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Skeletal isomerisation of oleic acid over ferrierite in the presence and absence of triphenylphosphine: Pore mouth catalysis and related deactivation mechanisms



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ABSTRACT

The formation and nature of coke (precursor) species has been studied during the skeletal isomerisation of oleic acid catalysed by protonated ferrierite, in the presence and absence of a triphenylphosphine promoter. UV–Vis and FT-IR spectroscopic analyses of the spent catalyst materials, complemented by NMR and mass spectrometry of the coke deposits extracted after HF dissolution, provide new insights into the deactivation mechanisms. Initial high catalyst activity and selectivity are quickly lost, despite conservation of the framework integrity, as a result of severe deactivation. Pore blockage is detected very early in the reaction, and only the pore mouth is actively employed. Additionally, polyenylic carbocations formed by hydrogen transfer reactions poison the active sites; they are considered to be the precursors to traces of condensed aromatics detected in the spent catalyst. Dodecyl benzene is the major "coke" constituent, and its precursor probably also competes for the active sites.

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1. Introduction

Branched-chain unsaturated fatty acids (BUFA) derived from natural vegetable oil sources are raw materials of great interest within the lubricant, surfactant and cosmetic markets, as they remain liquid after hydrogenation and have superior oxidative stability compared to unsaturated (liquid) fatty acids. Furthermore, they have useful interfacial properties and are compatible with a wide range of organic compounds. Some key applications include friction modifiers for fuel and lubricant oils, dispersants for pigments and metal powders, and emulsifiers for topical skincare products. The current commercial process for making BUFA is coupled to the production of oligomeric fatty acids, and maximum mass yields are limited to ca. 50%. Clays, such as montmorillonite, are typically used as catalyst in this process [1,2].

Decoupling of the skeletal isomerisation and oligomerisation production processes is highly desired yet challenging, as both

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reaction pathways go through the same carbocation intermediates. The use of zeolites as solid acids holds considerable promise in this respect, as discrimination between these two competing pathways could possibly be achieved by making use of their properties as shape-selective catalysts.

Table 1 summarises the main product classes that are obtained after a zeolite-catalysed skeletal isomerisation of a commercial oleic acid (OA), which mainly consists of *cis*-9-octadecenoic acid (1). Cis/trans isomerisation of the double bond to elaidic acid (5) occurs readily in the presence of acidic sites and is an important early-stage reaction. Beside the desired BUFA (4), a small amount of (alkyl branched) γ -lactones (6) are formed as a result of double-bond migration followed by lactonisation [3]. Other monomeric components include traces of stearic (2) and linoleic (3) acids, which are derived from the starting material and from hydrogen transfer reactions [4]. Higher molecular weight compounds include oligomerised fatty acids (dimeric C36 (7) and higher oligomers), as well as monoestolides (8) and polyestolides formed by the reaction of a carboxylic group and an activated doubled bond [5].

The dedicated production of BUFA from OA using zeolites has been investigated by several groups [6-10]. Yields are difficult to



Abbreviations: BUFA, branched-chain unsaturated fatty acids; OA, oleic acid; MO, methyl oleate; TPP, triphenylphosphine.

Table 1

Feedstock: Oleic acid (OA) Priolene™ 6936	
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(2) stearic acid (octadecanoic acid), 1.7 wt%	on
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	ÓН
(3) linoleic acid (<i>cis,cis</i> -9,12-octadecadienoic acid), 3.2 wt%	%
Crude monomeric fraction	
1	0
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(4) alkyl-branched isomer of oleic acid (BUFA) ^a	
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(5) elaidic acid (<i>trans</i> -9-octadecenoic acid) ^a	-
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(6) γ -stearolactone (5-tetradecyloxolan-2-one) ^b	•
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(7) isomer of C36 dimer acid ^a	
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(mono) estalida of alais asid ^a	

^a Compounds (**4**), (**5**), (**7**) and (**8**) are typical isomers of the indicated species. ^b Alkyl-branched isomers of (**6**) are also identified.

compare due to the limited analytical information given about the detailed product composition. In an early example [6], OA was converted to BUFA using zeolites such as protonated mordenite, with medium-sized channels and linear pore structures. Addition of a small amount of water was shown to promote the conversion to BUFA, postulated to be due to the conversion of Lewis acid sites into Brönsted ones. Comparison with the traditionally used clays demonstrated the superior selectivity of the zeolites to monomeric acids. Further improvements were obtained by crystal morphology manipulation, such as flat-plate crystals of L-type zeolites with the

pores along the shortest dimension; higher activity and selectivity were explained by the increase in pore diffusion rate [7–8]. OA conversion of up to 50% was disclosed with large-pore (Beta) zeolites [9], and up to 60% with mesoporous zeolites (MAS-5) [10]. Again, such structures are believed to be large enough for the OA to diffuse into, but still small enough to limit the formation of polymerised fatty acids. A further advantage is that less coke is reportedly formed with these large-pore zeolites.

Recently, a step change in both OA conversion (>95%) and selectivity towards BUFA (>70%) has been achieved by Ngo and co-workers using commercial, protonated ferrierite catalysts [11]. Selectivity towards the monomeric fraction could be further improved by the use of a bulky Lewis base as promoter, e.g. triphenylphosphine (TPP) [12]. It is believed that such a base interacts with the non-shape-selective acidic sites on the external zeolite surface. The size of the Lewis base prevents it from entering the zeolite framework and interacting with shape-selective acitive sites within the channels or, as will be shown here, in the pore mouths.

Protonated ferrierite thus seems to have an optimal structure and acidity for the skeletal isomerisation of OA. It is a mediumpore zeolite, characterised by two types of one-dimensional channels: the 10-membered (MR) channels $(4.2 \times 5.4 \text{ Å})$ and the 8-MR channels $(3.4 \times 4.7 \text{ Å})$, which cross perpendicularly; in addition, the latter contain spherical ferrierite cavities of 6–7 Å in size with 6- and 5-MR windows. Compared to other 10-MR zeolites, ferrierite has a low ratio of Lewis to Brönsted sites [13]. Its acidity has been characterised in detail using FT-IR spectroscopy and five distinct Brönsted acidic sites could be assigned, i.e. hydroxyl groups in 10-MR channels (20% of Si(OH)Al), at intersections between 10- and 8-MR channels (50% of Si(OH)Al), in the 8-MR channels, and finally in the 6-MR and 5-MR-windowed cavities [14]. However, overall acidity depends strongly on the accessibility of those sites [15]. FT-IR studies using bulky probe molecules also showed that the external surface of protonated ferrierite has terminal silanols (some with significant Brönsted acidity), as well as Lewis acid sites, but no bridging hydroxyl groups [16].

As ferrierite is much more expensive than the montmorillonite clay used in the current isomerisation process, catalyst stability and the possibility to reuse and/or regenerate the catalyst are key to the economic viability of BUFA production. While no studies have dealt with the details of ferrierite deactivation in BUFA production, the deactivation of zeolite materials in general has been extensively studied and the possible mechanisms have been reviewed [17,18]. For the skeletal isomerisation of OA, loss of activity or selectivity could be caused by build-up of organic deposits due to simple deposition (fouling), or by deposition after transformation ("coking"). An alternative mechanism is the poisoning of active sites by strong chemisorption of species. Finally, chemical and structural alterations could result from e.g. de-alumination and/or collapse of zeolite framework.

High activity and selectivity with ferrierite in the skeletal isomerisation of OA could only be obtained with the fresh catalyst, and direct reuse did not seem to be successful [11]. Later, successive solvent and acidic washings of the spent catalyst were reported to allow up to ten reuses without significant loss of activity and selectivity [12]. This result suggests that chemical or structural alterations of the zeolite are not the cause of deactivation. However, the actual deactivation mechanism was not discussed, and the combination of solvent and hydrochloric acid washing would be difficult to implement in an oleochemical production plant. Efficient catalyst recycling procedures first require a thorough understanding of the deactivation process, i.e. the alteration of the catalytic properties of the ferrierite during the reaction of interest. To date, such a study has not been reported for the zeolite-catalysed skeletal isomerisation of OA; only the poisoning of Beta zeolite by a carboxylic acid group has previously been described, by comparing the reaction of 1-octadecene to OA in the absence of water [19].

On the other hand, considerable research has been devoted to the deactivation of ferrierite in the skeletal isomerisation of butene [20]. The catalyst is known for its poor initial selectivity to isobutene, and its high selectivity and stability at higher times-on-stream (TOS). Process parameters (especially reaction temperature) were found to affect both the amount and nature of the "coke" [21]. Composition of "coke" (including slightly condensed aromatics with methyl substituents) and location (at the intersection of the 8- and 10-MR channels) were determined, and a reaction pathway was proposed to explain the high selectivity to isobutene of the coked rather than fresh catalyst (only 10% of the pore volume is accessible at maximum selectivity) [22]. Additionally, concentration and strength of Brönsted acid sites were found to affect "coke" formation as well as selectivity; indeed, higher isobutene selectivity and lower "coking" were observed with lower acid site density [23]. "Coke" nature, location, rate and mode of formation have been further investigated by various spectroscopies. Of these, in situ IR spectroscopy gave much valuable information. When combined with a tapered element oscillating microbalance (TEOM), both vacant Brönsted acid groups and "coking" could be monitored as a function of TOS [24]. FT-IR was also used to confirm accessibility of Brönsted sites of spent ferrierite following deuteroacetonitrile (CD₃CN) adsorption [25,26] and played a key role in the elucidation of the complex mechanism supporting increased selectivity at high TOS [26]. Although carried out in the gas phase at a higher temperature and with molecules of much smaller diameter, these studies provide important clues for our research.

Here, we present a detailed study of the deactivation pathways of ferrierite during skeletal isomerisation of OA, with the aim to provide pointers to ultimately improve its stability and to establish methods for its complete regeneration. OA and its methyl ester were reacted in a lab-scale batch reactor using conditions optimised by Ngo et al. [12] in the presence and absence of triphenylphosphine. The nature of the "coke" and its rate of formation were studied (amongst others) by a combination of UV–Vis and FT-IR spectroscopy. These findings were complemented by an analysis of the "coke" extract after HF dissolution of the spent zeolite materials. The causes for the activity loss could thus be systematically investigated, and reaction mechanisms explaining the deactivation proposed.

2. Experimental

2.1. Chemicals and catalyst material

OA with tradename PrioleneTM 6936 (92.2% C18:1 (1), 3.2% C18:2 (3), 0.2 C18:3 and 3.7% saturated fatty acids (mainly C18 (2)) and the methyl ester of OA (AV < 0.10 mg KOH/g, MO) were obtained from Croda. Triphenylphosphine (TPP, 99%) was obtained from Aldrich Chemicals. The zeolite material K⁺-Ferrierite (HSZ-720KOA) with a Si/Al ratio of 8.9, originates from Tosoh Corporation. K⁺-Ferrierite was activated prior to catalyst testing by conversion to its protonated form, further denoted as H-Fer, using an ion-exchange procedure with hydrochloric acid (HCl, 1 M) at room temperature (RT) [27], before air-drying for three days at RT.

2.2. Catalyst testing, sampling and catalyst recovery

The key parameters for all experiments are summarised in Table 2. Catalyst testing was carried out in an RC1 high-pressure reactor from Mettler Toledo, using the following amounts: 1000 g OA or its methyl ester MO, 50.0 g H-Fer, 3.75 g TPP and 10.0 g demineralised water (or/and methanol). After purging with nitrogen 3 times, the reactor was pressurised to about 1 bar and heated to (a maximum of) 260 °C at a rate of 6 °C/min, resulting in a pressure of about 11 bar. Reaction temperature was typically held for 6 h (unless otherwise stated), before the mixture was cooled to 80 °C and filtered under nitrogen for a minimum of 4 h. Spent catalyst from experiment 15 was collected and reused in experiment 16 after acetone washing; for practical reasons, the catalyst loading was reduced to 1.5 wt% and the promoter was omitted in both runs 15 and 16.

Because of the large differences in molecular weight of the different components in the crude reaction mixture, its composition was determined in two steps. First, the oligomer concentration in the crude reaction mixture was determined by high-temperature GC (HT-GC). The monomeric fraction was separated from the oligomers by distillation at a temperature of 260 °C under a pressure of <1 mbar. Subsequently, to reduce chemical complexity and facilitate analyses, a small amount of the collected monomeric fraction was diluted in ethyl acetate (40 mg/mL), hydrogenated at RT for 45 min using 40 mg Adam's catalyst (reduced in situ, hydrogen flow of 50 mL/min) and subjected to GC analyses.

Oleic acid ((1), with an initial mass fraction $X_{C18:1,0}$), linoleic acid ((3), $X_{C18:2,0}$) and linolenic acid ($X_{C18:3,0}$), are considered as

Table 2

Overview of the 16 experiments for the skeletal	isomerisation over H-Fer in the pre	esence and absence of TPP, with	different feeds; reaction temperature of 260 °C
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Exp.	Feed type	H-Fer loading (wt% on feed)	Additive	TPP loading (wt% on feed)	Reaction time (h)
1	OA	5	H ₂ O	0	0.5
2	OA	5	H ₂ O	0	1
3	OA	5	H ₂ O	0	2
4	OA	5	H ₂ O	0	6
5	OA	5	H_2O	0	12
6	OA	5	H_2O	0.375	0 ^a
7	OA	5	H ₂ O	0.375	0.5
8	OA	5	H ₂ O	0.375	2
9	OA	5	H ₂ O	0.375	6
10	OA	5	H ₂ O	0.375	12
11	OA + 3% C18:2 (3)	5	H_2O	0.375	6
12	OA + 9% C18:2 (3)	5	H ₂ O	0.375	6
13	MO	5	CH₃OH	0.375	6
14	MO	5	CH ₃ OH/H ₂ O ^b	0.375	6
15	OA	1.5	H_2O	0	6
16 ^c	OA	1.5	H ₂ O	0	6

^a 2 min at reaction temperature.

^b Weight ratio CH₃OH/H₂O = 3.5.

^c Spent catalyst from experiment 15 after filtration and acetone washing.

the reactive components of OA; positional and cis/trans isomers are implicitly included in the simplified nomenclature. Their mass conversion (y_t) was determined by quantification of the mass fraction of stearic acid ((**2**), $x_{C18,t}$) in the hydrogenated monomer fraction as a function of time *t*. The onset of the reaction (t = 0) is designated as the time when the reaction mixture reaches the temperature setpoint of 260 °C. A correction is made for the distillation yield of the monomeric species ($y_{M,t}$) as determined by HT-GC, and for the initial mass fraction of unreactive species, i.e. stearic acid ($X_{C18,0}$). The mass conversion of all unsaturated components, subsequently referred to simply as "conversion", is then given by:

$$y_t = 1 - \frac{\left[(x_{C18,t} + x_{C18:1,t}) \times y_{M,t} - X_{C18,0} \right]}{[X_{C18:1,0} + X_{C18:2,0} + X_{C18:3,0}]}$$
(E1)

Note that due to the closely similar molecular weights of these molecules, mole and mass conversions can be considered almost equivalent. The selectivity towards BUFA ($s_{B,t}$) is derived from the mass fraction of all hydrogenated BUFA ($x_{B,t}$) in the hydrogenated monomer fraction. Again, a correction was made for the distillation yield of the monomeric species ($y_{M,t}$):

$$s_{B,t} = \frac{[x_{B,t} \times y_{M,t}]}{[(X_{C18:1,0} + X_{C18:2,0} + X_{C18:3,0}) \times y_t]}$$
(E2)

30 g of H-Fer catalyst cake from each isomerisation reaction was transferred into a 500 mL erlenmeyer flask and suspended in 100 mL of acetone. After stirring for about 2 h at room temperature, the mixture was filtered (0.2 μ m polytetrafluoroethylene – PTFE – filter), using an extra 100 mL of solvent to rinse. The operation was repeated until no dry mass was detected following evaporation of the filtrate, after which the spent catalyst was air-dried for 24 h. The yield of spent catalyst after this washing series varied from 44 to 49% m/m (of the original cake). The white colour of the fresh H-Fer turned to light grey after reaction in the absence of TPP and remained light grey after washing. On the contrary, all spent catalysts from reactions involving TPP were characterised by a more yellow colouration (both before and after washing).

Spent catalyst from one selected experiment (entry 9 in Table 2) was calcined in air at 500 °C for 12 h [11]. For three selected experiments (4, 9 and 12, Table 2), 300 mg of acetone-washed spent catalyst was dissolved in hydrofluoric acid (HF) and the acidic solution extracted using dichloromethane. After neutralisation with calcium carbonate, addition of diethyl ether (10 mL) and filtration, the organic fraction was dried at reduced pressure (20 mbar) at 40 °C, leaving a greenish and odorous residue.

2.3. Analytical methods

The composition of the crude reaction mixtures was determined using high-temperature GC (HT-GC) after methylation using diazomethane. The GC was equipped with a cold on-column injection and a metal column with a non-polar stationary phase Cp-SimDist Ultimetal (Chrompack WCOT, 5 m × 0.53 mm × 0.17 μ m) and the components detected with a flame ionisation detector (FID) based on retention time. The carrier gas was He with a constant flow of 20 mL/min. The temperature programme used was as follows: initial temperature of 60 °C, hold for 1 min; temperature increase of 30 °C/min until 150 °C; hold 0 min; temperature increase of 12 °C/min until 380 °C; hold 10 min. The detector was set at 400 °C. The injection volume was 1 μ L for a concentration of 1 mg/mL.

The hydrogenated monomer fractions were analysed by GC after methylation with diazomethane. The GC was equipped with a split injection and a fused silica capillary column with a polar stationary phase FFAP-CB (Chrompack WCOT, $25 \text{ m} \times 0.32 \text{ mm} \times 0.30 \mu\text{m}$), and the components detected with FID based on

retention time. The carrier gas was He with a constant flow of 2.1 mL/min and a split flow of 75 mL/min. The temperature programme used was as follows: initial temperature of 120 °C, hold for 0 min; temperature increase of 8 °C/min until 250 °C; hold 20 min. The detector was set at 270 °C. The injection volume was 1 μ L for a concentration of 40 mg/mL.

For ICP-MS analysis, the crude mixtures were first digested using a closed vessel microwave system (CEM). 8.0 mL 70% HNO₃ and 2.0 mL 37% HCl were added to 0.5 g sample. The mixture was submitted to the following temperature programme: 10 min ramp to 120 °C; hold 5 min; 5 min ramp to 180 °C; hold 30 min. The resulting material was diluted to 50.0 mL with ultrapure water (18 M Ω cm at 25 °C). Elemental analyses were carried out using an ICP-MS (Agilent 7500ce with Shield Torch System) equipped with an Agilent Octopole Reaction System (ORS) with the option for adding reaction gases, Agilent Quartz torch and Shield Plate and Glass Expansion 'Micromist' nebulizer. The first sample of each series was determined by standard addition. The next samples were analysed by external calibration, with an internal standard. Al was measured at m/z 27; helium was used as collision gas and Ge (m/z 72) as internal standard.

TGA analyses of the (spent) catalysts were performed on a Mettler Toledo TGA/SDTA851 using a platinum pan (no lid). The measurements were performed under air (flow of 100 mL/min) at a heating rate of 10 °C/min from RT to 1000 °C. The first derivative was used to define the step limits of the "coke" losses.

Nitrogen physisorption on the (spent) catalyst materials was performed with an automated gas sorption system Micromeritics TriStar 3000. Before the measurements, the samples were out-gassed for 12 h at 250 °C (fresh catalyst only) or at 150 °C. Surface areas were calculated using the BET model. The external surface area (S_E), micropore surface area (S_μ), and micropore volume (V_μ) were determined by applying the *t*-plot method.

IR spectra of the (spent) catalyst materials were obtained by first pressing the material into a self-supporting wafer of 14–17 mg with a diameter of about 13 mm. The wafer was placed in a FT-IR cell connected to an oven. Adsorbed water was removed by heating it at 120 °C under vacuum (1.6 mbar) for 24 h. A Perkin– Elmer System 2000 was used to record the FT-IR spectra in transmission mode from 4000 to 400 cm⁻¹ (resolution of 4 cm⁻¹ and 25 scans), with the spectrum of the empty cell as background (ratio).

A Varian Cary 500 Scan spectrophotometer was used to record UV–Vis spectra of the (spent) catalyst materials in diffuse reflectance mode, in the range 200–800 nm (scan speed 600 nm/min and 1 cycle).

FT-IR spectra of the coke residues isolated after HF treatment were recorded on a FT-IR spectrometer (Digilab FTS 7000 series) equipped with a DTGS detector. The spectra of the film on KBr (128 scans) were recorded at RT between 4000 and 400 cm⁻¹, with a spectral resolution of 4 cm⁻¹.

Extracts obtained after HF dissolution were dissolved in CDCl₃ and ¹H, ¹³C and DEPT NMR spectroscopic measurements were conducted at 25 °C on a Varian Oxford AS400 MHz spectrometer. Chemical shifts (δ) are given in ppm referenced to the residual solvent signal.

For GC–MS analysis, the coke residues were re-dissolved in 1,1,2-trichloro-trifluoroethane (TTE) and the components separated by HT-GC. The GC was equipped with a cold on-column injection and a capillary column with a non-polar stationary phase ZB-1HT (Zebron Inferno, $30 \text{ m} \times 0.32 \text{ mm} \times 0.1 \mu\text{m}$). The carrier gas was He with a constant flow rate of 2.5 mL/min. The temperature programme used was as follows: initial temperature of 50 °C, hold for 1 min; temperature increase of 15 °C/min until 400 °C; hold 20 min. The injection volume was 0.5 μ L. The components were detected with a quadrupole MS detector (Agilent MSD 5975 B Inert) in electron ionisation mode (70 eV). The interface

temperature was set at 350 °C, the source temperature at 230 °C and the quadrupole temperature at 150 °C. The scan range was 29-1050 amu with 1.48 scans/s.

3. Results

3.1. Catalyst testing

The skeletal isomerisation of OA was carried out following the procedure of Ngo and co-workers [12], using a weight loading of 5% H-Ferrierite (H-Fer) an addition of water between 1.0% and 1.5% of water added with respect to OA. Table 2 gives an overview of the 16 experiments.

Conversion and selectivity (wt%) for the 6 h runs are summarised in Table 3, while the detailed compositions (wt%) of the crude mixtures are shown in Table 4. A control reaction was carried out in the absence of TPP (experiment 4), to assess its influence. TPP addition (experiment 9) resulted in a significant increase in the selectivity towards BUFA (from 70% to 88%), while conversion remained similar (95% and 92%). The total amount of lactones formed is only slightly lower in the reaction with TPP (9 wt%) compared to the one without (11 wt%). Therefore, the gain in BUFA yields can be almost fully attributed to the drop in oligomer yield. HT-GC analyses of distillation residues indicate that the higher molecular weight, oligomer fraction contains both estolides (product 8, Table 1) and dimers (product 7, Table 1), with an estolide:dimer weight ratio of 2.3 when using TPP, and 0.14 in its absence. As expected, the bulky base efficiently neutralises external acid sites, which are known to promote dimer acid formation [23]. The only bimolecular reaction that occurs is (poly)estolide formation, commencing at much lower temperature. A possible explanation is that the equilibrium between the TPP and the catalyst surface is not fully established at this early stage.

Linoleic acid (reactant **3**, Table 1) is found in most commercially important vegetable oils, and its influence on the mechanisms of deactivation therefore needs to be assessed. OA, which already

contains 3.2 wt% of linoleic acid (**3**), was spiked with additional linoleic acid, resulting in a marked decrease in both activity and selectivity. Comparison of experiments 9, 11 and 12 shows that increasing the concentration of linoleic acid in the feed leads to a concomitant loss in yield of BUFA. This result suggests that the presence of polyunsaturations in the feed is significantly accelerating catalyst deactivation.

The effect of the carboxylic acid functionality was assessed by using the methyl ester of OA, methyl oleate (MO), as feedstock in two reactions (i.e., experiments 13 with methanol only, and 14 with a methanol/water mixture). These reactions showed a considerable drop in conversion (57 and 72 wt%, respectively). Interestingly, in both experiments, the yield of the monomer fraction was very high (98 and 96 wt%, respectively); a possible explanation is the absence of an acid-base reaction between TPP and MO (unlike OA). leaving an excess of TPP available to block the external acid sites. Selectivity towards skeletal isomerisation was worsened if a methanol/water mixture was used; the gain in conversion resulted only in extra lactones (product 6, Table 1). The water therefore appears to have several functions; in addition to increasing the number of Brönsted sites as mentioned in the introduction, it also seems to promote the formation of esterification products, mostly lactones and to a minor extent estolides (product 8, Table 1).

Conversion and selectivity were further studied as a function of time (2 min to 12 h). Fig. 1 shows the crude product composition (with and without TPP) and conversion (with TPP). The reaction without promoter reached a maximum conversion of 94 wt% after 2 h, with the yield of branched products also at a maximum after 2 h of 63 wt%. At longer reaction times, the oligomer content of the mixture increased at the expense of the BUFA. The reactions with TPP were much slower, but resulted in a significant increase in BUFA yield, reaching a maximum of 75 wt% after 6 h. Importantly, in the presence of TPP, the oligomer content was found to remain constant (at around 5 wt%) once reaction temperature was reached (experiment 6), suggesting that most oligomers are

Table 3

Catalytic testing - Overview of conversion and selectivity determined after 6 h reaction at 260 °C for the skeletal isomerisation over H-Fer with different feeds.

_	-	-						
	Exp.	Feed type	H-Fer loading (wt%)	Additive	Promoter	Conversion (wt%)	Monomer yield (wt%)	BUFA selectivity (wt%)
	4	OA	5	H ₂ O	-	95	83	70
	9	OA	5	H_2O	TPP	92	95	88
	11	OA + 3%C18:2 (3)	5	H_2O	TPP	88	94	87
	12	OA + 9%C18:2 (3)	5	H_2O	TPP	79	92	79
	13	MO	5	CH₃OH	TPP	57	98	79
	14	MO	5	CH ₃ OH/H ₂ O ^a	TPP	72	96	63
	15	OA	1.5	H ₂ O	_	85	88	75
	16 ^b	OA	1.5	H ₂ O	-	56	90	60

^a Weight ratio $CH_3OH/H_2O = 3.5$.

^b Spent catalyst from experiment 15 after filtration and acetone washing.

Table 4

Catalytic testing - Detailed composition (wt%) of crude product determined after 6 h reaction at 260 °C for the skeletal isomerisation over H-Fer with different feeds.

Exp.	Stearic acid ^a (2)	Hydrogenated BUFA (4)	Lactones (6)	Oligomeric components (7 + 8)
4	5.7	61.7	11.3	17.1
9	8.7	74.7	8.8	5.1
11	12.8	70.4	7.6	5.6
12	20.9	57.3	10.0	7.8
13	41.5	41.7	13.4	2.0
14	27.1	42.0	25.6	3.6
15	15.1	59.2	10.2	11.6
16 ^b	41.8	31.2	13.5	10.2

^a From 3 sources: (1) present in the feed, (2) formed by H-transfer reactions during isomerisation, and (3) post-reaction, by hydrogenation of unreacted OA.

^b Spent catalyst from experiment 15 after filtration and acetone washing.



Fig. 1. Overview of the catalytic performances of H-Fer in the skeletal isomerisation of OA at 260 °C; Comparison of crude production composition versus: (a) reaction time in absence of TPP, (b) reaction time in presence of TPP and (c) conversion in presence of TPP (\blacklozenge) OA conversion (\blacktriangle) Monomeric fraction (\times) Hydrogenated BUFA (\blacklozenge) Oligomeric fraction.

formed during the heating stage. The TPP is probably first protonated by the abundant OA, and its adsorption onto the external acid sites therefore competes with this acid–base equilibrium. Up to three times less oligomer was formed with TPP.

In order to further assess the effect of catalyst deactivation on activity and selectivity, a reuse experiment (16) was carried out with spent catalyst collected from experiment 15 and subsequently washed with acetone. Conversion was found to drop by 34% (Table 3). While the ratio between the oligomer and monomer fractions remained unchanged, the selectivity towards BUFA also decreased, but to a lesser extent (20%, Table 3). These results demonstrate the severe deactivation of the catalyst after a single run.

3.2. Catalyst structural integrity

The XRD pattern recorded for the spent catalyst showed that the crystallinity was preserved under the reaction conditions. Aluminium content was determined by ICP-MS in the crude products, in the absence/presence of promoter and as a function of reaction time and feed (Table 5). Addition of TPP did not result in any significant differences in aluminium leaching after 6 h reaction (experiment 9 versus experiment 4). With OA, the aluminium content in the total product increased to 14 mg/kg after 12 h reaction (experiment 5), while with MO it remained very low (below 1 mg/ kg after 6 h, experiment 13). The carboxylic acid group is, as expected, responsible for some Al leaching. The maximum Al loss from the spent catalyst samples (estimated assuming 1.79 mmol/ g Al [13]) is 0.6 mol%; this seems too small to account for the severe deactivation observed.

The conservation of the catalyst structure was confirmed by nitrogen physisorption measurements (Table 6). All parameters recorded for a typical spent catalyst after calcination (calcined spent catalyst from experiment 9) are equivalent to those obtained for the freshly activated catalyst.

3.3. "Coke" formation

Thermogravimetric analyses (TGA) under air showed build-up or organic deposits on the spent catalysts, and the heating profiles provided some first insight into the "coke-like" nature of these deposits. All spent catalysts showed three successive phases of mass loss (Table 7 and Fig. 2, exemplified for experiment 9); the first from RT to 250 °C which is mostly due to water loss and possibly traces of acetone, the second one from 250 to 370 °C and the third one, the "soft coke" region, from 370 to 685 °C. Mass loss above 685 °C was not detected, which suggests that highly condensed polyaromatic residues are not formed in substantial amounts during the reaction [22]. Note that TPP is burning just below 300 °C under the applied TGA conditions, so it will only influence the second and not the third step, if present. The thermograms recorded for the experiments carried out without and with TPP (4 and 9 respectively) show very little difference in region 2, suggesting that most of the TPP is washed out during the acetone rinsing step of our protocol.

Overall, the amount of "coke" deposited after 6 h reaction with OA and TPP corresponds to 4.0% of the initial spent catalyst weight. In the absence of promoter, somewhat less "coke" is formed after

Estimation of maximum aluminium loss for the spent catalysts after 6 h reaction at 260 °C for the skeletal isomerisation of OA and MO with H-Fer (5 wt% on feed).

Exp.	Feed type	Additive	Promoter	Reaction time (h)	Measured Al in product (mg/kg)	Estimated ^a Al loss from catalyst (% mol/mol)
3	OA	H ₂ O	-	2	0.2	0.01
4	OA	H_2O	-	6	6	0.25
5	OA	H_2O	-	12	14	0.58
9	OA	H_2O	TPP	6	4	0.17
13	MO	CH₃OH	TPP	6	0.2	0.01

^a Assuming 1.79 mmol/g Al [13].

Table 5

31

26

259

26

20

22

33

24

Fable 6 N ₂ physisorption data of fresh and spent H-Fer before/after skeletal isomerisation of OA at 260 °C (5 wt% of H-Fer on feed).							
Exp.	H-Fer status	Promoter	Reaction time (h)	Out-gassing temp. ^a (°C)	BET area (m²/g)	S_E , external area (m ² /g)	V_{μ} , micropore volume (cm ³ /g)
-	Fresh	-	-	150	255	36	0.108
-	Fresh	-	-	250	254	33	0.108
4	Spent	_	6	150	28	25	0.001

150

150

250

150

^a Outgassing temperature used prior to N₂ physisorption measurements;

0

6

6

12

TPP

TPP

TPP

TPP

b Spent catalyst calcined at 500 °C for 12 h.

Table 7

6

9

9

10

Spent

Spent

Spent

Spent

Spent/calcined¹

Spent catalyst mass loss (%) recorded by TGA determined after 6 h reaction at 260 °C for the skeletal isomerisation of different feeds over H-Fer (5 wt% on feed).

Exp.	Feed type	Promoter	Mass loss region 2 (250–370 °C) (wt%)	Mass loss region 3 (370–685 °C) (wt%)
4	OA	-	1.5	2.3
9	OA	TPP	1.4	2.6
11	OA + 3%C18:2	TPP	1.2	2.9
	(3)			
12	OA + 9%C18:2	TPP	1.3	3.0
	(3)			



Fig. 2. Typical thermogram recorded for a spent catalyst sample after 6 h reaction with H-Fer and TPP (experiment 9); the 1st derivative used to define the step limits of the mass losses (1,2.3) is also shown.

6 h (~3.8 wt%). By comparison, in butene isomerisation, complete blockage of the pores of protonated Ferrierite (Si/Al = 13.8) was found to corresponded to 8 wt% of "coke" [22].

Addition of 9 wt% of extra linoleic acid to the feed (experiments 12 versus experiment 9) resulted in a 15% increase in mass loss in the second region (from 2.6% to 3.0%). This coincides with the loss of both activity and selectivity mentioned earlier and linoleic acid therefore seems to play some role in the catalyst deactivation.

N₂ physisorption data (Table 6) were recorded for a series of spent catalysts collected after 2 min to 12 h of reaction at reaction temperature, experiments 6 to 10) in the presence of TPP. The outgassing temperature prior to the physisorption measurements was decreased from 250 to 150 °C to minimise any loss of chemisorbed components. Surprisingly, all samples showed a BET surface area of 26–31 m²/g, corresponding to only about 10% of the initial value and hardly larger than the external area $(20-25 \text{ m}^2/\text{g})$; the micropore volume also almost completely disappeared (below

 $0.005 \text{ cm}^3/\text{g}$). These results suggest a very quick deactivation of the catalyst by severe blockage of the pores, already after 2 min of reaction time. The presence of TPP did not influence the speed and extent of pore blockage, as no significant differences in the physisorption data were found between experiments 4 and 9. This finding is confirmed by the TGA data; mass losses measured between 380 and 685 °C for the same series of spent catalysts collected as a function of reaction time, show that the "coke" content remained roughly constant from the moment the mixture in the autoclave reached the reaction temperature (data not shown). This suggests that most of the "soft coke" had already been formed at this point.

0.005

0.002

0.112

0.001

3.4. "Coke" composition

A combination of IR and UV-Vis spectroscopy was employed to determine the chemical nature of the "coke" components, after which the major ones were identified by NMR and GC-MS following extraction from the zeolite.

3.4.1. IR spectroscopy of the spent catalyst material

Fig. 3 shows the IR spectra of the spent catalyst recovered from experiment 9 before and after subtraction of the relevant H-Fer spectrum. The difference spectra show a series of negative peaks. suggesting that some "coke" components have adsorbed onto silanol (3747 cm⁻¹) and bridging Brönsted acidic OH groups (3609 cm⁻¹ for the 10 MR channels and 3601 cm⁻¹ for the intersections between 10 and 8 MR channels [14]); the intensity decrease should not be interpreted further, however, as the sample pretreatment conditions do not allow for the complete removal of adsorbed water. Its presence at residual level is confirmed by the band at 1640-1630 cm⁻¹ (H-O-H bending vibration). Unsurprisingly, a number of absorption bands can be seen corresponding to the vibrations characteristic for the functional groups from feed and products. The presence of long chain aliphatic carbon chains is confirmed by two sets of sharp vibrations: the first ones in the stretching range have very strong intensity (v_{asym} CH₃ at 2960 cm^{-1} , CH₂ at 2940–2936 cm^{-1} and v_{sym} CH₂ at 2866–2865 cm^{-1}), while those in the bending range have medium intensity ($\delta_{scissors}$ CH_2 or CH_3 at 1470–1468 cm⁻¹, CH_2 next to CO (COOH or COOR) at 1415–1407 cm $^{-1}$, δ_{sym} CH_3 at 1384–1380 cm $^{-1}).$ The C=O stretching region shows the presence of carbonyls originating from 3 types of carbonyl-containing functional groups: γ -lactones with a shoulder at 1772–1770 cm⁻¹, esters and/or estolides at 1752–1748 cm⁻¹ [28] and fatty acids and/or dimer fatty acids at 1711–1708 cm⁻¹. The latter is characteristic of carboxylic acids involved in hydrogen bonding, either between two fatty acids or with the catalyst.

New bands appeared as a result of the carbonaceous deposits. Vibrations that can be attributed to various double bonds were identified (Fig. 4a), of which only one small but sharp band at 1441 cm⁻¹ can be attributed solely to traces of the TPP promoter,



Fig. 3. IR spectra recorded for spent H-Fer collected after 6 h alkyl isomerisation of oleic acid in presence of TPP (experiment 9, a), for the fresh catalyst (b) and their difference (c).

by comparison of experiments 3 and 8 (both 2 h at reaction temperature). The strong band at 1513–1500 cm⁻¹ is assigned to highly conjugated double bonds. This could point at the presence of aromatics, although only one additional small, broad band can be found at 1583–1558 cm⁻¹. Alternatively, conjugated double bonds could be part of neutral and/or cationic long hydrocarbon chains [29-31]. In Fig. 4b, IR difference spectra of spent catalyst samples recovered during the reaction in the absence of TPP (experiments 1 to 5) show that the intensity of the C=C vibration at 1513-1510 cm⁻¹ decreased in the first two hours: the band also became broader in the course of the reaction with the appearance of a second peak above 1510 cm^{-1} . especially between 6 and 12 h. This could be explained by an increase in the aromatic "coke" and a simultaneous decrease in the conjugated double bonds in long hydrocarbon chains (neutral and/or cationic). Meunier et al. came to a similar interpretation of their IR data recorded during butene isomerisation with H-Fer [31].

The final feature of interest is a strong and sharp band at 1683-1673 cm⁻¹, which is found in all experiments except from those starting with MO (experiments 13 and 14, Fig. 4c). It originates from a C=O stretching vibration shifted to lower wavenumbers due to either very strong hydrogen bonding interactions and/or conjugation; this feature is tentatively assigned to a conjugated cyclic ketone thought to be a precursor to the alkybenzenes that are detected in the coke extracts (see below). Other assignments can be ruled out; C=C stretching of tri- or tetra-substituted olefins, or from a trans-configuration of the double bond, would be expected above 1665 cm⁻¹ based on studies of the alkylation of isobutane with n-butene over a HFAU zeolite [29]. However, the band is absent when starting with MO, indicating involvement of the carboxylic acid head group. The frequency is also too high to allow an assignment to CO_2^- asym stretching, which would be expected at 1650–1550 cm⁻¹. Without TPP, the first few hours of the reaction showed a significant increase in the band at 1683–1673 $\rm cm^{-1}$ to a maximum after about 6 h, followed by a decrease to a constant level after 6 h (Fig. 4b). In the presence of the promoter, this maximum is already reached after only 0.5 h (data not shown); it seems that the TPP is therefore favoring the formation of the species responsible for this specific band.

Surprisingly, addition of extra linoleic acid in the feed (experiments 11 and 12) did not result in much spectral variation in the infrared (data not shown), while both conversion and selectivity dropped significantly (Tables 3 and 4). Clearly, techniques other than IR are needed to provide insights into specific deactivation mechanisms.

3.4.2. UV–Vis spectroscopy of the spent catalyst material

Complementary information about unsaturated components and carbocations in the "coke" was provided by UV-Vis spectroscopy. H-Fer, TPP, acetone, lactones and linoleic acid [33] do not absorb in the 280-800 nm range, and any observed bands are therefore considered to originate from "coke" species. The spectra recorded for the spent catalysts show at least five absorption bands (Fig. 5a-c). Those at 290 nm. 355-360 nm and 440-445 nm are attributed to respectively monoenyl, dienyl and trienyl carbocations, formed through consecutive hydrogen transfer reactions [30,32]. The structures observed at 410–415 nm and 485–490 nm can be assigned to aromatic species (methyl-substituted benzenium cations for the former) [30,32]. The spent catalyst recovered after 2 h runs with OA, in the absence and in the presence of promoter (Fig. 5a, experiments 3 and 8, respectively), gave a very similar profile, with all absorption bands above 280 nm being somewhat more intense when the promoter was used. This suggests that the "coke" species that are detected in the UV-Vis spectra are mostly formed inside the catalyst structure through monomolecular processes.

The trends observed in the UV–Vis spectra of the spent catalyst samples as a function of reaction time correlate with those seen in the IR spectra. The intensities of all absorption bands attributed to enylic carbocations decreased, while those associated with aromatic species increased (Fig. 5b, exemplified for experiments 6, 7 and 9)). Addition of linoleic acid (**3**) (experiments 11 and 12, respectively) causes a significant increase in intensity of all absorption bands attributed to aromatic species, especially the one at 485–490 nm (Fig. 5c). This provides further evidence for the importance of the enylic carbocations as a precursor to "coke" formation and subsequent deactivation, the additional double bonds speeding up these processes.

3.4.3. IR, MS and NMR of the "coke" extract

Deposited and occluded organics were isolated by hydrofluoric acid destruction of selected spent catalysts, followed by extraction



Fig. 4. Overlay of part of the difference IR spectra recorded for spent H-Fer catalysts collected after: (a) 2 h alkyl isomerisation of oleic acid (OA) in absence of TPP (experiment 3) and in its presence (experiment 8); (b) alkyl isomerisation of OA in absence of TPP, for: 0.5 h, 1 h, 2 h, 6 h and 12 h (experiments 1, 2, 3, 4 and 5, respectively; and (c) 6 h alkyl isomerisation in presence of TPP of: OA/water (experiment 9), methyl oleate (MO), and methanol/water (experiment 14) and MO and methanol (experiment 13).

with dichloromethane and analysed by IR and NMR spectroscopy and mass spectrometry. The FT-IR spectra of all three "coke"



Fig. 5. Overlay of UV–Vis spectra recorded for the spent catalysts collected after: (a) 2 h alkyl isomerisation of oleic acid (OA) in absence of TPP (experiment 3) and in its presence (experiment 8); UV–Vis spectrum of H-Fer is also given; (b) alkyl isomerisation of OA in presence of TPP, for: 2 min, 0.5 h and 6 h (experiments 6, 7 and 9, respectively); and (c) 6 h alkyl isomerisation in presence of TPP for: OA, OA + 3% linoleic acid (**3**) (Exp. 9, 11, and 12, respectively); the spectra have been individually recorded and treated.

extracts are in many ways very similar to those recorded for the spent catalysts (Fig. 6, exemplified for experiment 9). The bands characteristic of long aliphatic carbon chains can be found both in the stretching range (just below 3000 cm^{-1}) and in the bending range (at $1458-1463 \text{ cm}^{-1}$, $1411-1412 \text{ cm}^{-1}$ and 1377 cm^{-1}). The carbonyl stretching range confirms the presence of a small amount of esters and/or estolides (shoulder at about 1750 cm^{-1}), along with the expected fatty acids (at $1708-1711 \text{ cm}^{-1}$).

However, the "coke" extracts spectra also differ from the spectra of the spent catalysts by a number of features. γ -lactones (**6**)

are probably opened by the hydrofluoric acid, as they were detected. In the absence of the characteristic catalyst bands, traces of TPP-related species can be clearly found (series of bands at 1485, 1439, 1109, 1063, 750, 693 and 532 cm⁻¹). Other aromatics species, at low concentration, are confirmed by a series of bands (1610–1510 cm⁻¹), which increase in intensity in the order: experiment 4 < experiment 9 < experiment 12. The fingerprint region suggests at least the presence of ortho- (~720 cm⁻¹), para-(800–815 cm⁻¹) and mono-substituted aromatics (700–695 cm⁻¹ and ~720 cm⁻¹). Another key difference with the IR spectra of the spent catalysts is the absence of the two absorption bands at 1675 and 1500 cm⁻¹, which are assigned to a conjugated cyclic ketone and (poly)enylic species, respectively. This proposal is consistent with their observed disappearance following HF destruction of the catalyst.

MS analysis of the "coke" extracts after high-temperature chromatography (HT-GC) shows traces of TPP and a relatively large peak assigned to its oxide, possibly formed during the acid treatment. More importantly, the chromatograms of all three residues are characterised by three major peaks of which two (of similar magnitude) correspond to linear saturated carboxylic acids; palmitic (hexadecanoic) acid and stearic acid (2). Both components are present in the feed, but additional stearic acid is formed from OA via hydride transfer during the reaction. Being linear, both diffuse quicker into the catalyst and would be preferentially retained due to their poor solubility in acetone. The third and largest peak is a C18-compound clearly identified from its ionisation fingerprint as dodecyl benzene, which must derive from the OA. Only a very small amount of condensed aromatics (e.g. substituted naphthalene) was found. Finally, HT-GC does not show any higher molecular weight components, but small amounts of C36 dimer acids (7) and estolides of OA (8) are detected by gel permeation chromatography. These species form mostly at the very beginning of the reaction and could contribute to early-stage blockage of the ferrierite channels.

The HT-GC–MS analyses thus strongly support the interpretation of both the IR and UV–Vis data of the spent catalysts. The proposed "coke" composition is also confirmed by the NMR data recorded for the three extracts (Fig. 7), in particular with regard to the presence of three types of aromatic compounds. The presence of dodecyl benzene explains the NMR peaks recorded between 7.11 and 7.26 ppm. The integration ratio between this latter range and the peak at 2.2–2.45 ppm (methylene alpha to the carboxylic group) is increasing in the order: 0.30 (experiment 4), 0.42 (experiment 9) and 0.54 (experiment 12). NMR peaks for condensed aromatics are expected above 7.20 ppm. The promoter is not detected as TPP (chemical shift expected at 7.34 ppm); however, a number of peaks above 7.20 ppm suggest the presence



Fig. 6. Part of IR spectrum recorded for the "coke" extract from the spent catalyst collected after 6 h skeletal isomerisation (experiment 9, OA, 5 wt% H-Fer and TPP).

of related species. Experiments without TPP show hardly any aromatic protons above 7.3 ppm. However, starting with a feed enriched in linoleic fatty acid led to an increase in the relative aromatic content, while intensity of the peaks associated with the TPP-related species remained constant. Based on the above data, there are at least two processes responsible for the formation of carbonaceous species: one leading to dodecyl benzene from the OA, and a second process that yields more condensed aromatics; the latter process is enhanced by the presence of additional double bonds on the fatty acid alkyl chains.

4. Discussion

The combination of both catalytic data and a number of analytical techniques has allowed the deactivation mechanism for the ferrierite catalyst during OA isomerisation to be determined. The physisorption measurements of the spent catalyst show the de facto disappearance of any micropore volume and the tenfold reduction in BET surface area, already at the onset of the reaction and independently of the addition of TPP. Based on TGA data, the "coke" content hardly increases thereafter, suggesting that the small amount of "coke" formed is enough to lead to the observed severe pore blockage. Despite this, very high initial conversions and selectivities towards BUFA are observed, clearly indicating that the internal pore volume is hardly used. Furthermore, as TPP can only adsorb onto the external sites, catalysis therefore must mostly take place within the pore mouths. In the absence of TPP, side reactions such as oligomerisation, catalysed by the external acidic sites. have a significant effect on the product composition. Catalysis involving the entrance of the pores has been previously proposed for the hydroisomerisation of long chain n-alkanes in the presence of Pt/zeolite bi-functional catalyst [34,35]. However, these examples involve gas-phase reactions under different conditions, with feed and products that are much more volatile and lack polar functional groups; a direct comparison is therefore not possible.

UV–Vis spectroscopy suggests that unsaturated carbocations play a key role in the deactivation of the catalyst. They are formed via hydride transfer (Scheme 1) and are detected from the start of the reaction. Their concentration is highest at the onset of the



Fig. 7. NMR spectra of "coke" extract from the spent catalysts collected after 6 h skeletal isomerisation with 5% H-Fer and: OA without TPP (experiment 4), OA and TPP (experiment 9) and OA/9% linoleic acid (**3**) and TPP (experiment 12).

reaction (when both OA concentration and acid site density are highest) and appears to decrease during the first two hours to a steady value. The (poly)envlic carbocations formed are very stable and remain almost irreversibly adsorbed at the active sites, competing with the carbocation precursor to alkyl isomerisation. They are detected by FT-IR in the spent catalyst, but (as expected) not in the extracts obtained after zeolite dissolution in HF. The (poly)enylic carbocations have been proposed to have a poisoning effect on zeolites used in liquid phase reactions [32,36]. Further evidence is provided by the reuse experiments: acetone washing of the spent catalyst leads to a drop of 34% in conversion, which is not the expected result if pore blockage is the sole mechanism of deactivation, because this has been shown to occur very early in the reaction without loss of activity (see above). However, an additional wash with HCl almost completely recovers the initial activity [12], indicating the presence of polar/charged organic species, which can only be displaced with highly acidic protons.

Additionally, carbocations with multiple double bonds are known to undergo cyclisation reactions [29,30], which could explain the formation of low levels of (condensed) aromatics, as revealed by IR of spent catalysts and confirmed by IR, MS and NMR measurements of the extract after destruction by HF. This hypothesis is strongly supported by two independent observations: firstly, the presence of TPP increases the concentration of polyenylic carbocations and condensed aromatics and reduces the rate of alkyl chain isomerisation. This is likely to be due to the reaction of TPP at the external surface, favouring monomolecular processes within the structure, including the formation of the polyenylic carbocations. Secondly, the concentration of both



Scheme 1. Proposed mechanisms for the deactivation of zeolite H-Fer during the skeletal isomerisation of oleic acid; top: Poisoning of active sites by monoenylic carbocations generated through H-transfer reactions; bottom: Formation of (long carbon chain) alkyl benzene molecules from unsaturated fatty acids after positional isomerisation of the double bond.

(poly)enylic carbocations and aromatics increases with the concentration of linoleic acid (**3**) in the feedstock, accompanied by a significant decrease in activity. This is due to the energetically favourable hydride extraction from conjugated double bonds, formed by positional isomerisation under the acidic conditions employed. However, based on the TGA data of the spent catalyst and NMR analyses of the extract after destruction by HF, the amount of (condensed) aromatics remains very limited and it is difficult to explain the observed severe catalyst blockage solely through this process.

MS and NMR characterisations of the extracts after destruction by HF also indicate the presence of a significant concentration of a long chain mono-substituted alkylbenzene, i.e., dodecyl benzene. This type of aromatic must derive ultimately from OA, and Scheme 1 proposes a mechanism for its formation via a cyclic conjugated ketone intermediate; this mechanism is supported experimentally by the detection in IR of a conjugated ketone (band at ~1675 cm⁻¹) within the spent catalyst material, which is absent when using MO as feedstock. Further evidence comes from the observation that TPP accelerates the formation of both the conjugated ketone and the long chain alkylbenzene, confirming the ketone as a likely intermediate species for this aromatic. The ketone would contribute to poisoning of the active sites, while the dodecyl benzene would participate in pore blockage.

5. Conclusions

The skeletal isomerisation of OA in the presence and absence of TPP has been investigated with protonated ferrierite as catalyst material. Details of the pore mouth catalysis and related deactivation processes have been investigated by a combination of analytical techniques, including UV–Vis and FT-IR spectroscopy. Our results confirm that this catalyst system shows superior activity and selectivity, compared to the numerous zeolite types previously investigated. Nevertheless, there is scope for improvement in its robustness to deactivation, and in designing a more efficient distribution of the reactive sites. While the ferrierite framework was found to be unaffected by the reaction, and little aluminium was leached, severe pore blockage was detected as soon as the mixture reached reaction temperature. Estolides, which are already formed during the initial heating phase, probably contribute to the first stage of blockage of the zeolite channels.

Coking reaches a constant level within the first minutes at reaction temperature, and this level increases with the concentration of polyunsaturated acids in the feed. Dodecylbenzene and other long chain alkylbenzenes were identified as the major coke constituents and are believed to be formed from OA via a cyclic conjugated ketone.

Pore mouth catalysis is confirmed by the use of TPP, which selectively blocks non-specific surface reactions. Addition to the reactant mixture increases the selectivity to BUFA, by binding reaction sites at the zeolite external surface where oligomerisation can occur. Since the pores are already blocked at the onset of the reaction, only the pore mouth is available for the isomerisation reaction. Polyenylic carbocations, formed through hydrogen transfer reactions between reactant species, are responsible for poisoning acid sites in the pore mouth and slowing down the skeletal isomerisation process. These polyenylic species eventually undergo cyclisation and are precursors to a very small amount of condensed aromatics. Consistent with this phenomena, higher levels of polyunsaturated acids in the feedstock enhance the above effects.

The elucidation of the mechanisms responsible for ferrierite deactivation during skeletal isomerisation of OA provides valuable insights for the industrial development of this new and promising route to BUFA.

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