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# Catalytic isomerisation of $\alpha$ -pinene oxide in the presence of ETS-10 supported ferrocenium ions



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## A R T I C L E I N F O

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## ABSTRACT

Ferrocenium ions,  $[Fc]^+$ , have been immobilised in the microporous titanosilicate ETS-10 by ion exchange of Na<sup>+</sup>/K<sup>+</sup> ions under hydrothermal conditions. The resultant hybrid inorganic-organometallic (ETS-10/ [Fc]<sup>+</sup>) material was characterised by elemental analysis, diffuse reflectance UV–Vis spectroscopy, FT-IR spectroscopy, powder X-ray diffraction, scanning electron microscopy, and thermogravimetric analysis. The ETS-10/[Fc]<sup>+</sup> sample was tested as a catalyst for the isomerisation of  $\alpha$ -pinene oxide (PinOx) at 35 °C. With  $\alpha,\alpha,\alpha$ -trifluorotoluene (TFT) as solvent, campholenic aldehyde (CPA) was the main product formed in 38% yield at 100% conversion and 30 min reaction. Other reaction products included *trans*-carveol, *iso*pinocamphone and *trans*-pinocarveol. The same PinOx conversion and CPA yield could be reached within 1 min reaction time by increasing the reaction temperature (to 55 °C) and the Fe:PinOx molar ratio. Other solvents (hexane, CH<sub>3</sub>CN, toluene) led to poorer results than TFT. Characterisation of the used catalyst, together with an analysis of the catalytic activity of the liquid phase obtained after contact of ETS-10/ [Fc]<sup>+</sup> with TFT, indicated that the ETS-10/[Fc]<sup>+</sup> sample was resistant toward leaching of iron-containing active species. When the recovered solid was reused in a second batch run, catalytic activity was lower than in the first run, while selectivity to CPA was higher.

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# 1. Introduction

ETS-10 (Engelhard Titanosilicate Structure 10) is a crystalline titanosilicate possessing a three-dimensional pore system of elliptical channels defined by 12-membered rings with a maximum pore diameter of 7.6 Å [1,2]. The framework structure, which was solved by Anderson et al. [3], consists of corner-sharing TiO<sub>6</sub> octahedra and corner-sharing SiO<sub>4</sub> tetrahedra. Each titanium atom contributes a net negative charge of -2 that is compensated by extraframework charge-balancing cations (Na<sup>+</sup> and K<sup>+</sup> in the assynthesised material). The O-Ti-O-Ti-O (titania) chains in ETS-10 can be considered as one-dimensional semiconducting quantum wires embedded inside an insulating matrix of SiO<sub>2</sub>. ETS-10 containing alkali cations exhibits catalytic activity for basecatalysed reactions such as the dehydration of tert-butanol [4], the dehydrogenation of alcohols [4,5], the aldol condensation of acetone [6], the transesterification of soybean oil [7], the isomerisation of p-glucose [8], and Knoevenagel condensation [9]. Furthermore, ETS-10 has been shown to be active in the photocatalytic decomposition of organic compounds [10–15]. Surprisingly, few studies have employed ETS-10 as a catalyst support. Most of these center around the immobilisation of nobel metal nanoparticles (NPs), e.g. Pt NPs in NO<sub>x</sub> mediated carbon oxidation [16] and *n*-hexane reforming [17], Ag NPs for bactericidal activity [18], Au NPs for oxidation of 1-phenylethanol with oxygen [19], and Ru NPs for the dry reforming of methane [20]. We recently reported that ferrocenium ions,  $[Fe(C_5H_5)_2]^+$ ([Fe]<sup>1</sup>) could be incorporated into FTS 10 by ion overbange [21].

([Fc]<sup>+</sup>), could be incorporated into ETS-10 by ion-exchange [21]. To the best of our knowledge, this was the first report describing the use of ETS-10 as a support for an organometallic species. The successful encapsulation of [Fc]<sup>+</sup> in ETS-10 is not surprising when the pore size characteristics of the support are examined in detail. Thus, a study on the photocatalytic activity of ETS-10 for the conversion of organic substrates with different molecular widths [13], backed up by theoretical analysis of the ETS-10 structure [22], indicates that the pore limiting diameter of ETS-10 is about 5.6 Å. This is almost an exact match with the shortest dimension of the [Fc]<sup>+</sup> ion, which can be considered a cylinder with dimensions of 6.8 Å  $\times$  5.65 Å [23]. Indeed, it is known, for example, that the





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ferrocenium cation can fully penetrate the cavity of the organic host cucurbit[7]uril [24], which has a cavity opening diameter of 5.4 Å [25], to form a highly stable inclusion complex.

Ferrocenium salts such as [Fc]PF<sub>6</sub> have attracted some interest as catalysts, especially for reactions promoted by Lewis acids, e.g. the Diels-Alder reaction [26], aminolysis of epoxides [27], cyanosilvation of carbonyl compounds [28], Strecker reactions of ketones and aldehvdes [29]. Mannich reaction of aldehvdes, anilines, and ketones to give  $\beta$ -amino-ketones [30], and ring-opening of epoxides with alcohols [31]. Recently, we started to explore organometallic complexes for the catalytic isomerisation of  $\alpha$ -pinene oxide (PinOx) to campholenic aldehyde (CPA), a reaction that is usually promoted by Lewis acid catalysts. Encouraging results were obtained for the indenyl allyl dicarbonyl derivative ( $\eta^{5}$ -Ind)Mo( $\eta^{3}$ - $C_3H_5$ (CO)<sub>2</sub> [32], the dimeric complex [{( $\eta^5$ -Ind)Mo(CO)<sub>2</sub>( $\mu$ -Cl)}<sub>2</sub>] [33] and methyltrioxorhenium(VII) [34]. CPA is useful as an aroma chemical and as a synthetic intermediate for other aroma chemicals and also for some pharmaceuticals [35,36]. In particular, CPA is used in the manufacture of commercial sandalwood-like fragrances, e.g. Sandalore<sup>®</sup> and Javanol<sup>®</sup> (Givaudan), Bacdanol<sup>®</sup> (IFF), Brahmanol<sup>®</sup> (Dragoso) and Polysantol<sup>®</sup> (Firmenich). The isomerisation of PinOx is a good test reaction and has been used to probe the Lewis acidity and catalytic activity of various materials, for example metalorganic frameworks [37]. We therefore chose this reaction to probe the catalytic potential of ETS-10-supported ferrocenium ions, and report the results in this paper.

#### 2. Experimental

## 2.1. Materials and methods

Ferrocenium hexafluorophosphate (97%), acetone (99%),  $\alpha$ , $\alpha$ , $\alpha$ -trifluorotoluene (TFT; anhydrous, >99%), toluene (anhydrous, 99.8%), acetonitrile (anhydrous, 99.8%), and *n*-hexane (anhydrous, 95%) were acquired from Sigma–Aldrich, and  $\alpha$ -pinene oxide (PinOx, 97%) was supplied by TCI. ETS-10 was prepared as described previously [38].

Elemental analysis for carbon and hydrogen were performed at the University of Aveiro using a Leco TruSpec 630-200-200 analyser. Fe contents were determined by ICP-OES at C.A.C.T.I., the University of Vigo, Spain. Powder X-ray diffraction (XRD) data were collected at ambient temperature using a PANalytical Empyrean instrument equipped with a PIXcel 1D detector set at 240 mm from the sample. Cu-K<sub> $\alpha$ 1.2</sub> X-radiation. ( $\lambda_1 = 1.540598$  Å;  $\lambda_2 = 1.544426$  Å) filtered with a nickel foil was used along with a standard transmission sample holder. Operating conditions for the X-ray tube were 45 kV and 40 mA. Intensity data were collected in continuous mode in the ca.  $3.5 \le 2\theta \le 70^\circ$  range, in  $0.02^\circ 2\theta$  steps with a counting time of 50 s per step. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) were carried out on a Hitachi S-4100 microscope. Samples were prepared by deposition on aluminium sample holders followed by carbon coating using an Emitech K 950 carbon evaporator. Thermogravimetric analyses (TGA) were performed using a Shimadzu TGA-50 system with a heating rate of 5 °C min<sup>-1</sup> under air. Room-temperature FT-IR spectra (range 4000–300 cm<sup>-1</sup>) were recorded with a Mattson 7000 spectrometer, using a globar source, a DTGS detector, and potassium bromide cells, with 4 cm<sup>-1</sup> resolution. Diffuse reflectance (DR) UV–Vis spectra were recorded in the range 220-850 nm at ambient temperature using a Jasco V-560 spectrometer equipped with a JASCO ISV-469 integrating sphere.

# 2.2. Synthesis of ETS-10/[Fc]<sup>+</sup>

A Teflon-lined stainless-steel autoclave was charged with ETS-10

(0.50 g), ferrocenium hexafluorophosphate (0.25 g, 0.76 mmol) and millipore deionised water (20 mL), and the mixture heated in an oven at 100 °C for 19 h. The resultant blue solid was isolated, washed with water (4 × 30 mL), acetone (4 × 30 mL), and finally vacuum-dried. Anal. Calcd for Na<sub>0.5</sub>K<sub>0.3</sub>(C<sub>10</sub>H<sub>10</sub>Fe)<sub>0.4</sub>(H<sub>3</sub>O)<sub>0.8</sub>[TiSi<sub>5</sub>O<sub>13</sub>]. 0.5H<sub>2</sub>O: C, 9.27; H, 1.44; Fe, 4.31. Found: C, 9.25; H, 1.60; Fe, 4.3%. Selected FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  = 3446 (br), 3155 (w), 3128 (w), 1639 (m), 1423 (m), 1025 (vs), 982 (sh), 858 (sh), 763 (s), 551 (s), 501 (w), 431 (s), 384 (m), 323 (w).

#### 2.3. Catalytic tests

The catalytic reactions were carried out in a magnetically stirred, closed borosilicate reaction vessel (10 mL capacity), which was immersed in an oil bath thermostated at 35 °C. Typically, the reactor was loaded with catalyst in an amount equivalent to 7.7  $\mu$ mol of iron,  $\alpha$ -pinene oxide (170  $\mu$ mol) and organic solvent (0.5 mL). The solvent and catalyst were mixed at 35 °C for 10 min prior to addition of PinOx (taken as the instant the reaction began). The course of the reaction was monitored using a Varian 3800 GC equipped with a BR-5 (Bruker) capillary column (30 m  $\times$  0.25 mm;  $0.25 \,\mu\text{m}$ ) and a flame ionisation detector, using H<sub>2</sub> as the carrier gas and cyclododecane epoxide as internal standard. The reaction products were identified by GC-MS (Trace GC 2000 Series (Thermo Quest CE Instruments) - DSQ II (Thermo Scientific)), equipped with a capillary DB-5 type column (30 m  $\times$  0.25 mm; 0.25  $\mu$ m) and using He as carrier gas. After a batch run, the solid phase was separated from the reaction mixture by centrifugation and washed  $(3 \times 1 \text{ mL})$ with *n*-hexane. For the reaction using TFT as solvent, the recovered solids were washed with *n*-hexane or TFT. The solids were dried at room temperature overnight and then under vacuum (0.1 bar) for 1 h, at 40 °C, giving the recovered solids referred to as ETS-10/ [Fc]<sup>+</sup>(W-Hex/run2) and ETS-10/[Fc]<sup>+</sup>(W-TFT/run2), respectively.

Contact tests were performed for ETS-10/[Fc]<sup>+</sup> by mixing the material with a solvent (without substrate) at 35 °C for 30 min. Afterwards, the mixture was centrifuged and the liquid phase was separated using a 0.22  $\mu$ m PTFE membrane, and transferred to a separate reactor, where it was preheated at 35 °C for 10 min. Subsequently, PinOx was added in a molar amount equivalent to that used under the typical reaction conditions. The solid obtained from the contact test was vacuum-dried at 40 °C for 1 h, characterised and used in a catalytic batch run.

## 3. Results and discussion

#### 3.1. Synthesis and characterisation

А mixture comprising ETS-10. ferrocenium hexafluorophosphate and water was heated at 100 °C for 19 h in a hydrothermal digestion bomb, giving a deep blue solid. This colour is characteristic of  $[Fc]^+$  and the presence of this ion was confirmed by electronic absorption measurements in the visible region, which showed an absorption maximum at 618 nm, equal to the absorption maximum of [Fc]PF<sub>6</sub> (Fig. 1). This band is assigned as a ligand-tometal charge-transfer transition. Further proof for the presence of [Fc]<sup>+</sup> ions in the hybrid material ETS-10/[Fc]<sup>+</sup> was obtained by measuring the FT-IR spectrum, which showed the characteristic bands of [Fc]<sup>+</sup> at 3128 and 1423 cm<sup>-1</sup>, corresponding to the C–H and C=C stretching modes of the cyclopentadienyl (Cp) ring (Fig. 2). Whereas the salt [Fc]PF<sub>6</sub> exhibits strong bands at 557 and  $833 \text{ cm}^{-1}$  due to PF<sub>6</sub>, these bands are absent for the sample ETS-10/ [Fc]<sup>+</sup>, which indicates that immobilisation of [Fc]<sup>+</sup> ions took place mainly through ion exchange of Na<sup>+</sup> and/or K<sup>+</sup> ions in ETS-10 (Fig. 3). Concerning the bands for the host framework, no significant changes occurred in the Si–O bands (at about 1025 cm<sup>-1</sup>),



**Fig. 1.** Diffuse reflectance UV–Vis spectra of ETS-10  $(- \cdot - \cdot -)$ ,  $[Fc]PF_6 (- - -)$ , and ETS-10/ $[Fc]^+$  (-----).

while, on the other hand, the Ti–O stretching mode at 725  $cm^{-1}$  underwent a shift to 763  $cm^{-1}$ .

Fig. 4 shows representative SEM images of as-synthesised ETS-10 and ETS-10/[Fc]<sup>+</sup>. ETS-10 displays the typical truncated bipyramidal crystal morphology, with crystal sizes ranging between 2.5 and 5  $\mu$ m. The ETS-10/[Fc]<sup>+</sup> sample presents similar morphology. EDS analyses carried out on different crystals of ETS-10/[Fc]<sup>+</sup> generally showed a



**Fig. 2.** FT-IR spectra in the ranges 250–1550 cm<sup>-1</sup> and 2750-4000 cm<sup>-1</sup> of (a) ETS-10, (b) [Fc]PF<sub>6</sub>, and (c) ETS-10/[Fc]<sup>+</sup>. The frequencies of selected bands are indicated.



Fig. 3. Ion-exchange scheme showing the structure of ETS-10 (polymorph B) and ferrocenium ion,  $[Fc]^+$ .

constant composition, although some iron rich particles were found. Average Fe/Ti, Si/Ti and (Fe + Na + K)/Ti atomic ratios were 0.45, 5 and 1.2, respectively. Values of 5 and 1.2 were also obtained for the Si/Ti and (Na + K)/Ti ratios in the ETS-10 starting material. Microanalysis and ICP-OES measurements for ETS-10/[Fc]<sup>+</sup> gave a carbon content of 9.25% and an iron content of 4.3%, which indicate a ferrocenium loading of 0.8 mmol g<sup>-1</sup>. Taking these data together with the EDS-determined atomic ratios allows us to propose the formula (Na,K)<sub>0.8</sub>([Fc])<sub>0.4</sub>(H<sub>3</sub>O)<sub>0.8</sub>[TiSi<sub>5</sub>O<sub>13</sub>].0.5H<sub>2</sub>O for the hybrid material.



Fig. 4. Representative SEM images of (a) ETS-10 and (b) ETS-10/[Fc]+.

Thermogravimetric analysis of ETS-10/[Fc]<sup>+</sup> revealed a weight loss of 3.4% from ambient temperature to 250 °C, attributed to loss of water, followed by a loss of 10.6% up to 500 °C, attributed to decomposition of encapsulated ferrocenium ions (Fig. 5). The TGA curve for as-synthesised ETS-10 is shown for comparison, and reveals a 13.3% weight loss from ambient temperature to 300 °C, but no mass loss step in the temperature range of 300–500 °C.

Fig. 6 shows the powder XRD patterns of the starting materials (as-synthesised ETS-10 and  $[Fc]PF_6$ ) and the ETS-10/ $[Fc]^+$  sample. After treatment with  $[Fc]^+$ , the reflections characteristic of ETS-10 are maintained at the same positions, although there are significant changes in the relative intensities of some peaks. No reflections characteristic of  $[Fc]PF_6$  are present, providing further evidence for the successful encapsulation of  $[Fc]^+$  ions within the channels of the titanosilicate host material.

#### 3.2. Catalysis

The ETS-10/[Fc]<sup>+</sup> sample was tested as a catalyst for the isomerisation of  $\alpha$ -pinene oxide (PinOx), using TFT as solvent, at 35 °C (Table 1). Campholenic aldehyde (CPA) was the main product formed in 38% yield at 100% conversion and 30 min reaction (Scheme 1). Other reaction products included trans-carveol, isopinocamphone and *trans*-pinocarveol. The turnover frequency (TOF, calculated from the conversion at 1 min reaction) was 17 mol  $mol_{Fe}^{-1}$  min<sup>-1</sup>. With ETS-10 (without [Fc]<sup>+</sup>) as catalyst, the PinOx reaction was sluggish (15% conversion at 24 h), and CPA yield was less than 3%. Hence, the active species which promote the isomerisation reaction contain iron. The catalytic performance of ETS- $10/[Fc]^+$  was compared with that for the ferrocenium salt ([Fc]PF<sub>6</sub>) on the basis of the same initial molar ratio Fe:PinOx of 1:22. The salt [Fc]PF<sub>6</sub> led to slightly higher reaction rate and lower CPA selectivity than ETS-10/[Fc]<sup>+</sup>, which may be due to differences in the chemical nature of the iron species and/or catalyst stability (Table 1).

Increasing the initial Fe:PinOx molar ratio from 1:22 to 1:6.3, and the reaction temperature from 35 °C to 55 °C, led to similar CPA yield (38%) at 100% conversion, but in a shorter period of time (1 min,



**Fig. 5.** TGA curves of as-synthesised ETS-10 (—), ETS-10/[Fc]<sup>+</sup> (- –), ETS-10/ [Fc]<sup>+</sup>(W-TFT/run2) (- –), and ETS-10/[Fc]<sup>+</sup>(W-Hex/run2) (- -).



Fig. 6. Powder XRD patterns of (a)  $[Fc]PF_{6}$ , (b) ETS-10, (c) ETS-10/ $[Fc]^+$ , (d) ETS-10/ $[Fc]^+$ (W-TFT/run2), (e) ETS-10/ $[Fc]^+$ (W-Hex/run2), and (f) ETS-10/ $[Fc]^+$ -TFT<sub>ct</sub>.

Table 1). Several iron based heterogeneous catalysts have been previously investigated for the isomerisation of PinOx to CPA: iron oxide supported on TiO<sub>2</sub> [39], SiO<sub>2</sub> [40], Zr–SiO<sub>2</sub> [40], mesoporous SiO<sub>2</sub> [41] and MCM-41 [42]; iron(II) and iron(III)-containing MCM-41 [43]; FeCl<sub>3</sub> supported on SiO<sub>2</sub> or TiO<sub>2</sub> nanoparticles [44]; iron(III)-containing mesoporous and microporous nickel phosphate molecular sieves [45]; iron-containing zeolites [46] and iron(III)-containing MOFs [47]. In comparison to titania-supported iron oxide, the results for ETS-10/ [Fc]<sup>+</sup> are fairly good; the former led to 38% CPA yield at 95% conversion, using cyclohexane as solvent, at 70 °C and 325 min [39].

For ETS-10/[Fc]<sup>+</sup>, the type of solvent (TFT, hexane, toluene,  $CH_3CN$ ) influenced significantly the catalytic reaction (Table 1). The reaction of PinOx was sluggish with hexane or  $CH_3CN$  as solvent, at 35 °C. Considerable improvements were observed for toluene or TFT (higher reaction rates and CPA yields), the latter leading to the best catalytic results. For all solvents tested, the solids were recovered and characterised by FT-IR spectroscopy, and exhibited weak bands attributed to the cyclopentadiene ring of the supported species (3128 and 1423 cm<sup>-1</sup>, Fig. 7). The differences in catalytic results for the different solvents may be due to competitive adsorption effects, and/or differences in catalyst stability.

In order to check for leaching of active species, a contact test (described in Section 2.3) was performed for ETS-10/[Fc]<sup>+</sup> using TFT as solvent (without substrate), at 35 °C. The liquid phase obtained after separating the catalyst by filtration was colourless, suggesting that no iron-containing species were desorbed from the catalyst into the liquid phase. The substrate PinOx was added to the liquid phase obtained from the contact test and the solution was left to react under typical conditions for 4 h. The results were comparable with those obtained without catalyst, giving only 10% conversion and 2% CPA yield, with TFT as solvent. Hence, ETS-10/[Fc]<sup>+</sup> seems to be stable towards metal leaching. The solid obtained from the contact test of ETS-10/[Fc]<sup>+</sup> with TFT (denoted ETS-10/[Fc]<sup>+</sup>-TFT<sub>ct</sub>)

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Catalytic isomerisation of PinOx in the	e presence of ETS-10/[Fc] <sup>+</sup> and [Fc]PF <sub>6</sub> .
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Catalyst	Fe:PinOx <sup>a</sup>	T/°C	Solvent	Time	Conv. (%) <sup>b</sup>	CPA Sel. (%) <sup>c</sup>
ETS-10/[Fc]+	1:6.3	55	TFT	1 min	100	38
ETS-10/[Fc]+	1:22	35	TFT	1 min/30 min	76/100	35/38
ETS-10/[Fc]+	1:22	35	Hexane	4 h	10	18
ETS-10/[Fc]+	1:22	35	Toluene	24 h	59	47
ETS-10/[Fc]+	1:22	35	CH₃CN	24 h	19	28
ETS-10/[Fc] <sup>+</sup> (W-Hex/run2) <sup>d</sup>	1:22	35	TFT	24 h	41	51
ETS-10/[Fc] <sup>+</sup> (W-TFT/run2) <sup>d</sup>	1:22	35	TFT	4 h/24 h	56/74	62/57
ETS-10 <sup>e</sup>	-	35	TFT	1 h/24 h	4/15	16/15
[Fc]PF <sub>6</sub> <sup>f</sup>	1:22	35	TFT	1 min/30 min	94/100	25/29

<sup>a</sup> Initial amount of catalyst based on Fe:PinOx molar ratio.

<sup>b</sup> PinOx conversion at the indicated reaction time.

<sup>c</sup> CPA selectivity at the indicated reaction time.

<sup>d</sup> Catalysts correspond to the solids recovered after a batch run using ETS-10/[Fc]<sup>+</sup> as catalyst and TFT as solvent; the used solid was washed with hexane or TFT, and dried at 40 °C, giving ETS-10/[Fc]<sup>+</sup>(W-Hex/run2) and ETS-10/[Fc]<sup>+</sup>(W-TFT/run2), respectively.

<sup>e</sup> Catalyst used in a similar mass amount as that used for ETS-10/[Fc]<sup>+</sup>.

<sup>f</sup> Catalyst used in a similar molar amount of iron as that used for ETS-10/[Fc]<sup>+</sup>.

was characterised by FT-IR spectroscopy (Fig. 7) and powder XRD (Fig. 6). The FT-IR spectrum shows bands attributed to the cyclopentadiene ring of the supported species, while the powder XRD pattern is unchanged from that for ETS-10/[Fc]<sup>+</sup>, confirming that the hybrid material has good stability towards metal leaching under the catalytic reaction conditions used.

The solid ETS-10/[Fc]<sup>+</sup>-TFT<sub>ct</sub> was tested for the isomerisation of PinOx under typical conditions, and led to 29% conversion and 44% CPA selectivity, which was poorer than that observed for the original catalyst (76% conversion and 35% CPA selectivity). Possibly, the chemical nature of the supported iron species changes and/or active sites are passivated by adsorption of reaction products. PinOx can undergo cationic ring-opening polymerisation to give ether polymers [48]. To the best of our knowledge there are no reports on the polymerisation of PinOx in the presence of iron catalysts. Nevertheless, in an attempt to improve the catalyst recovery by simple washing, the solid recovered from a 30 min batch run of the reaction of PinOx (with TFT as solvent) was washed (W) with

hexane or TFT, and vacuum-dried at 40 °C, giving ETS-10/[Fc]<sup>+</sup>(W-Hex/run2) and ETS-10/[Fc]<sup>+</sup>(W-TFT/run2), respectively. The washed and dried solids were characterised and tested in a second batch run. The FT-IR spectra and powder XRD patterns (Fig. 6) of ETS-10/[Fc]<sup>+</sup>(W-Hex/run2) and ETS-10/[Fc]<sup>+</sup>(W-TFT/run2) were similar to those for the original catalyst ETS-10/[Fc]<sup>+</sup>. The PinOx conversion at 24 h was greater for ETS-10/[Fc]<sup>+</sup>(W-TFT/run2) than for ETS-10/[Fc]<sup>+</sup>(W-Hex/run2) (Table 1), suggesting that TFT is a more efficient solvent than hexane for the catalyst recovery. However, the reaction for the two solids was slower than for the original catalyst. TGA (Fig. 5) and elemental analysis (carbon content of 10 wt%) data for ETS-10/[Fc]<sup>+</sup>(W-TFT/run2) were similar to those for ETS-10/[Fc]<sup>+</sup>, suggesting that the catalyst was efficiently washed and dried, and did not contain reaction products. The same applies for the solid obtained from the catalytic reaction with hexane as solvent, washed with hexane and vacuum-dried 40 °C



Scheme 1. Products formed in the isomerisation of PinOx catalysed by ETS-10/[Fc]+.



**Fig. 7.** Selected regions of the FT-IR spectra of the solids recovered after a batch run using ETS-10/[Fc]<sup>+</sup> as catalyst and the solvent (a) TFT, (b) toluene, (c) CH<sub>3</sub>CN or (d) hexane, and of (e) ETS-10/[Fc]<sup>+</sup>-TFT<sub>ct</sub>.

(carbon content of 9.6 wt%). The lower catalytic activity may be due to changes in the chemical nature of the supported iron species. Nevertheless, the CPA selectivity at ca. 75% conversion was greater for ETS-10/[Fc]<sup>+</sup>(W-TFT/run2) than for the original catalyst (57% and 35% selectivity, respectively, Table 1).

#### 4. Conclusions

In this work, the immobilisation of ferrocenium cation  $([Fc]^+)$  in the channels of ETS-10 has been achieved by performing a single ion exchange cycle with an aqueous solution of ferrocenium hexafluorophosphate under hydrothermal conditions. The ETS-10/ [Fc]<sup>+</sup> sample exhibited catalytic activity for the liquid-phase isomerisation of  $\alpha$ -pinene oxide (PinOx), under moderate reaction conditions (35–55 °C, air). In comparison to the salt  $[Fc]PF_6$ , the supported catalyst ETS-10/[Fc]<sup>+</sup> was less active, and slightly more selective to campholenic aldehyde (38% yield at 100% conversion). The catalyst is stable toward metal leaching, based on contact tests. However, the used catalyst (washed with TFT and dried) exhibited lower activity than the original one, suggesting that the chemical nature of the supported iron species changed. Nevertheless, the recovered catalyst led to significantly higher CPA selectivity than the original catalyst (57% and 35%, respectively, at ca. 75% conversion). These results indicate that hybrid inorganic-organometallic materials based on ferrocenium ions immobilised in porous supports may warrant further investigation as solid Lewis acid catalysts for the isomerisation of  $\alpha$ -pinene oxide.

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