



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

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 double bond [5].

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

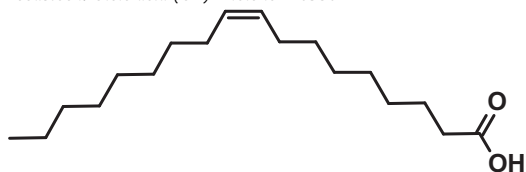
Abbreviations: BUFA, branched-chain unsaturated fatty acids; OA, oleic acid; MO, methyl oleate; TPP, triphenylphosphine.

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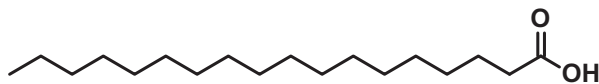
E-mail address: b.m.weckhuysen@uu.nl (B.M. Weckhuysen).

Table 1
Reactants and main products for the zeolite-catalysed skeletal isomerisation of OA.

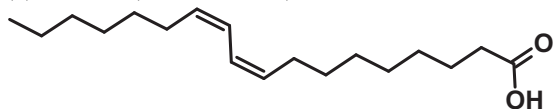
Feedstock: Oleic acid (OA) Priolene™ 6936



(1) oleic acid (*cis*-9-octadecenoic acid), 92.2 wt%

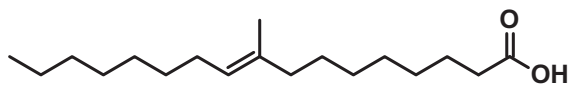


(2) stearic acid (octadecanoic acid), 1.7 wt%

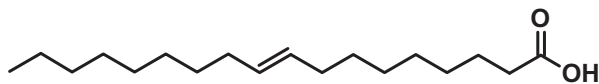


(3) linoleic acid (*cis,cis*-9,12-octadecadienoic acid), 3.2 wt%

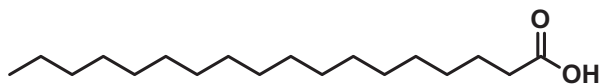
Crude monomeric fraction



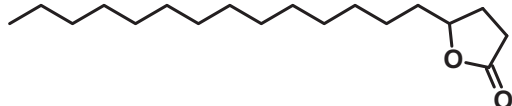
(4) alkyl-branched isomer of oleic acid (BUFA)^a



(5) elaidic acid (*trans*-9-octadecenoic acid)^a

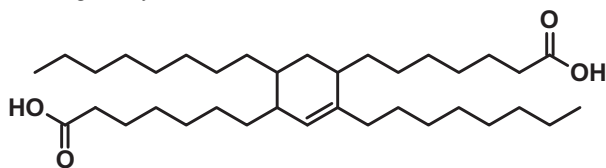


(2) stearic acid (octadecanoic acid)

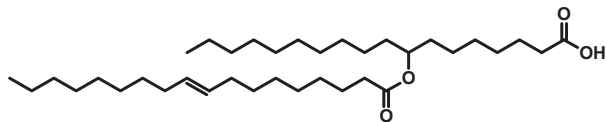


(6) γ -stearolactone (5-tetradecyloxolan-2-one)^b

Crude oligomeric fraction



(7) isomer of C36 dimer acid^a



(8) (mono)-estolide of oleic acid^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 Brønsted 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 active 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 medium-pore zeolite, characterised by two types of one-dimensional channels: the 10-membered (MR) channels ($4.2 \times 5.4 \text{ \AA}$) and the 8-MR channels ($3.4 \times 4.7 \text{ \AA}$), 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 Brønsted sites [13]. Its acidity has been characterised in detail using FT-IR spectroscopy and five distinct Brønsted 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 Brønsted 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

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