

## Iron Based Catalysts

Different iron based catalysts were tested to study its catalytic activity at high temperatures to reach vapour phase systems and favour thermodynamics. This study of iron based catalysts for our reaction also included the use of  $\text{Fe}^{3+}$  supported catalysts, concretely, iron supported on  $\gamma\text{-Al}_2\text{O}_3$  and active carbon (AC). The shortness and superficiality of this chapter may subtract importance to it. However, these preliminary results gave the clue to show which path should be followed along this research work, which in the last steps achieved to the obtaining of tri-unsaturated FAEE.

### 3.4.1 Introduction

In biocatalysis, most of fatty acid desaturases (enzymes responsible of dehydrogenation reactions) belong to a large set of membrane-bound proteins with several histidines and di-iron coordination site. Although the structure of these sites

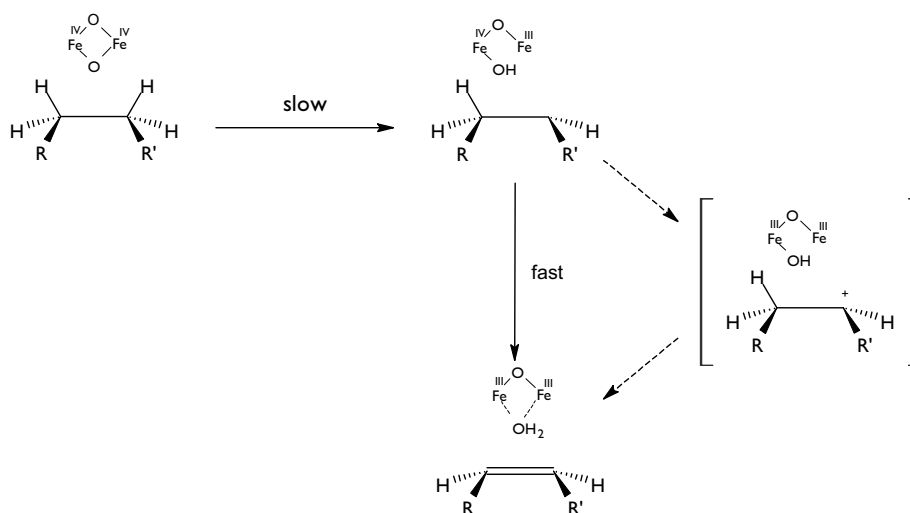


Figure 3.4.1 Generic mechanism for desaturation.

is not well defined yet, it is thought to be high valent di-iron oxo complexes [1-5]. A general mechanism for fatty acid desaturation is shown in Fig. 3.4.1. Moreover, there was another reason to choose iron based catalysts: their reported

dehydrogenating properties in the synthesis of styrene [6-9]. Therefore, it was decided to test different iron based catalysts, such as iron oxides and iron supported catalysts. To start with this study, iron oxide nanoparticles were synthesized and characterized (see *Annex VII*). Nevertheless, no interesting catalytic activity results were obtained. Furthermore, the oxidative conditions required to regenerate iron oxide [7, 10, 11] catalysts were an important preventing factor to use such catalysts. Another oxide, cerium oxide, was synthesized in order to be tested as a catalyst. Since the synthesis of this material was self-designed, some characterization had to be done in order to ensure its chemical composition and textural properties. The characterization results turned out to be very interesting. This fact induced the appearance of the publication shown in *Annex VI*.

The following step consisted in testing iron supported catalysts. The catalytic activity of two different supported catalysts was studied at 250 °C and 340 °C.

### 3.4.2 Experimental

Both supports were previously dried at 120 °C. The catalysts were prepared by Incipient Wetness Impregnation (IWI) of the supports using an aqueous solution of  $\text{Fe}(\text{NO}_3)_3$  (Aldrich, Germany) to obtain a final metallic load of 5 %. The catalytic study was performed at 250 °C and 340 °C and with  $0.11 \mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{s}^{-1}$ . Argon was used as inert carrier with a flow of 0.225 mL/s. The surface area determined by BET method was 848  $\text{m}^2/\text{g}$ .

### 3.4.3 Results and Discussion

The experiment performed with  $\text{Fe}^{3+}/\gamma\text{-Al}_2\text{O}_3$  at 270 °C gave no positive results. As the temperature increased to 350 °C, conversion values around 10 % were obtained. Most of the products were fruit of isomerization reactions and degradation was observed. A negligible amount of aromatic FAEE, which at that moment were still *unknown*, was detected. Now then the results obtained in the experiments using  $\text{Fe}^{3+}/\text{AC}$  showed that those new *unknown* peaks should be structurally determined because of the acquired importance as a product of the reaction (see *Chapter 3.2*) The result of the structural analyses showed that those compounds were aromatic FAEE.

Total conversion of di-unsaturated FAEE (ethyl linoleate) versus reaction time is presented in Fig. 3.4.2. The catalytic activity reached a value around 100 % at the beginning of the reaction. After 30 minutes of reaction, the catalyst suffered an

important deactivation reaching a plateau at around 30 % after a reaction time of 4 hours. The hydrogenation reaction became more important as time went by. Its selectivity value smoothly increased from 38 % to 51 %. On the other hand, the reaction of aromatization of FAEE presented a selectivity value of 32 % at the beginning of the reaction. Along the evolution of time, the value decreased to reach

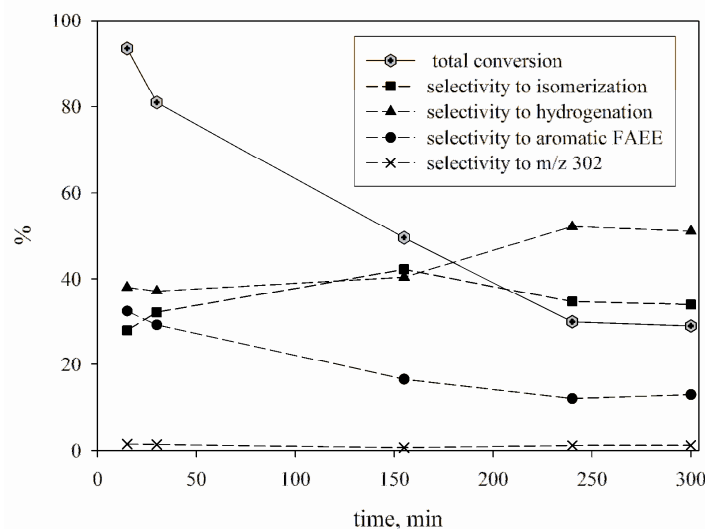
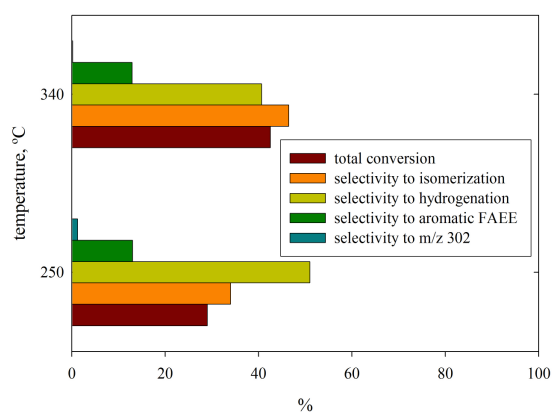


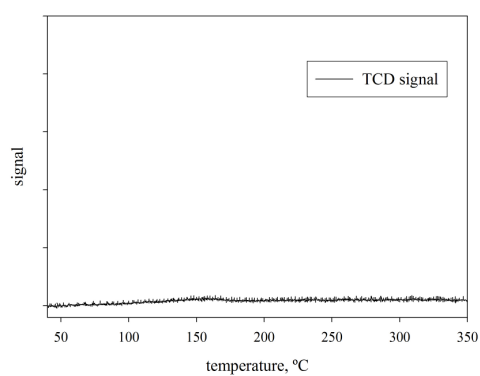
Figure 3.4.2 Catalytic activity of ethyl linoleate at 250 °C.

a 13 % value. Another relevant reaction which takes place, as in other cases, is the isomerization reaction. This reaction presents a regular trend along the time and its selectivity value is around 30 % reaching a maximum of 42 % after 155 minutes of reaction. Finally, a low and relatively constant selectivity around 1 % was obtained in the case of compounds of  $m/z = 302$ . The effect of temperature in the conversion of ethyl linoleate is shown in Figure 3.4.3. As expected, the total conversion was higher at 340 °C than at 250 °C. Isomerization reached a higher value (47 %) at 340 °C, while hydrogenation became more important at lower temperature, presumably, due to hydrogen spill-over on the catalyst surface. The obtaining of aromatic FAEE was the same in both cases, with a conversion value of 13 %. It is worth to point out the obtaining of compound with  $m/z = 302$  at 340 °C.



**Figure 3.4.3** Total conversion of ethyl linoleate after 5 hours reaction.

Now then, was the hydrogen balance consistent with the results? If it is supposed that the required hydrogen for the hydrogenation reaction was that



**Figure 3.4.4** TCD signal during the thermal study of the stability of ethyl linoleate.

released by the dehydrogenation reaction, then the balance was not consistent. This fact induced to consider another source of hydrogen. Did the hydrogen come from the catalyst? If it was so, a decrease of the hydrogenation conversion should be observed, which had not been detected. Another possible cause of the lack of

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balance in hydrogen terms could be the decomposition of starting material due to temperature to give some molecular hydrogen. For that reason, a thermal study of the stability of ethyl linoleate (0.1 mL) was performed by placing in a quartz reactor ethyl linoleate in an oven under inert conditions and in the absence of light. The outlet of the reactor was connected to a TCD detector and to a mass spectrometer in order to detect the possible releasing of gases (Fig. 3.4.4). Apparently, no important released gases were detected indicating the stability of the starting material along the reaction time and conditions.

#### 3.4.4 Conclusions

Iron supported active carbon catalysts with a metal load of 5 % presented catalytic activity when using ethyl linoleate as a starting material at 250 °C and 340 °C in a continuous vapour system under inert conditions. The total conversion was of 40 % at 340 °C; this value acquired a lower value (32 %) at 250 °C. The products may be classified into four family compounds, which are isomers of di-unsaturated FAEE, aromatic FAEE, hydrogenated FAEE, such as, mono-unsaturated FAEE, and, finally, compounds, whose  $m/z$  in MS analyses was 302.

Hydrogenation reaction appeared to be more important at lower temperatures, while selectivity towards aromatization of FAEE appeared to be the same in both cases reaching a value of 13 %. In the case of isomerization, the contrary occurred, that is, isomerization was higher at 340 °C than at 250 °C with values of 47 % and 34 %, respectively. Finally, compounds with  $m/z = 302$  were only detected at 240 °C with a nearly negligible value (1 %).

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