An efficient ring opening reaction of methyl epoxystearate promoted by synthetic acid saponite clays†

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The acid-catalysed reaction of methyl 9,10-epoxystearate ring opening using synthetic saponite acid clay as catalyst, has been studied for the first time. In the presence of methanol, 90% of the epoxide substrate is converted after 5 min and the main reaction product is the vicinal hydroxyether, methyl methoxyhydroxystearate, with 84% of selectivity. In the absence of alcohol the ring opening reaction proceeds slower, leading to a mixture of methyl 9- and 10-oxostearate as main products, and a 9,10-epoxystearate conversion of 66% after 1 h. The performance of acid saponite, an environmentally benign catalyst, is exceedingly higher than those of strong mineral acids, such as H_2SO_4, widely used for this reaction.

Introduction

The diminishing fossil reserves and the awareness of global environmental problems have made the exploitation of alternative renewable resources an urgent goal.[1] In this strategy, oleochemistry plays a major role in the great challenge represented by the chemistry of renewable raw materials as building blocks to obtain fine chemicals and biofuels.[2]

The functionalisation of double bonds of unsaturated fatty acid methyl esters (FAMEs) provides an interesting tool for the preparation of molecules containing different functional groups. The formation of oxirane rings on double bonds is a well-established industrial reaction,[3] generally used for the preparation of epoxidised oils as additives for plastic materials.[4] Epoxidised fatty acid methyl esters (epoxy FAMEs) are key intermediates in the synthesis of fatty acid derivatives, since by ring opening or rearrangement they can give rise to a broad variety of valuable compounds with functionalised alkyl chains.[5,6] In the last few years, the use of heterogeneous catalysts in the epoxidation of fatty acid methyl esters have received great attention. Large-scale processes based on heterogeneous catalysts are desirable, because they do not need difficult separation and recycling steps. In addition, the use of selective solid catalysts can lead to a global reduction in the production of wastes thanks to the formation of less undesired by-products and to simpler purification protocols.[7] In previous works, we

optimized the synthesis of epoxidized fatty acid methyl esters using titanium silica catalysts (Scheme 1, from **1** to **2**).[8]

In this report, we focus our attention onto the ring opening of methyl 9,10-epoxystearate (**2**) in the presence of a solid catalyst (Scheme 1). The tests were performed on the epoxy FAME synthesized from methyl oleate over a Ti-MCM-41 catalyst in the presence of *tert*-butylhydroperoxide (TBHP), as previously described.[8] With this methodology, the conversion attains 95% after 24 hours of reaction, with selectivity >95% to methyl 9,10-epoxystearate.

Epoxide ring opening is typically performed under acid conditions with nucleophilic molecules, such as water or alcohols. The transformation leads to diols and hydroxyethers derivatives, respectively (Scheme 1). Rearranged epoxides bear a castor oil-like structure and can find applications similar to those where ricinoleic derivatives are used, namely as precursors of biopolymers, lubricants, polyurethane foams and casting resins. In particular, diol derivatives of FAMEs find application in the preparation of polyols for bio-based polymers[9] or in the synthesis of fine chemicals.[10] Hydroxyether derivatives can be used as components for alternative mineral additive-free base lubricants,[11] for casting resins[12] or as additives for biofuels.[13] Up to now, strong mineral acids have been employed as catalysts for this reaction, but the set-up of an efficient heterogeneous catalytic process could lead to more sustainable technologies. The optimisation of a heterogeneous solid acid is still a challenge and many reports in open and patent literature focus on this topic.[14–16]

Saponite clays are layered hydrous silicates of aluminium and magnesium and show interesting features. They have a marked acidity, generated by isomorphous substitution of Si(IV) by Al(III) ions in tetrahedral sheets, and a good thermal stability. There are many advantages in the use of natural acid-activated saponite clays, thanks to their large availability and low price, but their use for technological applications requires several extensive purification steps, due to their extremely variable

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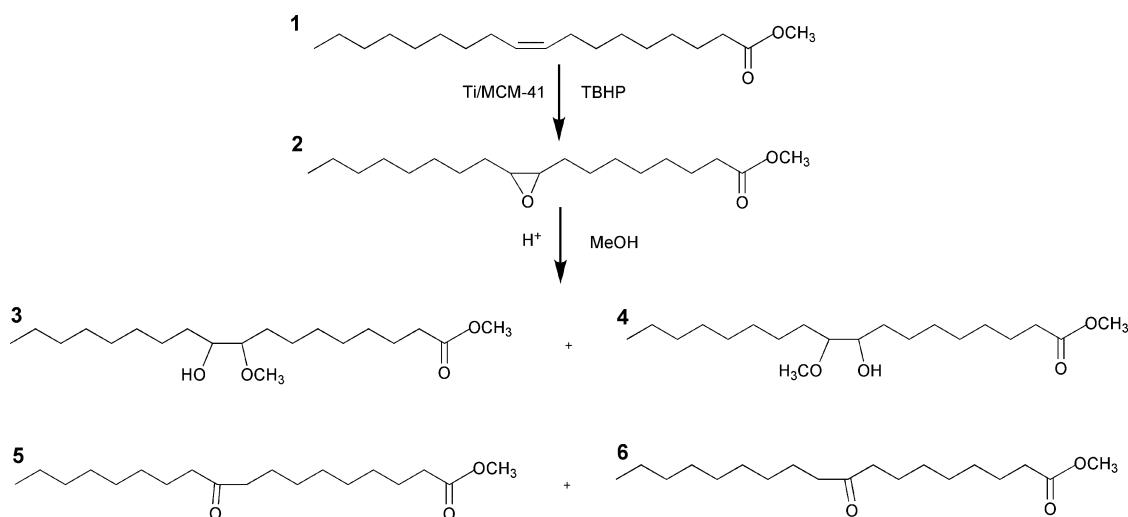
Scheme 1 Synthetic pathway for ring opening of methyl 9,10-epoxystearate from methyl oleate.

chemical composition and the presence of impurities. Different simple and less time-consuming methods for the preparation of synthetic clays with controlled chemical composition for tailored purposes have therefore been developed.[17] Here we report on the epoxide-ring opening of a fatty acid methyl ester using synthetic acid saponites as catalysts, and compare their performance with both solid acids having different structure and acid strength and a solution of highly concentrated sulfuric acid.

Experimental

The synthesis of methyl 9,10-epoxystearate (**2**) starting from methyl oleate (**1**) was performed using Ti-MCM-41 (1.8 wt% Ti; 950 m^2 g^{-1} surface area; 2.5 nm pore diameter), in the presence of anhydrous *tert*-butylhydroperoxide (TBHP; Aldrich, 5 M solution in decane) as oxidant.[8] Methyl oleate (Aldrich, 99%) was used as received. Ti-MCM-41 was prepared by grafting titanocene dichloride, Ti(Cp)$_2$Cl$_2$ (Fluka, purum >95%) onto MCM-41.[18] Ethylacetate (Carlo Erba, RPE, 10 mL) was used as solvent for the epoxidation. After filtration of Ti-MCM-41 catalyst, the final solution was evaporated overnight under vacuum.

Synthetic saponite sample Na-SAP with a gel composition of 1SiO$_2$: 0.835MgO : 0.056Al$_2$O$_3$: 0.056Na$_2$O : 20H$_2$O and a nominal cationic exchange capacity (CEC) of 104.9 meq/100 mg was prepared and optimized in our laboratory, as reported in the literature.[19] Part of the Na-SAP material was exchanged in three HCl aqueous solutions of different concentrations, 0.01M, 0.1M and 1M, and have been named H-SAP (A), H-SAP (B) and H-SAP (C), respectively[19] (see also ESI).† A further series of tests was carried out over another H-SAP material obtained by exchanging a second batch of Na-SAP clay in a 0.01 M hydrochloric acid solution. The results confirmed a very good reproducibility of the synthesis procedure of the heterogeneous catalyst.

An aluminium-containing SBA-15 mesoporous silica was prepared with a Si/Al ratio of 20 following the procedure reported in the literature.[20] Triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (P123), was purchased from Aldrich

(see also ESI).† Zeolite H-BEA, having a Si/Al ratio of 13, was provided by Polimeri Europa S.p.A. in its acidic form after template removal at 550 °C in air. A commercial sample of amorphous SiO$_2$–Al$_2$O$_3$ (14.7 wt% Al$_2$O$_3$, 475 m^2 g^{-1} surface area; 0.79 mL g^{-1} pore volume; grade 135 Sigma Aldrich) and montmorillonite K10 (Sigma Aldrich) were also tested as solid acid catalysts and used without any further modification. H$_2$SO$_4$ (98%, 6 μL corresponding to 0.22 mmol H$^+$ in the reaction medium) was purchased from Prolabo.

The concentration of Brønsted acid sites calculated by FT-IR of adsorbed NH$_3$ by using the equation $C = A/(\varepsilon\rho)$, where A is the integrated intensity of the FT-IR band at 1445 cm^{-1} (δ NH$_4^+$ ions), ε is the extinction coefficient ($\varepsilon = 13.0$ cm μmol^{-1})[21] and ρ is the pellet density (g cm^{-2}).

Ring opening of epoxystearate (0.500 mL, >95%) was carried out in a glass batch reactor (stirring rate 500 rpm) at 363 K using toluene as solvent (puriss., Riedel de Haën, 3 mL), previously dried on molecular sieves (Siliporite, 3A). All solid catalysts (50 mg) were pretreated at 150 °C for 1 h *in vacuo*, before running catalytic tests. Methanol (0.100 mL) used for reactions as in Table 1 was purchased from Fluka (>99.8%). Samples were taken after a reaction time of 5, 10, 15, 30 min and 1 h, and reaction products were determined by GC analysis (HP5890; HP-5 column, 30 m × 0.25 mm; temperature programme: 60 °C 0 min, 40 °C min^{-1} to 140 °C 0 min, 8 °C min^{-1} to 195 °C 30 min; FID or MS detectors, head pressure 160 kPa). The products were identified by comparison with standards (**2**) or by the analysis of the MS fragmentation patterns (**3** to **6**). Separation of oxostearates and epoxystearate (retention times: 16.9 min and 17.2 min) was also confirmed by single ion chromatography on the GC-MS. Standard deviations were ±2% and ±3% in conversion and selectivity values, respectively. *n*-Decane (Janssen Chimica, 99.8%) was used as internal standard.

A conventional, montmorillonite K10 clay,[14,15] was tested under the same conditions and used as a reference material. This clay, from natural origin, shows a lower initial rate and a longer time of reaction to reach the complete conversion of epoxystearate with respect to the synthetic H-SAP (A) clay.

However, a direct comparison between the catalytic performance of synthetic saponite and natural montmorillonite is difficult because of their different chemical composition, structure and morphology. This comparison is beyond the scope of the present manuscript.

Due to the presence of some *tert*-butanol in the batch of methyl epoxystearate synthesized using TBHP as oxidant, in all reactions of Table 1 and Table 2 *tert*-butoxyhydroxystearate (1–4% yield) was always detected as side-product in epoxide ring opening. Methyl 9,10-dihydroxystearate was a side-product obtained in 1–2% yield in all the presented tests. No detectable amounts of oligomerized or polymerized species have been observed in solution under the reaction conditions used here.

Results and discussion

Preparation and characterization of saponite catalysts

Three different H-exchanged saponites (H-SAP (A), H-SAP (B) and H-SAP (C)) were obtained from one batch of parent Na-containing synthetic saponite (Na-SAP) by cationic exchange with an aqueous solution of 0.01, 0.1 and 1.0 M hydrochloric acid, respectively.[19]

While the ionic exchange under mild conditions does not alter significantly the structure of saponite (Fig. 1A, curve a), samples
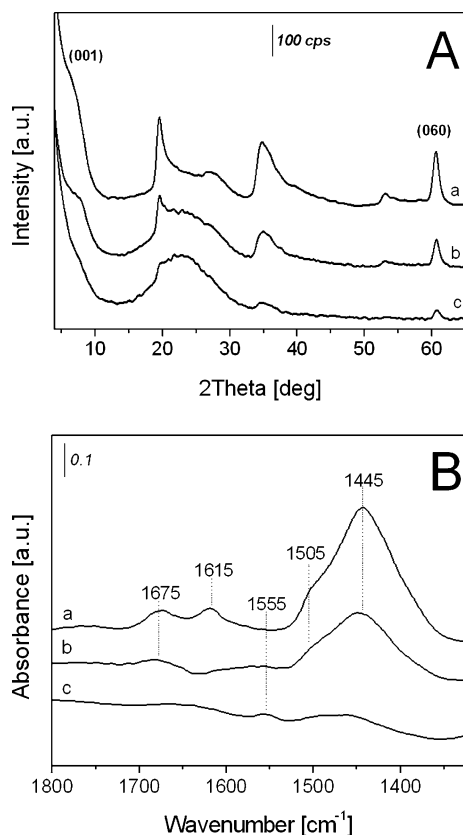

exchanged with more concentrated acid solutions (0.1 and 1 M HCl solutions) are characterised by an increasing amount of amorphous phase, as indicated by the broad signal in the 20–30 2θ degrees range in the XRD patterns (Fig. 1A, b–c). This effect is due to a progressive collapse of the saponite framework, leading to the formation of an amorphous silica phase.[19,22]

The concentration of the catalyst acid sites was estimated by using FT-IR spectroscopy of adsorbed NH_3 at room temperature. IR spectra of NH_3 adsorbed on all samples are reported in Fig. 1B.

The IR spectrum of H-SAP (A) (Fig. 1B, a) in the 1800–1300 cm^{-1} range is dominated by an intense band at 1445 cm^{-1} with a shoulder at 1505 cm^{-1}, accompanied by weak absorptions at 1675 and 1615 cm^{-1}. The bands at 1445 and 1505 cm^{-1} are attributed to an asymmetric bending of NH_4^+ ions, while the band at 1675 cm^{-1} is related to the symmetric bending mode of NH_4^+. This suggests that Brønsted acid sites strong enough to give a proton transfer to ammonia molecules are present on the saponite surface upon treatment under acid conditions, as already reported in ref. 19. The absorption at *ca.* 1615 cm^{-1} can be assigned to the bending mode of ammonia adsorbed on Lewis acid centers and/or interacting with silanol groups.[23]

Fig. 1B shows that the intensity of the bands related to ammonium ions decreases progressively as the concentration of the HCl solution used for the ion exchange increases. This behaviour indicates that the acid treatment in 0.1 and 1 M HCl solutions leads to a modification of the surface acid sites of the sample. The band at 1555 cm^{-1}, especially observed for samples treated in more acidic media (0.1 and 1 M HCl solutions), are due to Si-NH_2 species formed by NH_3 reaction with distorted siloxane bridges, which can be formed during the activation treatment by condensation of vicinal silanols.[24]

The total concentration of Brønsted acid sites can be estimated from the IR data of adsorbed NH_3 using the extinction coefficient reported in the literature.[21] It was calculated that H-SAP (A) contains *ca.* 0.32 mmol g^{-1} of Brønsted surface acid sites, whereas in H-SAP (B) and H-SAP (C) the amount of these sites is reduced to 0.16 and 0.06 mmol g^{-1}, respectively (Table 1).

The use of CO as FTIR probe molecule allowed us to have a scaling of the acidity of surface sites of the different saponite samples (Fig. 2).

The IR data indicated that the activation under mild acid conditions (H-SAP (A)) leads to the formation of Brønsted sites whose acidity is comparable to that of the most acid

Table 1 Transformation of methyl 9,10-epoxystearate over saponite catalysts in the presence of methanol[a]

Entry	Catalyst	$[H^+]^b$/mmol g^{-1}	C^c (%)	S^d (%) 5 and 6	S^e (%) 3 and 4
1	H-SAP(A)	0.32	98	14	84
2	H-SAP(B)	0.16	53	34	61
3	H-SAP(C)	0.06	22	27	50
4	Na-SAP	n.d.	21	35	48

[a] Catalyst (50 mg) pre-treated at 150 °C for 1 h in air; Me-epoxystearate (500 μL); methanol (100 μL); toluene (3 mL); 85 °C. [b] Concentration of Brønsted acid sites (see Experimental). [c] Conversion after 1 h. [d] Selectivity to 10-oxostearate and 9-oxostearate (5 and 6) at 1 h. [e] Selectivity to methoxyhydroxystearate (3 and 4) at 1 h.

Fig. 1 A: XRD pattern of (a) H-SAP (A), b) H-SAP (B) and (c) H-SAP (C). B: IR spectra of NH_3 adsorbed on (a) H-SAP (A), (b) H-SAP (B) and (c) H-SAP (C). Spectra collected upon admission of NH_3 (90 mbar) and subsequent outgassing at r.t., are reported after subtraction of the spectrum of bare samples, *i.e.* prior NH_3 adsorption, used as reference.
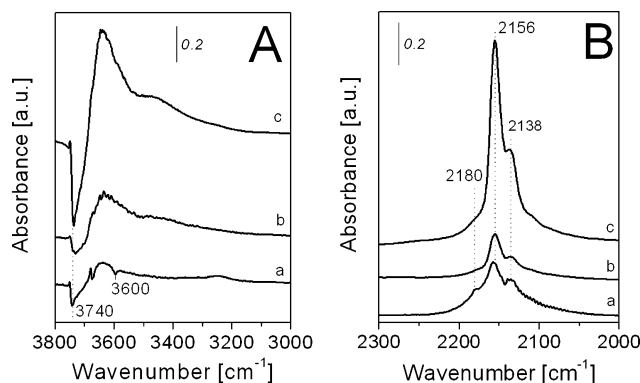
Fig. 2 IR spectra of CO adsorbed at 100 K (60 mbar) on (a) H-SAP (A), (b) H-SAP (B) and (c) H-SAP-(C) samples. Spectra are reported in the ranges 3800–3000 cm^{-1} (frame A) and 2300–2000 cm^{-1} (frame B).

Table 2 Transformation of methyl 9,10-epoxystearate using different acid catalysts in the presence of methanol[a]

Entry	Catalyst	[H$^+$]/mmol g^{-1}	C^b (%)	S^c (%) 5 and 6	S^d (%) 3 and 4
1	H-SAP(A)	0.32	>98	14	84
5	SiO$_2$-Al$_2$O$_3$	0.66	60	—	85
6	H-BEA	0.77	58	3	85
7	Al-SBA-15	0.66	58	—	88
8	H$_2$SO$_4$	—^{e}	26	59	39
9	No catalyst	—	>2	—	—

[a] Solid catalyst (50 mg) pre-treated at 150 °C for 1 h in air; Me-epoxystearate (500 µL); methanol (100 µL); toluene (3 mL); 85 °C. [b] Conversion after 1 h. [c] Selectivity to 10-oxostearate and 9-oxostearate (5 and 6) at 1 h. [d] Selectivity to methoxyhydroxystearate (3 and 4) at 1 h. [e] 6 µL H$_2$SO$_4$ 98% corresponding to ca. 0.22 mmol H$^+$.

zeolites, accompanied with the presence of sites with medium acidity (Al–OH), in agreement with the literature.[19] When the samples are treated under more severe acid conditions (H-SAP (B) and H-SAP (C)) the distribution of surface OH groups appeared significantly modified: a progressive decreasing of strong Brønsted acid sites was observed, in fact, as the concentration of HCl solution increases, while Al–OH sites with medium acidity were formed. The different acid behaviour of H-SAP materials can be explained on the basis of the structural modification occurring to the saponite framework upon exchange under different acid conditions (Fig. 1A). It is worth pointing out that the destructuration phenomena are also accompanied by progressive dealumination of the saponite framework.[19] The Si/Al ratio of H-SAP samples indeed passes from about 11 for H-SAP (A) to 71 for the sample treated under the most acid conditions (H-SAP (C)).

Transformation of methyl epoxystearate

The catalytic ring-opening of methyl 9,10-epoxystearate **2** was studied in the presence of methanol over H- and Na-containing saponites (Table 1, entries 1–4). H-SAP (A) shows the best catalytic activity, leading to almost complete conversion of the epoxide after 1 hour. This is in accordance with the results observed by FT-IR spectroscopy of adsorbed NH$_3$ and CO probe molecules: cationic exchange with H$^+$ species under mild conditions (0.01 M aq. HCl) maximizes the number of strong Brønsted acid sites. H-SAP (B) and H-SAP (C), prepared under strong acid conditions show a lower catalytic activity and H-SAP (C) gives almost the same conversion value after 1 hour as Na-SAP itself. Such loss in catalytic activity is strictly related to the decrease of Brønsted acid sites in the saponite clays (Table 1), as described above (Fig. 1B and Table 1, column 3).

The reaction products found under the tested conditions are shown in Scheme 1 and selectivities to these compounds are presented in Table 1. The main product was in all cases methyl methoxyhydroxystearate (**3** and **4**). 10-Oxostearate (**5**) and 9-oxostearate (**6**) products were obtained by isomerisation of the epoxide ring, catalysed by Brønsted acid sites.

Attempts to force the production of **3** and **4** by increasing the amount of methanol in the reaction mixture (5 : 1 mol mol^{-1} stoichiometric ratio CH$_3$OH : epoxy FAME) were unsuccessful.

A fraction of oxostearates **5** and **6** was always observed with a selectivity of *ca.* 15%.

The data obtained over H-SAP(A) have been compared with those recorded over a series of conventional and widely-used solid catalysts (Table 2), namely a commercial silica–alumina mixed oxide, SiO$_2$–Al$_2$O$_3$ (entry 5), a protonic beta zeolite (H-BEA, entry 6) and a mesoporous ordered aluminosilicate Al-SBA-15 prepared in our laboratory (entry 7). In Table 2 the results obtained in the presence of H$_2$SO$_4$ (entry 8), used as industrial catalyst for this reaction, are also shown.

Entries 5, 6 and 7 (Table 2) show that the three reference solid catalysts all give similar results and have a poorer performance than H-SAP (A). In particular, Fig. 3 shows the most relevant differences in epoxide conversion throughout the reaction time for a selection of catalysts. 90% of the epoxide is already converted over H-SAP (A) after 5 minutes. It is worth noting that H-SAP (A) shows results that are outstandingly higher than those obtained in the presence of H$_2$SO$_4$ under comparable conditions. As a matter of fact, under the conditions and with the methanol to epoxy FAME ratio here tested, H$_2$SO$_4$ leads to conversion values as low as those obtained on H-SAP (B) and H-SAP (C) (Table 2), but with a poorer selectivity to vicinal hydroxyethers **3** and **4**. In the presence of an amount of H$^+$ species that is *ca.* 14 times as high as the amount introduced with H-SAP (A) (*i.e.* 0.22 mmol H$^+$ for 6 µL H$_2$SO$_4$ *vs.* 0.016 mmol
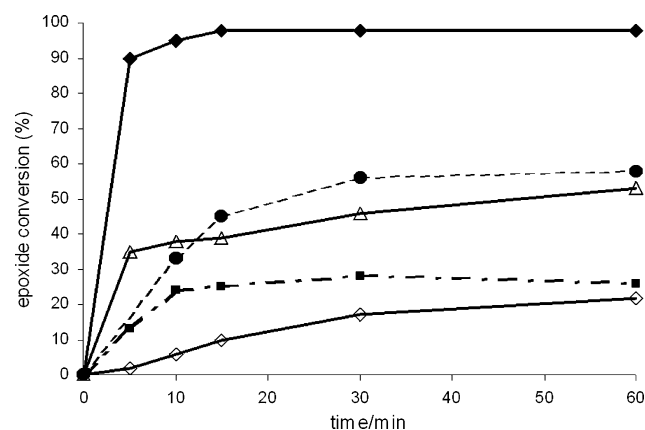

Fig. 3 Profile of methyl 9,10-epoxystearate conversion *vs.* reaction time for a selection of catalysts in the presence of methanol. H-SAP(A) (◆), H-SAP(B) (△), H-SAP(C) (◇), H-BEA (●) and H$_2$SO$_4$ (■).

H⁺ for 50 mg H-SAP (A)), methyl oxostearate (mixture of 9- and 10-isomers) is the product obtained preferentially.

The layered material prepared under mild acid conditions (H-SAP (A)) displays Brønsted acid sites which are strong and accessible at the same time, whereas these two features are not present together in the other solid catalysts employed in this work (Table 2). As derived by FT-IR spectroscopy of CO adsorbed at 100 K, H-BEA zeolite shows Brønsted acid sites whose acidity is lower than that of H-SAP(A), the downward shift of the OH stretching vibration upon CO interaction ($\Delta \nu_{OH}$) being around 300 and 340 cm⁻¹, respectively.[25,19] The acid strength of Brønsted acid sites of H-SAP (A) is similar to that observed in most acid zeolites (see for instance H-Mordenite[26]).

NH₃ adsorption indicates that H-BEA zeolite contains a larger number of Brønsted acid sites with respect to H-SAP(A) material (Table 2, entry 6). However, the microporous nature of zeolitic materials limits the accessibility of the epoxystearate molecules to the catalytic sites. This justifies the lower catalytic activity of H-BEA with respect to H-SAP (A). On the other hand, the mesoporous Al-SBA-15 is characterized by large pores (around 8 nm) and is able to easily accommodate epoxystearate molecules. Nevertheless, even though Al-SBA-15 contains an amount of Brønsted acid sites that is almost twice as high than those of H-SAP (A) (Table 2, entry 7), the weak nature of its surface acid sites[27] (the downward shift of the OH stretching vibration upon CO interaction at 100 K ($\Delta \nu_{OH}$) being around 150–200 cm⁻¹), in comparison to H-SAP (A) and protonic zeolites, limits its catalytic activity.

The role of Brønsted acid site of saponites during the ring-opening reaction is evident in Fig. 4, where a clear dependence of the conversion (both after 5 and 60 min) on the concentration of protonic sites is reported. Analogously, a diminution of the amount of acid sites in the reaction mixture, by using, for instance, a lower amount of catalyst, implies a proportional diminution in the epoxide conversion.
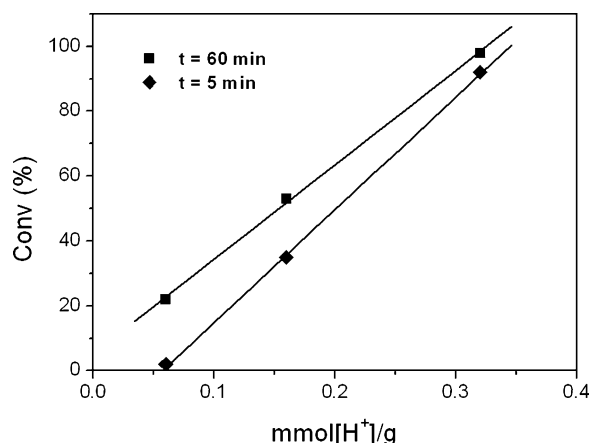

Fig. 4 Dependence of activity on concentration of H⁺ acid sites. Conversion after 5 min (♦) and 60 min (■). Reaction conditions as in Table 1; entry 1, 2 and 3.

Acid-catalysed rearrangement of epoxystearate in the absence of methanol gives a mixture of methyl 10- and 9-oxostearate (**5** and **6**) as the main product. This reaction was performed with H-SAP (A) (Table 3, entry 10), SiO₂–Al₂O₃ (entry 11) and H₂SO₄ (entry 12). In the absence of alcohol, the rearrangement

Table 3 Transformation of methyl 9,10-epoxystearate using different catalysts in the absence of methanol[a]

Entry	Catalyst	C^b (%)	S^c (%) **5** and **6**
10	H-SAP(A)	66	87
11	SiO₂–Al₂O₃	12	50
12	H₂SO₄[d]	50	70
13	no catalyst	<2	—

[a] Catalyst (50 mg) pre-treated at 150 °C for 1 h in air; Me-epoxystearate (500 µL); no alcohol; toluene (3 mL), 85 °C. [b] Conversion after 1 h. [c] Selectivity to 10-oxostearate and 9-oxostearate (**5** and **6**) at 1 h. [d] 6 µL H₂SO₄ 98%.

of epoxide is slower, but, also in this case, H-SAP (A) is the best catalyst, with a 9,10-epoxystearate conversion of 66% (entry 10).

Conclusions

Synthetic saponite clays proved to be interesting heterogeneous acid catalysts and a possible alternative to strong mineral acids in the ring-opening of methyl 9,10-epoxystearate. In particular, in the presence of methanol, 90% of methyl epoxystearate conversion is obtained in only 5 minutes and good selectivities to vicinal hydroxyethers are obtained from epoxidised FAMEs. A combination of spectroscopic and catalytic results show that the conversion is strictly related to both the concentration and strength of accessible Brønsted acid sites on saponite materials. The catalytic sites of protonic saponites have an acid strength comparable to that of the most acidic zeolites, together with a high accessibility, similar to that of mesoporous materials. Such features pave the way to the use of these strongly acid materials in other acid-catalysed transformations of bulky and richly functionalised molecules, such as those used in fine and specialty chemistry.

Acknowledgements

Notes and references

1 J. C. Warner, A. S. Cannon and K. M. Dye, *Env. Impact Assess. Rev.*, 2004, **24**, 775; D. R. Dodds and R. A. Gross, *Science*, 2007, **318**, 1250.
2 U. Biermann, W. Friedt, S. Lang, W. Lühs, G. Machmüller, J. O. Metzger, M. Rüsch, gen. Klaas, H. J. Schäfer and M. P. Schneider, *Angew. Chem., Int. Ed.*, 2000, **39**, 2206; G. W. Huber and A. Corma, *Angew. Chem., Int. Ed.*, 2007, **46**, 7184; R. Luque, L. Herrero-Davila, J. M. Campelo, J. H. Clark, J. M. Hidalgo, D. Luna, J. M. Marinasa and A. A. Romero, *Energy Environ. Sci.*, 2008, **1**, 542; A. Behr, A. Westfeschtel and J. Perez-Gomez, *Chem. Eng. Technol.*, 2008, **31**, 700.
3 X. Pages-Xatart-Pares, C. Bonnet, and O. Morin, Synthesis of new derivatives from vegetable oil methyl esters *via* epoxidation and oxirane opening in *Recent Developments in the Synthesis of Fatty Acids Derivatives*, ed. G. Knothe and J. T. P. Derksen, AOCS Press, Champaign, IL, USA, p. 141.
4 K. M. Doll and S. Z. Erhan, *Green Chem.*, 2008, **10**, 712.
5 B. K. Sharma, K. M. Doll and S. Z. Erhana, *Green Chem.*, 2007, **9**, 469.
6 J. Filley, *Bioresour. Technol.*, 2005, **96**, 551.

7 M. Guidotti, R. Psaro, M. Sgobba, and N. Ravasio, in *Catalysis for renewables: from feedstock to energy production*, ed. G. Centi and R. A. van Santen, Wiley-VCH, Weinheim, 2007, p. 257.

8 M. Guidotti, R. Psaro, N. Ravasio, M. Sgobba, E. Gianotti and S. Grinberg, *Catal. Lett.*, 2008, **122**, 53.

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

10 G. F. H. Kramer, O. Jurrius, T. C. de Rijk, J. T. P. Derksen and F. P. Cuperus, *Biotechnol. Tech.*, 1997, **11**, 293.

11 A. Kleinova, P. Fodran, L. Brncalova and J. Cvengros, *Biomass Bioenergy*, 2008, **32**, 366.

12 B. Gruber, R. Hoefer, H. Kluth and A. Meffert, *Fat Sci. Technol.*, 1987, **89**, 147.

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

14 L. A. Rios, P. P. Weckes, H. Schuster, H. Hausmann and W. F. Hoelderich, *Appl. Catal., A*, 2003, **253**, 487.

15 J. M. R. Gallo, S. Texeira and U. Schuchardt, *Appl. Catal., A*, 2006, **311**, 199.

16 A. Martinez, P. Esteve and A. Corma, *Span. Pat.* ES 96-9601086, 1999.

17 J. T. Kloprogge, S. Komarneni and J. E. Amonette, *Clays Clay Miner.*, 1999, **47**(5), 529.

18 T. Maschmeyer, F. Rey, G. Sankar and J. M. Thomas, *Nature*, 1995, **378**, 159.

19 C. Bisio, G. Gatti, E. Boccaleri, L. Marchese, L. Bertinetti and S. Coluccia, *Langmuir*, 2008, **24**, 2808.

20 Y. Yue, A. Gédéon, J.-L. Bonardet, N. Melosh, J.-B. D'Espinose and J. Fraissard, *Chem. Commun.*, 1999, 1967.

21 O. Bortnovsky, Z. Melichar, Z. Sobalik and B. Wichterlova, *Micropor. Mesopor. Mater.*, 2001, **42**, 97.

22 M. A. Vicente Rodriguez, J. de Dios Lopez Gonzalez and M. A. Banares Munoz, *Microporous Mesoporous Mater.*, 1995, **4**, 251; O. Prieto, M. A. Vicente and M. A. Banares-Munoz, *J. Porous Mater.*, 1999, **6**, 335.

23 A. Zecchina, L. Marchese, S. Bordiga, C. Pazé and E. Gianotti, *J. Phys. Chem.*, 1997, **101**, 10128.

24 Z. Shan, P. Waller, W. Zhou, J. C. Jansen, P. Yeh, G. Tartaglione, L. Marchese and T. Maschmeyer, *Chem.–Eur. J.*, 2004, **10**, 4970.

25 C. Bisio, G. Martra, S. Coluccia and P. Massiani, *J. Phys. Chem. C*, 2008, **112**, 10520.

26 M. Maache, A. Janin, J-C. Lavalley and F. Benazzi, *Zeolites*, 1995, **15**, 507.

27 K. Góra-Marek and J. Datka, *Appl. Catal., A*, 2006, **302**, 104.