

N°333 / OC / PC

TOPIC(s) : Homogenous, heterogenous and biocatalysis / Industrial chemistry

Cu-based catalyst for the selective hydrogenation of canola and sunflower vegetable oils.

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## PURPOSE OF THE ABSTRACT

As attested in other studies vegetable, oils are a viable alternative to petroleum in the preparation of interesting industrial products [1][2]. However, to stabilize the degree of oxidation of oils or their derivatives (FAME) and to properly use them, lowering the degree of unsaturation is necessary. Anyway complete saturation of the raw materials and the isomerization secondary reaction must be avoided. Saturated compounds and trans-isomers change the cold properties of the oils and other important properties (cetane number, viscosity). High concentration of cis-monoenes can be obtained via selective hydrogenation. In this work, heterogeneous catalysis for hydrogenation was considered. In particular, copper was chosen as active phase for this reaction, since its activity towards complete saturation is lower than other transition metals and its use is a green alternative respect other more common active phases (Ni, Pt, Pd,?)[3].

10%w/w load copper based catalysts, supported on silica, were produced with two different synthesis' paths: the Hydrolysis-Precipitation (HP) method [4] and the Ammonia Evaporation (AE) method [5]. Each catalyst is characterized with different techniques: XRD for crystalline phases identification, Raman and FTIR for non-crystalline phases identification. BET-BJH for surface area and pore size distribution, the catalysts from HP and AE show high surface area around 300-350 m<sup>2</sup>/g with pore size in the range of 100-120 Å and 30-40 Å, respectively. From ICP-AES characterization, catalysts show copper load of 9-9.5%w/w. TPR curves and TEM images were also carried out.

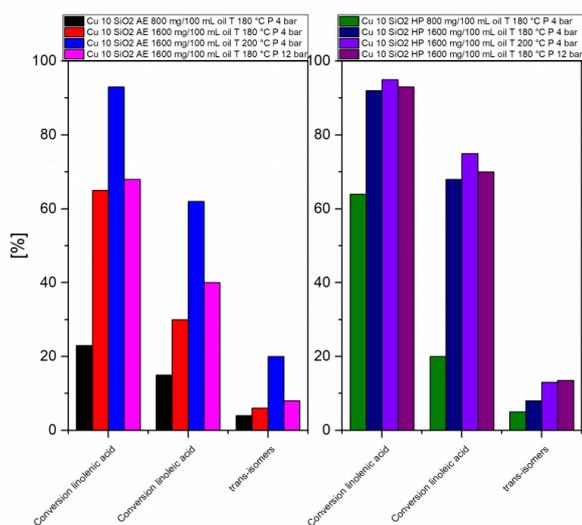
The lab scale apparatus mainly consists of a batch reactor of 600 mL (Parr Reactor 4560). The reactor was charged with 180 g of canola oil and tests are carried out in a pure hydrogen atmosphere as reported in previous works [6,7]. Here, the catalyst concentration in the oil was studied (from 800mg/100mL to 1600 mg/100mL) and the operating conditions (pressure at 4 and 12 bar and temperature at 180 and 200°C) were changed one by one. The tests duration was of 4h. The reactor was purged with nitrogen to eliminate all the air contained in the oil and in the reactor and brought to the test conditions with nitrogen. When the test conditions are reached, the hydrogen is fed in the reactor and, at established time, sampling is performed. Blank test with no catalyst has been also performed and tests with a commercial sunflower oil (180 °C and 4 bar) were conducted to evaluate how the reaction evolves when a low amount of linolenic acid is in the reaction media.

The samples withdrawn from the reactor are trans-esterified following IUPAC Standard and analysed in a Varian 3400 GC equipped with a SUPELCO 2380 capillary column and a FID detector.

The conversion of linolenic acid and linoleic acid, and the final concentration of trans-isomers formed, are reported (Figure 1). As confirmed in literature [3], no stearic acid was detected after reaction. The increase in copper content leads to a higher conversion. Higher temperature reaction has an important positive effect on the activity of the two catalysts. Pressure, has a less important and negative effect on the behaviour of the HP

catalyst, while is important with AE catalyst [5]. These results are related to the catalyst characterization and more specially to the surface area and the active phase dispersion.

## FIGURES



**FIGURE 1**

Figure 1

Conversions of linolenic acid and linoleic acid, and final concentration of trans-isomers versus operating conditions.

**FIGURE 2**

## KEYWORDS

Vegetable oils | Selective hydrogenation | Heterogeneous catalysis | Batch reactor

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