2SO_4. The selectivity of the epoxides was determined by GC (Agilent 6890 Series; HP-5 column, 30 m 0.25 mm; FID detector) using mesitylene (Sigma, 99%) as an internal standard. GC peaks were identified by comparison with peaks of authentic samples of reference standards and by means of GC-MS analysis.

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Notes and references

1 U. Biermann, W. Friedt, S. Lang, W. Luhs, G. Machmuller, J. O. Metzger, M. R. Klaas, H. J. Schafer and M. P. Schneider, *Angew. Chem., Int. Ed.*, 2000, **39**, 2206–2224.

2 F. D. Gunstone and F. B. Padley, *Lipid Technologies and Applications*, Marcel Dekker, New York, 1997, pp. 759–769.

3 G. Lligadas, J. C. Ronda, M. Galia, U. Biermann and J. O. Metzger, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 634–645.

4 S. Warwel, F. Bruse and M. Kunz, *Fresenius Environ. Bull.*, 2003, **12**, 534–539.

5 P. Daute, R. Picard, J. D. Klamann, P. Wedl and A. Peters, *US Pat.*, 7071343 B2, 2006.

6 B. K. Sharma, K. M. Doll and S. Z. Erhan, *Green Chem.*, 2007, **9**, 469–474.

7 B. R. Moser and S. Z. Erhan, *Eur. J. Lipid Sci. Technol.*, 2007, **109**, 206–213.

8 *Recent developments in the synthesis of fatty acid derivatives*, ed. G. Knothe and J. T. P. Derksen, AOCS press, Champaign, IL, 1999.

9 Z. S. Petrovic, A. Zlatanic, C. C. Lava and S. Sinadinovic-Fiser, *Eur. J. Lipid Sci. Technol.*, 2002, **104**, 293–299.

10 R. L. Musante, R. J. Grau and M. A. Ba1tanás, *Appl. Catal., A*, 2000, **197**, 165–173.

11 R. E. Kirk, D. F. Othmer, H. F. Mark and A. Standen, *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley-VCH, New York, 1965.

12 V. V. Goud, A. V. Patwardhan, S. Dinda and N. C. Pradhan, *Chem. Eng. Sci.*, 2007, **62**, 4065–4076.

13 V. V. Goud, A. V. Patwardhan and N. C. Pradhan, *Ind. Eng. Chem. Res.*, 2007, **46**, 3078–3085.

14 B. Singh, S. L. Jain, P. K. Khatri and B. Sain, *Green Chem.*, 2009, **11**, 1941.

15 S.-S. Weng, G.-Y. Lin, H.-C. Li, K.-C. Yang, T.-M. Yang, H.-C. Liu and S.-H. Sie, *Appl. Organomet. Chem.*, 2012, **26**, 455–460.

16 A. M. Pansuriya, M. M. Savant, C. V. Bhuva, N. Kapuriya, J. Singh and Y. T. Naliapara, *Lett. Org. Chem.*, 2009, **6**, 619–623.

17 S. B. Patil, P. R. Singh, M. P. Surpur and S. Samant, *Synth. Commun.*, 2007, **37**, 1659–1664.

18 S. B. Patil, P. R. Singh, M. P. Surpur and S. Samant, *Synth. Commun.*, 2006, **36**, 2163–2168.

19 G. D. Yadav and H. B. Kulkarni, *Polymers*, 2000, **44**, 153–165.

20 G. D. Yadav and M. S. Krishnan, *Org. Process Res. Dev.*, 1998, **2**, 86–95.

21 J. Gangadwala, S. Mankar, S. Mahajani, A. Kienle and E. Stein, *Ind. Eng. Chem. Res.*, 2003, **42**, 2146–2155.

22 K. G. Chandra and M. M. Sharma, *Catal. Lett.*, 1993, **19**, 309–317.

23 (*a*) J. A. L. da Silva, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 2011, **255**, 2232–2248; (*b*) H. Toshikazu, *Chem. Rev.*, 1997, **97**, 2707–2724.

24 R. Sen, R. Bera, A. Bhattacharjee, P. Gütlich, S. Ghosh, A. K. Mukherjee and S. Koner, *Langmuir*, 2008, **24**, 5970–5975.

25 M.-C. Hsiao and S.-T. Liu, *Catal. Lett.*, 2010, **139**, 61–66.

26 G. Grivani, G. Bruno, H. A. Rudbari, A. D. Khalaji and P. Pourteimouri, *Inorg. Chem. Commun.*, 2012, **18**, 15–20.

27 C. D. Nunes, P. D. Vaz, V. Félix, L. F. Veiros, T. Moniz, M. Rangel, S. Realista, A. C. Mouratoa and M. J. Calhorda, *Dalton Trans.*, 2015, **44**, 5125–5138.

28 N. Belaidi, S. Bedrane, A. Choukchou-Braham and R. Bachir, *Appl. Clay Sci.*, 2015, **107**, 14–20.

29 S. Verma, M. Aila, S. Kaul and S. L. Jain, *RSC Adv.*, 2014, **4**, 30598–30604.

30 C. Cordelle, D. Agustin, J.-C. Daran and R. Poli, *Inorg. Chim. Acta*, 2010, **364**, 144–149.

31 P. P. Upare, J.-W. Yoon, M.-Y. Kim, H.-Y. Kang, D. W. Hwang, Y. K. Hwang, H. H. Kung and J.-S. Chang, *Green Chem.*, 2013, **15**, 2935–2943.