



# Article Selective Catalytic Hydrogenation of Vegetable Oils over Copper-Based Catalysts Supported on Amorphous Silica

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**Abstract:** This work aims to study the selective catalytic hydrogenation of vegetable oils to maximize oleic acid content and expand the range of non-edible uses. Oleic acid (C18:1) is suitable for use as a biodegradable lubricant and is a building block in producing polymers and plastics from renewable resources. The challenge is the synthesis of heterogeneous catalysts, allowing for a maximum yield of C18:1 and low formation of the corresponding saturated acid (stearic acid). New copper-based catalysts on silica were synthesized via two synthesis methods: hydrolysis precipitation and ammonia-evaporation. Experimental tests were carried out at a lab scale operating in a semi-batch mode. The best conversion reached 90% for C18:3 and 80% for C18:2 HP Cu-silica catalyst results, the best candidate for an industrial case study. Good results were obtained in the selectivities of oleic acid production and cis/trans isomers ratio. The modified return on the investment of the designed hydrogenation plant provides the revenues of the capital costs in less than one year.

Keywords: selective catalytic hydrogenation; copper-based catalysts; oleic acid

# 1. Introduction

The Paris Climate Agreement is a global safeguard for the planet and human health [1]. Every action on climate or the environment must last and be made with the consideration that the world population is continuously growing.

The products obtained by industrial activities often remain in the environment as waste and can persist for long periods; one relevant example is plastic [2].

Globally, the production of waste in 2016 was estimated to be near 2.01 billion tonnes, with an increment concerning 2012 of +45% (1.3 billion tonnes in 2012). With the growing population, waste will inevitably increase. By 2030, it will reach 2.59 billion tonnes produced yearly. Almost 12% of solid wastes are composed of plastic, the first contaminant in the oceans, not considering  $CO_2$  captured by the sea, and more than 60% globally is untreated [3].

Using biomass to produce energy, chemicals, materials, and the next generation of bio-plastic materials [4] is one of the critical issues for sustainable development [5,6]. Indeed, bio-based resources are renewable and potentially  $CO_2$ -neutral. Catalytic processes implemented on biomass feedstocks minimize by-products and fulfill multiple green chemistry principles, operating as an advanced biorefinery [7].

The valorization of vegetable oils represents a sustainable alternative to traditional petrochemicals and a renewable building block in industrial applications. Partially hy-



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). drogenated oils can produce many bio-based compounds (polymers, soaps, lubricants, polyalcohols, etc.) [8].

The main compounds of vegetable oils are triglycerides, i.e., fatty acids with 14–22 carbon atoms. Among the fatty acids, a specific interest exists for oleic acid due to its stability in the presence of oxygen, which avoids spontaneous polymerization, and it has a lower melting point than saturated fatty acids. These characteristics facilitate industrial use in continuous transformation processes [9] for bio-lubricants at low viscosity and high oxidative and thermal stability [10]. Building blocks for bio-based plastics include sebacic acid, 11-aminoundecanoic acid, and azelaic and pelargonic acids derived from oleic acid. The great potential of these compounds for polymerization is well recognized; the olefin metathesis reaction allows for the direct synthesis of monomers [11].

Vegetable oils have an intrinsically variable composition among oleic acid (C18:1), linoleic acid (C18:2), linolenic acid (C18:3), and stearic acid (C18:0). Other possible compounds can be arachidonic acid (C14:0) and palmitic acid (C16:0). Erucic (C22:1) and behenic acid (C22:0) are also present in non-canola rapeseed oil. The presence of polyun-saturated fatty acids (PUFA) determines essential properties for bio-lubricants (viscosity and thermal instability) and biofuels (pour point); the decrease in PUFA reduces their perishability and improves the oxidation instability [12,13]. The relative oxidation rates of (C18:1):(C18:2):(C18:3) are 1:40:100. The fluidity strongly depends on the content of saturated compounds and the extent of isomerization; a higher amount of these compounds is linked to increased oil viscosity and comports the formation of solid phases in the worst scenarios [14].

Selective heterogeneous catalytic hydrogenation is a crucial process for various biocompatible products [15–18]. Nowadays, industrial processes are limited to high oleic vegetable oils due to technical constraints, such as inadequate selectivity of only one of the two double bonds of linoleic acid (C18:2) to yield C18:1 fatty acids [13] or difficulties in solid catalyst recovery [19].

The core of the process is the catalyst; Veldinsk et al. [20] proposed an attempt to classify the principal catalytic active phases by combining the observations of many scientists (Table 1).

**Table 1.** Ranking of the active phases.

Characteristic	
Activity	Pd > Rh > Pt >> Ir > Ru = Ni >> Cu
Selectivity	Cu > Pd > Rh > Pt >> Ir > Ru = Ni
Cis/trans selectivity	$Cu \approx Pd > Rh > Ru = Ni >> Ir > Pt$

Numwong et al. [21] found a similar trend among Pd, Pt, and Ni: for activity, Pd > Pt >> Ni and for trans selectivity, Pd >> Ni > Pt, placing the Pd as the best alternative for both activity and selectivity.

To reduce the content of unwanted by-products, such as trans-isomers and stearic acid, research in this field proceeds following two different paths: the use of noble metal catalysts, mainly Pd [22,23] and Pt [24,25], or the use of Cu, which is cheaper and exhibits a lower activity toward complete saturation [26] or eventually with the addition of solvents (critical–near-critical) or additives [27].

Several supporting materials have been recently investigated (SiO<sub>2</sub> [28], Al<sub>2</sub>O<sub>3</sub> [29], TiO<sub>2</sub> [25], carbon [30], etc.). Mesoporous silica exhibiting high surface area, uniform pore size-tunability [31], and surface functional groups [32,33] was studied.

Copper-based catalysts provide peculiar reaction results in terms of monoene formation [34]. The first copper catalyst tested was copper chromate; this catalyst was extensively studied by Koritala et al. [35–43]. The copper-based catalysts work at a higher temperature than the nickel ones; selectivity depends on the reaction pressure. The products obtained are liquid down to -15 °C [15]. Cu supported on SiO<sub>2</sub> and Cu-Zn-Al oxides showed activity and selectivity linked to copper dispersion and the porous structure of the support. Poorly dispersed Cu catalyst presents inactivity toward soybean oil hydrogenation; at the same time, narrower pores imply more difficult mass transport and lower activity [15]. Cu on silica showed the best catalytic performances in hydrogenating high linolenic and linoleic oils [44].

Many different techniques exist for the preparation of copper supported on silica: incipient wetness impregnation (IWI) [45], chemisorption–hydrolysis method (CH) [46], ammonia-evaporation (AE) [47,48], precipitation gel method (PG) [49], hydrolysis precipitation method (HP) [50], and urea hydrolysis deposition–precipitation (UHDP) [51]. All these synthesis methods produce Cu/SiO<sub>2</sub> with a high copper surface and high active phase dispersion on the support. Ammonia-evaporation [47,48] (45 m<sup>2</sup>/g <sub>Cu</sub> and crystallite size smaller than 7 nm) and hydrolysis precipitation techniques [50] (72 m<sup>2</sup>/g <sub>Cu</sub> and crystallite size smaller than 10 nm) reached the best results. In this work, they were then chosen as synthesis methods to prepare Cu-based catalysts for the selective partial hydrogenation of vegetable oils.

This work's aims are as follows:

- Synthesize new Cu-based catalysts supported on amorphous silica following green chemistry principles. For this reason, two different synthesis methods are used and compared: hydrolysis precipitation (HP) and ammonia-evaporation (AE);
- Perform an experimental test campaign in a semi-batch reactor to evaluate the conversion and selectivity as a function of temperature, pressure, and catalyst/oil mass ratio, with particular attention to low pressure and a low loading of the catalyst given with the scope of reducing the impact of the process;
- Fully characterize the developed catalysts correlating their properties to the activities and selectivities;
- Select the best-performing catalyst for designing an industrial-scale plant and optimizing the operating parameters, with particular attention to the reaction time, avoiding complete fatty acid saturation;
- Design a semi-continuous process, including the introduction of a loop reactor to improve mass transfer, optimize heat recovery, and reduce operative costs.

## 2. Materials and Methods

The attention was focused on the following classes of copper catalysts supported on silica.

As reported in the literature, copper and, more specifically, copper supported on silica showed good performances in the hydrogenation of FAME and vegetable oils [15,27,34,44,52,53]. Among all synthesis methods, hydrolysis precipitation [50] and ammonia-evaporation [54] were chosen. These two methods produce a high dispersion of copper species on the support surfaces with a small dimension of the active phase crystallites. Therefore, they are considered particularly suitable for the hydrogenation of oils.

Both methods started from a "liquid" silicon oxide precursor; the silica is formed during the precipitation of the copper species. Copper and silica can form copper phyllosilicates, increasing copper dispersion in the silica matrix. The support and the active phase are precipitated simultaneously during the synthesis [54].

#### 2.1. Hydrolysis Precipitation Method (HP)

The precursors were Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Sigma Aldrich<sup>®</sup>, Merck KGaA, Darmstadt, Germany, purity 99%), tetra-ethyl-orthosilicate (TEOS) (Sigma Aldrich<sup>®</sup>, Merck KGaA, Darmstadt, Germany, purity 98%), and ethanol (Sigma Aldrich<sup>®</sup>, Merck KGaA, Darmstadt, Germany, purity 99.9%) and deionized water as solvents.

HP synthesis steps were the following:

 A required amount of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was dissolved in deionized water (20 mL), and the solution was then added to a solution of TEOS. The TEOS:EtOH:H<sub>2</sub>O ratio was 1:1:1 by weight. After stirring for 1.5 h at 400 rpm, the mixture and an (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> solution (0.25 M) were added dropwise to deionized water at 80  $^{\circ}$ C. The pH was maintained between 7 and 7.5.

- The resulting suspension was stirred at 80 °C for 18 h, separated with filtration, and washed with deionized water, checking the conductivity of the permeate.
- The recovered solid was dried for 24 h at 105 °C and then calcined at 550 °C under static air, with a heating rate of 5 °C/min and 6 h of dwell.

#### 2.2. Ammonia-Evaporation Method (AE)

Copper precursor salt was Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Sigma Aldrich<sup>®</sup> purity 99); silica precursor was an aqueous colloidal dispersion of silica gel nanoparticles named LUDOX AS-40 (Sigma Aldrich<sup>®</sup> silica concentration  $30\%_{w/w}$ ) and  $28\%_{w/w}$  aqueous ammonia solution (Sigma Aldrich<sup>®</sup>).

AE synthesis followed these steps:

- Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was dissolved in distilled water (50 mL), and ammonia solution was added till the resulting solution presented a pH between 11 and 12. The solution was stirred at room temperature for 30 min, forming the tri-ammonium copper nitrate.
- The amount of silica precursor was added to the copper ammonia complex solution and stirred for 4 h at room temperature, then heated at 90 °C to evaporate the ammonia up to a pH value between 6 and 7.
- The precipitate was separated with filtration and washed with deionized water, and the recovered solid was dried for 24 h at 105 °C, then calcined at 550 °C under static air.

Table 2 lists all materials synthesized, with their nominal composition. From here on, the following nomenclature applies for their identification; copper catalysts were named  $CuxSiO_2XX$ , where *x* was the nominal weight percentage of Cu present in the sample and *XX* was the type of synthesis (e.g., Cu5SiO<sub>2</sub>AE nominally contained 5%<sub>*w/w*</sub> of copper supported on silica prepared with the AE method).

**Table 2.** List of synthesized catalysts (nominal phase: Cu-silica): name, nominal loading of  $Cu_{w/w}^{*}$ .

Name	Nominal Cu Loading [ $\%_{w/w}$ ]
Cu5SiO <sub>2</sub> HP	5
Cu10SiO <sub>2</sub> HP	10
Cu5SiO <sub>2</sub> AE	5
Cu10SiO <sub>2</sub> AE	10

2.3. Characterization Methods

All synthesized catalysts were characterized via the following:

- V.A.R.I.A.N. 720-ES ICP-AES ICP-AES (Inductively Coupled Plasma—Atomic Emission Spectroscopy), equipped with a custom-designed charge coupled device (CCD) highly sensitive photon detector. The estimated detection limit for the quantified Cu was 5 μg/L. The samples were mineralized in a mixture of concentrated strong acids, then diluted in deionized water to be ready for nebulization operated by the device.
- A MICROMERITICS ASAP 2420 to determine surface area and porosity, recording N<sub>2</sub> adsorption and desorption isotherms at  $-196 \,^{\circ}$ C. ASAP 2420 software v2.09 performed calculations of surface area (S<sub>BET</sub>), pore volume (V<sub>BJH, des</sub>), average pore diameters (D<sub>av, BJH</sub>) and pore size distribution. Degassing of the powder was performed before the analysis under a weak vacuum with a 10  $^{\circ}$ C min<sup>-1</sup> heating ramp until 250  $^{\circ}$ C, and it dwelled overnight (at least 8 h).
- X-ray diffractometer BRUKER AXS D8 ADVANCED, using CuK $\alpha_1$  radiation to detect crystalline phases with a Bragg–Brentano geometry. XRD spectra were recorded in a Bragg angle range from 20° and 90° at 0.0158° scanning step and a sampling time of 1s per step (3 s for amorphous phases). Phase identification was performed with the DIFRAC.EVA V5.2.0.3 software, including the JCDPS (Joint Committee on Powder

Diffraction Standards) database. The spectra acquired on powder samples allowed for the estimation of average crystallite sizes (L) of the main detected phases with Scherrer equation [55].

- Raman spectrometer HORIBA JOBIN YVON LabRam ARAMIS, equipped with two lasers at 532 nm (green) and 785 nm (red) and coupled with an optical confocal microscope. The range of acquired signals was from 200 cm<sup>-1</sup> to 1850 cm<sup>-1</sup>, and the spectra were compared to results from the literature for copper [56] and silica catalysts [57–61] and online databases collected by RRUFF Project [62], the WURM Project [63], and the database of the University of Parma [64].
- FT-IR NEXUS 870 THERMONICOLET: Fast Fourier Transform Infrared Spectroscopy Attenuated Total Reflectance (FTIR-ATR). Measures were obtained in the medium infrared field, ranging from 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>.
- MICROMERITICS AUTOCHEM II 2920 analyzer for temperature programmed reduction (TPR) and temperature programmed desorption (TPD-N<sub>2</sub>O) of 200mg of catalyst (50–150 μm). TPR started with a 10 °C min<sup>-1</sup> ramp heating up to 450 °C, letting it dwell for 2 h at 450 °C under 50 NmL min<sup>-1</sup> flow of reducing gas (10%vol H<sub>2</sub> in Ar). A TCD (Thermal Conductivity Detector) measured H<sub>2</sub> consumption and then recorded temperature versus time profile, elaborated with AUTOCHEM II software v4.02. The metallic copper surface was characterized by N<sub>2</sub>O temperature programmed desorption of 400 mg of catalyst (50–150 μm) reduced under 10%vol H<sub>2</sub> in Ar (50 NmL min<sup>-1</sup> flow rate) at 300 °C overnight after a 3 °C min<sup>-1</sup> ramp [65,66]. Before the N<sub>2</sub>O TPD, a flow rate of 2% N<sub>2</sub>O in Ar (50 NmL min<sup>-1</sup>) was sent to the TCD detector; the TCD signal was acquired until a stable signal was reached. The loop was therefore purged with Ar, and then, the sample was oxidized with the same flowrate of 2% N<sub>2</sub>O in Ar (50 NmL min<sup>-1</sup>) for 1 h at 50 °C.
- THERMO VG MULTILAB 2000, which performed XPS (X-ray Photoelectron Spectroscopy), determining silica-supported catalysts' superficial elemental composition and electronic state. The instrument could operate under an ultra-high vacuum.
- ZEISS GEMINI SEM 500 device equipped with OXFORD ENERGY 250 INCAx-act detector and combined with scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), operating at 15 kV, BSE (Back Scattering Electron) Z-contrast mode.
- JEOL 2100 LaB<sub>6</sub> (lanthanum hexaboride filament), operating a 200 kV, with punctual resolution equal to 0.2 nm in parallel mode and 2–3 nm works in STEM (scanning transmission electron microscopy) mode, equipped with an SDD detector (30 mm<sup>2</sup>) for elemental analyses with in situ EDS.

## 2.4. Reaction Tests

The selected vegetable oils were canola rapeseed (*B. napus*) and sunflower (*H. annuus*). Canola rapeseed oil was chosen because it is more exploitable at the industrial level. On the other hand, sunflower oil allows for a higher C18:1 yield, starting from a relatively low initial percentage of C18:1 and a higher content of polyunsaturated compounds (mainly C18:2).

Before each hydrogenation test, each catalyst (2 g of the catalyst with granulometry between 50–150  $\mu$ m) was pre-reduced with ex situ dry reduction in <sup>1</sup>/<sub>2</sub> inch AISI 316L stainless steel fixed bed reactor under 200 NmL min<sup>-1</sup> (30%<sub>v/v</sub> of H<sub>2</sub> in N<sub>2</sub>), following indications available in the literature [37,41,44,53] and the results of TPR experiments.

The laboratory-scale apparatus for vegetable oil hydrogenation tests is described in previous work [67]. In Table 3, the operation conditions of reactivity tests are reported.

Test Number	Catalysts	Oil	Catalyst Concentration (mg/mL <sub>oil</sub> )	Temperature (°C)	Pressure (bar)	Test Duration (min)
$ \begin{array}{c} 1\\ 2\\ 3\\ 4 \end{array} $	Cu5SiO <sub>2</sub> AE	Canola	4	180 200	4 12 4 12	240
5 6 7 8	Cu5SiO <sub>2</sub> HP	Canola	4	180 200	4 12 4 12	240
9 10 11 12	Cu10SiO <sub>2</sub> AE	Canola	4	180 200	4 12 4 12	240
13 14 15 16	Cu10SiO <sub>2</sub> AE	Canola	8	180 200	4 12 4 12	240
17 18 19	Cu10SiO <sub>2</sub> AE	Canola	2	180 200	4 12 4	240
20 21 22	Cu10SiO <sub>2</sub> AE	Sunflower	4	180 200	4 12 4	360
23 24 25 26	Cu10SiO <sub>2</sub> HP	Canola	4	180 200	4 12 4 12	240
27 28 29 30	Cu10SiO <sub>2</sub> HP	Canola	8	180 200	4 12 4 12	240
31 32 33	Cu10SiO <sub>2</sub> HP	Canola	2	180 200	4 12 4	240
34 35 36	Cu10SiO <sub>2</sub> HP	Sunflower	4	180 200	4 12 4	360

**Table 3.** Reactivity test conditions: catalyst concentration in oil, temperature, pressure, and test duration.

All collected samples were trans-esterified with a standardized method (AOAC 969.33 [68]) and analyzed with GC-FID with a Varian 3400 GC equipped with flame-ionization detector (FID) and with a Supelco<sup>®</sup> SP-2380 GC capillary column (30 m × 25  $\mu$ m) (Sigma Aldrich<sup>®</sup>, Merck KGaA, Darmstadt, Germany). The peaks' areas were calculated with the Software VARIAN Star GC-MS v6.02. The GC-FID was periodically calibrated with an external standard, and the retention times of the FAME are in Table 4.

Component	Retention Time [min]
Myristic FAME	4.12
Palmitic FAME	5.23
Stearic FAME	6.81
Elaidic FAME	7.33
Oleic FAME	7.62
<i>t,t</i> Linoleic FAME	8.23
<i>c,t</i> Linoleic FAME	8.58
<i>t,c</i> Linoleic FAME	8.70
c,c Linoleic FAME	9.12
Behenic FAME	9.65
Linolenic FAME	10.81
Erucic FAME	15.22

Table 4. Retention times of the FAME individuated with gas chromatography.

Reactivity performances were evaluated in terms of linolenic acid conversion (Equation (1)), linoleic acid conversion (Equation (2)), and Iodine Value variation.

$$X_{C18:3} = \frac{(C18:3)_0 - (C18:3)_t}{(C18:3)_0} * 100,$$
(1)

where  $(C18:3)_0$  and  $(C18:3)_t$  are the relative percentage of linolenic acid at the initial time (t = 0) and at a given time t.

$$\chi_{C18:2} = \frac{\sum_{j} (C18:2)_{0} - \sum_{j} (C18:2)_{t}}{\sum_{j} (C18:2)_{0}} * 100,$$
(2)

where  $\sum_{j}(C18:2)_{0}$  and  $\sum_{j}(C18:2)_{t}$  are the relative percentage of linoleic acid and its isomers at the initial time (t = 0) and at a given time t.

Iodine Value (IV) is the mass of iodine in grams consumed by 100 g of a chemical substance to saturate the unsaturation in its fatty acids. The higher the IV value, the more double bonds are present in oils. The international standard ISO 3961:2018 [69] provides the IV calculation starting from GC analysis (Equation (3)):

$$IV = (x_{C16:1} \cdot 0.950) + (x_{C18:1} \cdot 0.860) + (x_{C18:2} \cdot 1.732) + (x_{C18:3} \cdot 2.616) + (x_{C20:1} \cdot 0.785) + (x_{C22:1} \cdot 0.723),$$
(3)

where  $w_{Cx:y}$  are the percentages of the different unsaturated compounds typically found in vegetable oils.

To evaluate the selectivity toward various acids under mild conditions [70–72], a simple pseudo-first order scheme of series reactions, omitting isomerization of double bonds, was taken into account [73] (Equation (4)):

$$(C18:3) \xrightarrow{k_3} (C18:2) \xrightarrow{k_2} (C18:1) \xrightarrow{k_1} (C18:0), \tag{4}$$

explicatable as follows:

$$\frac{d(C18:3)}{dt} = -k_3 \cdot (C18:3), \tag{5}$$

$$\frac{d(C18:2)}{dt} = k_3 \cdot (C18:3) - k_2 \cdot (C18:2), \tag{6}$$

$$\frac{d(C18:1)}{dt} = k_2 \cdot (C18:2) - k_1 \cdot (C18:1).$$
(7)

This set of differential equations (Equations (5)–(7)) was numerically integrated with MAPLE<sup>®</sup> 018 V2.1 software.

$$S_{Ln} = k_3/k_2,$$
 (8)

$$S_{Le} = k_2 / k_1$$
, (9)

$$SII = \frac{(trans)_t - (trans)_0}{\Delta IV_t},$$
(10)

$$\Delta IV_t = IV_0 - IV_t \tag{11}$$

where  $IV_0$  and  $IV_t$  are the iodine values at the initial time (t = 0) and at a given time t.

# 3. Results and Discussion

3.1. Characterization of Catalysts

The theoretical loading of the active element is compared with the ICP-AES measurement, quantifying the Cu content in the synthesized catalysts (Table 5). The amount of copper is often higher than the nominal loading introduced during the synthesis, especially for the AE. It is probably due to the synthesis procedure; a hypothesis is that part of the silica is washed away during the filtering.

**Table 5.** Cu%<sub>*w*/*w*</sub> of silica-supported catalysts.

 $(\Delta IV)$  (Equation (11)) were defined as follows:

Sample	Nominal Loading	<b>ICP-AES</b> Measure
Cu5SiO <sub>2</sub> HP	5	$5.8\pm0.2$
Cu10SiO <sub>2</sub> HP	10	$10.8\pm0.3$
Cu5SiO <sub>2</sub> AE	5	$6.5\pm0.1$
Cu10SiO <sub>2</sub> AE	10	$11.7\pm0.2$

The  $N_2$  adsorption and desorption curves show a shape intermediate between Type II and Type IV(a) from the IUPAC classification of physisorption isotherms [74]. Figure 1 reports an example; samples curves are reported in Figure S1 (see Supplementary Materials). The hysteresis loop is associated with complex structures with a network effect between the pores. All catalysts present the flat line characteristic of mesoporous materials. The pore volume distribution's relation to pore size confirms this deduction in Table 6.

Table 6 reports values of the BET surface ( $S_{BET}$ ), BJH cumulated pore volume calculated for the desorption branch ( $V_{BJH,des}$ ), and estimation of average pores diameter ( $D_{av,BJH}$ ). BET surface values are reliable, whereas macroporosity and network effects affect the BJH volume.

An increase in the copper load seems to have a beneficial role in the surface area of the catalysts. At the same nominal metal fraction, HP synthesis products show higher surface area, pore volume, and average diameter than the corresponding AE ones. In addition to different pH (7–7.5 for HP against 6–7 for AE), the lower synthesis temperature during the  $SiO_2$  formation can explain the lower area in AE samples. The obtained materials have surface area values in line with the literature values [50,54,58].

X-ray diffractograms of calcined samples (not reported here) showed a strong contribution of the SiO<sub>2</sub> amorphous phase.



Figure 1. BET adsorption/desorption isotherms of Cu10SiO<sub>2</sub>HP catalyst.

**Table 6.** BET surface area ( $S_{BET}$ ), BJH cumulative volume ( $V_{BJH, des}$ ), and average pore diameters ( $_{Dav, BJH}$ ) for as-synthesized materials.

Materials	$\begin{array}{c} S_{BET} \\ [m^2g^{-1}] \end{array}$	V <sub>BJH, des</sub> [cm <sup>3</sup> g <sup>-1</sup> ]	D <sub>av, BJH</sub> [nm]
Cu5SiO <sub>2</sub> HP	342	1.58	18.7
Cu10SiO <sub>2</sub> HP	359	1.71	20.3
Cu5SiO <sub>2</sub> AE	208	0.55	10.6
Cu10SiO <sub>2</sub> AE	256	0.69	10.8

The infrared spectra recorded between 4000 cm<sup>-1</sup> and 400 cm<sup>-1</sup> (Figure 2) for each as-synthesized sample are similar and ascribable to the silica. However, the presence of CuO alters the wavelength of these bands of silica (more evident for HP catalysts), lowering the 1112 cm<sup>-1</sup> band to 1060, identified as follows [75–77]:

- At 450 cm<sup>-1</sup> and 800 cm<sup>-1</sup>, the symmetric stretching of siloxane groups (Si-O-Si);
- At 1060 cm<sup>-1</sup>, the asymmetric stretching of the same siloxane groups;
- The shoulder at 960 cm<sup>-1</sup>, the angular deformation of the Si-OH silanol group.

In the spectra, there are no bands of organics phases; this is important for HP catalysts because it highlights that all the TEOS is converted into SiO<sub>2</sub>.

In Figure 2, the characteristic infrared bands of CuO (575 cm<sup>-1</sup>, 500 cm<sup>-1</sup>, and 460 cm<sup>-1</sup>) are overlapped with the intensive band of Si-O-Si stretching, but they are recognizable at a shoulder of 580 cm<sup>-1</sup>.

FTIR-ATR spectra of  $Cu5SiO_2HP$  and  $Cu5SiO_2AE$  (not reported) are similar to silica with minor modifications due to the lower concentration of the metallic phase.

Raman spectroscopy is combined with FTIR analysis to integrate the information between the two techniques for copper-based catalysts. As-synthetized samples present the Raman bands of copper phyllosilicate called chrysocolla [78,79] (Figure 3). Chrysocolla and copper hydroxide structures are usually found together; sometimes, the copper hydroxide could be reformed by decomposing the copper phyllosilicate [60]. The reduced samples (HPR and AER, respectively) show less intense bands, and the Cu<sup>+</sup> oxide bands appear formed from the reduction of chrysocolla or phyllosilicates-like phases, as illustrated in the literature [50,54,80].



Figure 2. FTIR-ATR spectra of Cu10SiO<sub>2</sub>HP, Cu10SiO<sub>2</sub>AE.



**Figure 3.** Raman spectra for Cu-based catalysts with highlighted bands of SiO<sub>2</sub>, copper phyllosilicate, Cu<sub>2</sub>O, and Cu(OH)<sub>2</sub> [68,70,76].

Table 7 gathered all the results of the TPR reduction temperature for the as-synthesized samples. The stronger the interactions between the active phase and support, the higher the reduction temperatures of H<sub>2</sub> consumption peaks of TPR data were. Therefore, the copper phase is not strongly bonded to the silica substrate because no reduction temperature (232–242 °C) increase compared to the CuO bulk reduction temperature (between

220–250 °C) is observed [54,66,81,82]. The presence of chrysocolla does not affect the reduction temperature of the samples [50,54,60], and only a single reduction peak is recognizable. HP samples exhibit slightly higher reduction temperatures than AE samples linked to higher copper interaction with SiO<sub>2</sub> thanks to the higher dispersion of copper silicate.

Table 7. Reduction temperatures for the reducible Cu species and metallic copper surface area.

Material	Cu T <sub>red</sub> (°C)	Cu Surface (m² <sub>Cu</sub> /g <sub>Cu</sub> )
Cu5SiO <sub>2</sub> HP	242	-
Cu10SiO <sub>2</sub> HP	239	55
Cu5SiO <sub>2</sub> AE	232	-

An XRD analysis on silica-supported catalysts after TPR confirms the reduction of all the reducible species (Figure 4). HP and AE present a small amount of metallic copper Cu and Cu<sub>2</sub>O in Cu supported on silica catalysts. As indicated by Hope et al. [60] and Yunjun et al. [50], the formation of reduced species of copper is related to the reduction of CuO and copper phyllosilicates. Only the most intense peak of Cu<sub>2</sub>O at 36° is differentiable from the spectra of Cu at 42.3°. Peaks are only barely distinguishable for samples with  $10\%_{w/w}$ .



Figure 4. X-ray diffractometer of all samples after TPR.

In the AE samples, the ray relative to  $Cu_2O$  is more intense than  $Cu^0$ . Comparing these results to as-synthesized catalysts, one can hypothesize that the materials synthesized with AE contain a more significant amount of chrysocolla phase than the HP ones, the reduction of the sample giving place to more copper oxide. Instead of reducing HP samples, more metallic copper is formed.

The broad peaks do not permit an accurate crystallite size estimation. For  $Cu_2O$  or  $Cu^0$ , the peaks are too large, and the values are such that the predicted value is smaller than 3 nm, which is the limit of the accuracy of the Scherrer equation.

Figure 5a–c show the XPS spectra relative to as-synthesized Cu10SiO<sub>2</sub>AE and Cu10SiO<sub>2</sub>HP samples, respectively. For these catalysts, the peaks at 942.5 eV and 962.4 eV are identifiable as CuO peaks, and the Cu<sup>2+</sup> strong satellites are also present and probably linked to phyllosilicate. After the reduction (Figure 5b–d) of Cu10SiO<sub>2</sub>AE and Cu10SiO<sub>2</sub>HP samples, respectively, the intensity of the Cu<sup>2+</sup> satellites decreases. The weak satellites are visible after the reduction of the Cu10SiO<sub>2</sub>AE catalyst, which happens when Cu<sub>2</sub>O is formed in large quantities on the support. For the Cu10SiO<sub>2</sub>HP catalyst, the satellites are less intense after reduction, and consequently, more Cu<sup>0</sup> is obtained on the superficial layer.

As shown in Figure 5e–f, the two LMM spectra (L-inner level-M-inner level-M-inner level electron transition), produced by the Auger effect, present an asymmetrical and broad peak, suggesting the coexistence of  $Cu^+$  (the lower peak) and  $Cu^0$  (the higher peak) as stable species. Table 8 shows the ratio  $Cu^+/(Cu^+ + Cu^0)$ ; HP has more metallic copper on its surface after reduction.

SEM-EDS analyses in Figure 6 show the external silica textures of  $Cu10SiO_2HP$  (Figure 6a) and  $Cu10SiO_2AE$  (Figure 6b), respectively. The  $Cu10SiO_2AE$  material has a much smoother surface with some aggregates with similar elemental composition to the bulk of the homogeneous support (see analyses spectra 14 to 16).

Figure 7 shows that the two syntheses present a different arrangement of the silica matrix, more cohesive for HP than for the AE catalyst. Figure 7a suggests the integration of the copper inside the matrix and reveals more evident crystalline structures smaller than 3–5 nm, as highlighted by peaks of XRD spectra in Figure 4. Because of their small size, these crystalline structures could be associated with CuO crystals.

The as-synthesized sample of Cu10SiO<sub>2</sub>AE shows a lamellar structure (Figure 7b), and some crystals were observed on the border of the materials. The EDS analyses of both reduced samples suggest that the particles smaller than 7 nm (Figure 8a,b) are composed of metallic copper or Cu<sub>2</sub>O, confirming the XPS results.

## 3.2. Catalyst Reactivity Tests

## 3.2.1. Effect of Copper Loading, Temperature, and Pressure

The results of catalytic reactivity tests in terms of the maximum percentage of oleic acid  $(C18:1)_{max}$ , corresponding linolenic selectivity  $(S_{Ln})$ , specific isomer index (SII), maximum conversion of linolenic ( $\chi$ C18:3) and linoleic ( $\chi$ C18:2) acids, total mass percentage of trans isomers ( $TT_{max}$ ), and total mass percentage of stearic acid ( $TS_{max}$ ), under the operating conditions reported in Table 3, are summarized in Table 9.

The increase in copper loading has a beneficial effect on the activity of the catalysts, which results in more significant amounts of linoleic and linolenic acid converted (Table 9 tests 1–4 vs. tests 9–12 and tests 5–8 vs. tests 23–26).

Compared to the Lindlar catalyst [67], copper silica catalysts are more active at higher temperatures. The effect of temperature is already visible even with a moderate increase (180 °C vs. 200 °C). A higher temperature favors the decomposition of canola oil, estimated at around 220 °C [83]. Among the tests carried out at 200 °C, Test 25 performed at 4 bar showed a good content of final oleic acid, with a high conversion of linolenic acid and almost half conversion of linoleic acid, with a small amount of trans isomers and stearic acid formed (TT<sub>max</sub> and TS<sub>max</sub> equal to 14.6% and 4.1%, respectively).



**Figure 5.** XPS of 10%Cu catalysts on silica: shifted raw data (black), peaks fitting (blue), peak sum (red), background (grey dash). (a) XPS of Cu10SiO<sub>2</sub>HP Cu 2p region; (b) XPS of reduced Cu10SiO<sub>2</sub>HPR Cu 2p region; (c) XPS of Cu10SiO<sub>2</sub>AE Cu 2p region; (d) XPS of reduced Cu10SiO<sub>2</sub>AER Cu 2p region; (e) XPS of Cu10SiO<sub>2</sub>HPR reduced Cu LMM; (f) XPS of Cu10SiO<sub>2</sub>AER reduced Cu LMM; Survey data in Figure S2.



Material Cu10SiO<sub>2</sub>HPR

**Table 8.** Cu<sup>+</sup> and Cu<sup>0</sup> distribution obtained with deconvolution with software CasaXPS 2.3.25 on reduced samples.



(b)

Figure 6. (a)  $Cu10SiO_2HP$  secondary electron images with EDS analysis; (b)  $Cu10SiO_2AE$  secondary electron images with EDS analysis; EDS results in Table S1.

At 180 °C, the pressure increase has a positive effect on conversions, more relevant for AE catalysts (Test 1:  $\chi$ C18:3 = 15.8 and  $\chi$ C18:2 = 7.3 vs. Test 2:  $\chi$ C18:3 = 30.8 and  $\chi$ C18:2 = 15.5). At 200 °C, changing pressure mainly affects the conversion of linoleic acid (see Test 3 vs. Test 4, Test 7 vs. Test 8, Test 11 vs. Test 12, and Test 25 vs. Test 26 of Table 9). The pressure effect is more relevant in the conversion of linoleic acid (C18:2) than linolenic acid (C18:3) because the first one is more suitable to form the conjugated diene as an intermediate reaction [34].

 $(Cu^+/Cu^0 + Cu) * 100$ 

 $45.4\pm0.2\%$ 



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Figure 8. TEM micrographs of reduced (a) Cu10SiO<sub>2</sub>HP and (b) Cu10SiO<sub>2</sub>AE.

Concerning selectivities, Cu10SiO<sub>2</sub>AE performs better than Cu10SiO<sub>2</sub>HP in terms of the isomer formation of SII and S<sub>Ln</sub> (Table 9). The SII selectivity, the IV value, and the total trans percentage obtained for Cu10SiO<sub>2</sub>AE catalysts (Test 9 SII = 0.32,  $\Delta$ IV = 42, and the TT = 12%) and Cu10SiO<sub>2</sub>HP (Test 23 SII = 0.41,  $\Delta$ IV = 40, and the TT = 10.9%) are in line with Ravasio et al. values (SII = 0.44,  $\Delta$ IV = 45, and the TT = 15–20% [80]). Concerning selectivities, they can be linked to the capacity of the catalyst to form conjugated dienes and to hydrogenate them. In particular, Cu10SiO<sub>2</sub>HP has a higher degree of hydrogenation of the conjugated dienes than Cu10SiO<sub>2</sub>AE, and it is also faster in forming these compounds. Using first-order kinetic constant ratios is a simple way to describe and compare the reaction data with the literature.

Test Number	Catalyst	Catalyst Concentration (mg/mLoil)	Т (°С)	P (bar)	Oil <sup>1</sup>	(C18:1)max (%)	SLn	SII	χC18:3 (%)	χC18:2 (%)	TTmax (%)	TSmax (%)
1	щ		180	4	С	70.1	6.7	0.18	15.8	7.3	0.6	2.1
2	$O_2A$		180	12	С	71.4	6.1	0.13	30.8	15.5	2.2	4.0
3	15Si	4	200	4	С	79.1	6.9	0.26	76.7	26.8	4.0	3.4
4	Ū		200	12	С	78.5	6.8	0.17	78.5	30.4	2.7	5.0
5	Ь		180	4	С	68.3	6.1	0.32	65.3	20.5	9.0	1.6
6	O <sub>2</sub> H		180	12	С	69.7	6.5	0.35	66.3	23.5	7.8	1.5
7	15Sic	4	200	4	С	79.1	6.1	0.31	82.3	36.7	9.5	1.7
8	Ū		200	12	С	80.2	6.5	0.35	83.1	38.9	8.5	1.9
9			180	4	С	71.9	6.9	0.32	35.8	13.4	12.1	2.2
10			180	12	С	78.8	6.0	0.39	79.8	33.4	8.2	4.0
11		4	200	4	С	78.7	6.3	0.35	82.2	35.8	15.4	3.4
12			200	12	С	79.9	6.7	0.42	83.3	48.7	12.3	5.4
13			180	4	С	77.5	7.0	0.56	67.8	45.7	14.8	3.5
14	Æ	0	180	12	С	87.8	6.8	0.48	80.3	65.2	20.2	3.1
15	$O_2^A$	8	200	4	С	78.6	6.8	0.58	69.8	57.6	17.3	4.7
16	10Si		200	12	С	88.6	6.7	0.54	84.5	79.5	24.0	5.3
17	Cu		180	4	С	71.4	-	-	21.1	5.8	4.8	2.1
18		2	180	12	С	73.2	-	-	24.3	8.3	6.8	2.1
19			200	4	С	78.4	7.1	0.18	54.3	23.3	11.8	2.9
20			180	4	S	59.6	-	0.87	-	42.1	27.0	6.0
21		4	180	12	S	67.2	-	0.89	-	60.2	28.5	4.7
22			200	4	S	69.1	-	0.88	-	62.2	33.4	8.0
23			180	4	С	76.2	5.1	0.42	73.0	35.0	10.9	3.6
24		4	180	12	С	80.1	6.5	0.50	74.5	38.4	9.7	5.2
25		4	200	4	С	84.5	5.4	0.51	86.4	48.5	14.6	4.1
26			200	12	С	86.2	6.3	0.58	87.5	61.3	12.4	5.5
27			180	4	С	88.8	5.8	0.75	89.8	78.5	13.2	4.1
28	Ĥ	Q	180	12	С	89.2	5.7	0.62	91.8	82.5	14.8	5.4
29	$O_2F$	0	200	4	С	90.7	5.5	0.82	92.6	82.3	18.8	5.5
30	10Si		200	12	С	91.3	5.7	0.69	93.3	90.4	23.0	5.3
31	Cu		180	4	С	69.2	-	-	17.5	4.2	3.8	1.9
32		2	180	12	С	71.0	-	-	20.1	7.2	4.5	2.0
33			200	4	С	72.3	6.0	0.20	37.2	26.2	12.5	2.1
34			180	4	S	67.3	-	0.51	-	48.2	15.2	7.0
35		4	180	12	S	69.1	-	0.72	-	55.1	23.4	4.1
36			200	4	S	70.6	-	0.83	-	60.4	28.1	6.3

Table 9. Test results of SII index and conversions calculated after tests (SLe is always near zero).

 $^{1}$  C = canola oil, S = sunflower oil.

By comparing the results of the Lindlar catalyst ( $S_{Ln} = 1.3-2.2$ ) [67], the  $S_{Ln}$  ranges between 5.1 and 7.1. This parameter is correlated with the different reaction mechanisms described by Dijkstra et al. [34,52]; for copper catalysts, the hydrogenation does not process through the direct hydrogenation of the double bond, but an initial reaction step is the formation of a conjugated diene inside the polyunsaturated acids. This mechanism was described by Dijkstra [34], and the currently accepted explanation involves the abstraction of an allylic hydrogen atom followed by the addition of such an atom to a terminal atom of a pentadienyl or octatrienyl system. The double bonds can then scramble through the triglyceride chain until formed conjugated dienes are hydrogenated, removing the possibility of mobile conjugated double bonds on the chain and terminating the reaction. A Horiuti–Polanyi mechanism currently describes the hydrogenation step of the reaction. This mechanism involves a reversible addition of the first hydrogen atom to one of the double-bonded carbon atoms, followed by an irreversible addition of a second hydrogen atom to another formerly double-bonded carbon atom [52]. However, the selectivity S<sub>Ln</sub> values align with the results found by Mounts et al. [41]. Koritala et al. [35] found a kinetic constant, k<sub>1</sub>, of Equation (4) of oleic acid saturation near zero, producing a negligible formation of undesirable stearic acid. Vice versa, in the present work, the kinetic constant, k<sub>1</sub>, of oleic acid consumption is three orders of magnitude higher than k<sub>2</sub>, which is almost zero, ranging from  $1.01 \times 10^{-5}$  to  $2.89 \times 10^{-5}$ . Consequently, with canola oil, the maximum formation of stearic acid is 5.5% in Tests 26 and 29.

#### 3.2.2. Effect of Catalyst Concentration

Based on the presented data, Cu10SiO<sub>2</sub>AE and Cu10SiO<sub>2</sub>HP, achieving high conversion of dienes and trienes, were selected for industrial application.

Testing at a lower concentration (2 mg<sub>catalyst</sub>/mL<sub>oil</sub>) at 180 °C at 4 and 12 bar, no evident activity is found for both catalysts with the linolenic conversion,  $\chi$ C18:3, below 25% and the linoleic conversion,  $\chi$ C18:2, below 9%. At 200 °C, the conversion of C18:3 reaches 54.3% for Cu10SiO<sub>2</sub>AE (Test 19) and 37.2% for Cu10SiO<sub>2</sub>HP (Test 33), respectively. In Test 33, the conversion of C18:2 is also more significant, and 26.2% of linoleic acid is converted. Under these conditions, a small amount of TTs is formed (see Test 33 SII = 0.20 in Table 9).

The increase in catalyst concentration does not significantly increase C18:3 conversion, reaching more than 83% of the conversion at 4 mg <sub>catalyst</sub>/mL<sub>oil</sub>, confirming that the catalyst is already active at a low concentration.

Although Cu10SiO<sub>2</sub>HP conversion is already high at low concentrations (87.5% in Test 26), a further significant increase is noted with 8 mg <sub>catalyst</sub>/mL<sub>oil</sub>, reaching 93.3% in Test 30, representing the best performance of the whole experimental plan. This result confirms that the HP synthesis is better than the AE under the operating conditions investigated in this work. These promising results could be ascribable to the synergic effect of the higher surface area (Table 6), higher Cu dispersion (Figures 7 and 8), and higher reducibility (Table 8) combined with a stronger interaction with the silica support (Table 7).

At 200 °C and 12 bar, the total  $TT_{max}$  reaches 23% (in Test 30 of Table 9), representing the worst case, where nearly 15% of the product is elaidic acid and the remaining fraction percentage consists of linoleic acid isomers.

The 8 mg<sub>catalyst</sub>/mL<sub>oil</sub> concentration of the catalysts allowed for the conversion of more than 50% of the linoleic acid under all investigated conditions. It is interesting to compare other values at  $\chi$ C18:2 = 50% (see Table 10). Notwithstanding that the amount of catalyst is doubled, it is worth noting that the concentration of oleic acid remains in the range of 66.0–69.9. This evidence indicates that severe pressure conditions are unnecessary, and this information allows for considerable savings in terms of equipment and process management costs at the industrial level.

Under similar operating conditions to Tests 9 and 23 (180 °C and 6 bar), the catalyst Cu/SiO<sub>2</sub> found in the literature [80] showed an almost complete conversion of C18:3 and C18:2 ( $\chi$ C18:3 = 100% and  $\chi$ C18:2 = 81%) in C18:1 after 3 h of the reaction. It is worth noting that, despite very close copper content in the catalysts, the catalyst concentration in the reaction medium is five times lower than the concentration adopted by Ravasio et al. [80] (20 mg <sub>catalyst</sub>/mL<sub>oil</sub>).

The reaction times at 50% of C18:2 conversion decrease as the temperature, pressure, and concentration of the catalyst increase, except for Tests 29 and 30. Definitively, the experimentation reveals that, at the same pressure,  $Cu10SiO_2HP$  is more active than  $Cu10SiO_2AE$ .

Test Number	Catalyst	Catalyst Concentration (mg/mL <sub>oil</sub> )	T (°C)	P (bar)	t (min)	IV	SII	C18:0 (%)	C18:1 (%)		
9			180	4	-	-	-	-	-		
10		4	100	12	209	110.2	0.25	1.8	67.5		
11	AE	4	200	4	168	109.4	0.26	2.0	68.3		
12	iO <sub>2</sub> ,		200	12	135	111.3	0.17	1.8	66.0		
13	10S		180	4	109	110.5	0.35	2.5	67.4		
14	U U	8	0	0	100	12	91	110.0	0.27	3.1	67.8
15	-		8	200	4	86	109.7	0.40	4.3	68.9	
16	-		200	12	74	109.4	0.36	3.7	69.1		
23			180	4	159	110.1	0.23	1.5	67.9		
24		4	100	12	137	110.6	0.17	1.5	68.7		
25	Ĥ	4	200	4	124	109.2	0.26	1.5	69.0		
26	iO <sub>2</sub> 1		200	12	111	108.9	0.18	1.8	69.3		
27	10S		180	4	82	109.6	0.31	1.6	68.1		
28	Ū Ū	0	180	12	74	108.6	0.24	2.0	67.9		
29		8	200	4	55	109.2	0.45	3.0	69.7		
30				200	12	56	110.3	0.41	2.8	69.9	

Table 10.	Test results,	SII and IV	at 50%	conversion	of linoleic	(C18:2)	for Cul	10SiO <sub>2</sub> AE and
Cu10SiO <sub>2</sub> I	HP at 4 mg <sub>cata</sub>	<sub>alyst</sub> /mL <sub>oil</sub> a	nd 8 mg <sub>c</sub>	<sub>atalyst</sub> /mL <sub>oil</sub>	•			

Except for Test 10 vs. Test 12 (SII = 0.25 vs. SII = 0.17), the isomerization selectivity increases with temperature and decreases with pressure (Table 10) with a concomitant increase in stearic acid production. It is also highlighted that the reaction time needed to reach 50% of C18:2 conversion augments accordingly to decrease temperature and pressure. The SII calculated values at the same linolenic acid conversion confirm that the Cu10SiO<sub>2</sub>HP is more active than Cu10SiO<sub>2</sub>AE and has similar SII. Consequently, Cu10SiO<sub>2</sub>HP produces a higher amount of TTs and TS.

#### 3.2.3. Effect of Different Oil

Cu10SiO<sub>2</sub>AE (Tests 20–22 of Table 3) and Cu10SiO<sub>2</sub>HP (Tests 34–36 of Table 3) are tested, with sunflower oil having a higher linoleic acid content and no linolenic acid in its composition.

The results are in line with sunflower data obtained with the Lindlar catalyst [67]. After 6 h of hydrogenation, the Cu10SiO<sub>2</sub>HP exhibits a slightly higher linoleic conversion than the Cu10SiO<sub>2</sub>AE (i.e.,  $\chi$ C18:2 = 50.2% vs. 43.3% of Test 34 vs. Test 20, Table 9). By comparing the tests at the same conditions, the SII selectivity is higher for Cu10SiO<sub>2</sub>HP. The TT<sub>max</sub> contents are much higher than canola oil for both catalysts due to a longer reaction time (360 vs. 240 min). In the end, the C18:2 isomers' production is higher for Cu10SiO<sub>2</sub>AE. This behavior could be related to the formation of a conjugated diene, as reported for the mechanism of a reaction of copper catalysts proposed by Dijkstra, where the hydrogenation of polyunsaturated oils proceeds through the conjugation of the double bonds, in turn caused by a hydrogen extraction followed by a hydrogen addition [34] and the consecutive hydrogenation of the conjugated dienes, which follows the mechanism proposed by Horiuti–Polanyi. It involves the first hydrogen reversible addition and a second irreversible hydrogen addition. This mechanism should explain why the hydrogenation observed for oils with high linolenic content, such as canola oil, is much faster [53], as linolenic acid contains more double bonds that can form conjugated dienes.

Furthermore, Dijkstra [27] suggested that the observed higher content of trans isomers is linked not to the isomerization of cis-monoenes but to the conjugation reaction. The interpretation of hydrogenation data indicates that the Cu10SiO<sub>2</sub>HP catalyst is more active toward reducing conjugated double bonds when a low amount of linolenic acid is present. The higher activity could be related to a greater reduction of Cu on the catalyst surface (Figure 5). S<sub>Le</sub> results for all sunflower tests are higher than the canola tests, reaching values higher than 1000, closer to the hypothetical infinite selectivity found by Koritala [35,42].

#### 3.2.4. Reusability and Stability of the Catalyst: Cyclic Tests

By evaluating all the results obtained in the previous paragraphs, the  $Cu10SiO_2HP$  catalyst showed the best performance. For this catalyst, the reusability was analyzed over cyclic activity. The catalyst was recovered after a hydrogenation run with centrifugation. The powder was washed with ethanol and acetone to separate the hydrogenated oil and reused in a new hydrogenation run.

Figure 9 reports the trend of the conversions of  $\chi$ C18:2 and  $\chi$ C18:3 for Test 29 repeated over five cycles. It is possible to observe a slight decrease in the conversions under the consecutive hydrogenation runs, with  $\chi$ C18:2 varying from 82.3% down to 79.5% and  $\chi$ C18:3 decreasing from 92.6% to 89.4%. The selectivities slightly changed over the hydrogenation runs; in particular, the SII selectivity changed from 0.82 at the first run to 0.85, denoting a mild decrease in the selectivity toward the formation of isomers. It is interesting to report that the S<sub>Ln</sub> overall does not change. In terms of TTs and TS, it was found that the maximum total trans changed from 18.8 up to 21.3, in line with SII results, but the total stearate decreased from 5.5 to 4.1, indicating a not compromising decrease in the activity toward complete hydrogenation.



**Figure 9.** Conversion  $\chi$ C18:2 and  $\chi$ C18:3 over five hydrogenation run cycles.

Lastly, in Figure 10, the TEM and SEM images of the catalyst are reported after five hydrogenation runs. In Figure 10a, the TEM image shows that the average dimensions of the copper nanoparticles remained almost unaltered, but fewer metallic particles are present when comparing it with Figure 8. From the SEM point of view, the particles appear less cohesive than in the pre-test figure (Figure 6a); this could be ascribed to the centrifugation process used to recover all the powder between each run.



Figure 10. (a) TEM image and (b) SEM image of Cu10SiO<sub>2</sub>HP catalyst after five cycles.

Overall, the Cu10SiO<sub>2</sub>HP seems to be quite stable after consecutive hydrogenation runs. A small make-up of the catalyst can be implemented to compensate for the loss of activity.

## 3.3. Industrial Applications

An industrial pilot application case study was developed by evaluating all the experimental data and choosing the Cu10SiO<sub>2</sub>HP catalyst. Tests at 200 °C and 4 bar with 4 mg<sub>catalyst</sub>/mL<sub>oil</sub> or 8 mg<sub>catalyst</sub>/mL<sub>oil</sub> (Test 25 and Test 29, respectively) provide the best results regarding the catalyst activity and selectivity. In Test 29, with a higher catalyst concentration in the oil, the almost complete linolenic and linoleic acid conversion was achieved after three hours (Figure 11). Since the difference in the relative composition of products becomes negligible from 180 min of reaction and a further increase in reaction time also comports an increase in undesired by-products (Table 11), the pilot hydrogenation plant was designed based on the optimized time (three hours) of the hydrogenation reaction.

The above information (Table 11 and Figure 9) combined with the analysis of the saturated components not involved in the reaction (C14:0, C16:0, C20:0, and C22:0) are the bases of the mass balances developed for the industrial design.

The hydrogenation process diagram is reported in Figure 12, and the description of each unit is available in Pasqual Laverdura (2019) [84]. The vegetable oil from storage is fed to the plant under flow control conditions and is preheated up to 160 °C, recovering part of the heat from the effluent hydrogenated product.

The plant size was 2.4 tonnes of vegetable oil, FAME, or fatty acids, estimated enough for a pilot plant scale. The hydrogenation reaction is carried out for 3 h in a loop reactor. All the secondary procedures of reaction charge/discharge and reactor cleaning between one hydrogenation run and the next one are hypothesized to take almost one hour. Definitively, the complete cycle of hydrogenation takes nearly four hours. The filtered catalyst could be recovered after every cycle.

In one 24 h day, six hydrogenation runs can be performed, and the production in a working day should be 14.76 tonnes of hydrogenated product. The venting must be considered to remove possible unwanted gases accumulated inside vessels.



**Figure 11.** Hydrogenation results Test 29: On the left-hand side (**a**), the relative percentage of C18 compounds vs. time; on the right-hand side (**b**), the conversions of linolenic and linoleic acid ( $\chi$ C18:2,  $\chi$ C18:3) and iodine value (IV) vs. time.

**Table 11.** Relative composition for C18 compounds of Test 29 at the start of the hydrogenation at 180 and 240 min.

Time (min)	C18:0	t-C18:1	C18:1	iso-C18:2	C18:2	C18:3
0	1.3	0.00	67.8	0.1	20.6	10.3
180	3.7	13.5	90.2	2.9	2.2	0.9
240	3.9	17.1	92.1	2.0	1.2	0.8

Estimations of the CAPEX, OPEX, and COP for the designed plant were carried out, affected by an error of  $\pm 30\%$ . The CAPEX cost of the main equipment is calculated based on the present price of stainless steel AISI SA-240-Gr.316. The cost of S and T heat exchangers is related to the cost per square meter of exchange surface; the cost of the impeller is estimated with Peters and Timmerhaus correlations [85].

The total direct cost for the equipment is  $365,000 \notin$ ; all the other indirect costs are expressed as a percentage of the equipment cost (Table 12).

The estimated operative costs include raw material, electricity, steam, hydrogen through electrolysis, catalyst, cooling water, and two operators for every work shift of 8 h for 245 shifts/operator/year and 300 working days/year at three shifts/day.

The total revenue produced by the plant and the total costs during one year of activity is listed in Table 13.

The modified return on the investment of 179% of the hydrogenation plant means that the revenue of the CAPEX was reached in less than one year.



**Figure 12.** The designed hydrogenation scheme layout [84]. (M: motor, LPS: low pressure steam, ◊ numbers stream index, TC, FC, LC: temperature, flow, and level controls).

Table 12. To	otal investment	costs distribution	following Peters and	Timmerhaus rules [85].
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Investment Cost	€	
Equipment cost (EC)	365,000 €	
Installation cost	36,500€	10% EC
Piping, Instruments and controls	73,000 €	20% EC
Electric system	18,250 €	5% EC
Total direct costs TDC	495,000€	
Engineering, supervision, site	49,000	10% TDC
Construction expenses	24,750	5% TDC
Total costs direct + indirect	570,000 €	
Contractor's fee	68,500	12% TDC + TIC
Contingencies	28,500	5% TDC + TIC
Working Capital (Total Investment)	667,000€	

Table 13. Calculation of the modified return on the investment (ROI<sub>m</sub>).

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Entry		m.u.
Sell revenues	4,392,000	€
Costs	3,060,000	€
R-C	1,332,000	€
Depreciation (linear 5 years)	133,400	€
ROI <sub>m</sub> = (Net Revenues)/CAPEX	1.79	

## 4. Conclusions

New catalysts containing Cu on a  $SiO_2$  support were studied, and two different synthesis methods were investigated: the AE (ammonia-evaporation) and the HP (hydrolysis precipitation) methods. Between the two syntheses, the HP catalyst gave the best results in oil hydrogenation activity and selectivity toward linoleic acid under all tested operating conditions.

The effect of temperature was significant in both synthesized catalyst families, and a slight increase in temperature from 180 to 200 °C improves the catalyst activity. However, the pressure effect was less relevant, reaching 82.3% of the conversion of linoleic at a relatively low pressure (4 bar).

The highest conversions (93.3% for C18:3 and 90.4% for C18:2) were reached at 8 mg<sub>catalysts</sub>/mL<sub>oil</sub>. The reaction time of three hours was exploitable for industrial hydrogenation processes. The maximum amount of total trans isomers under the most drastic conditions explored (200 °C and 12 bar of pure H<sub>2</sub>) is about 23%. The results of the Cu10SiO<sub>2</sub>HP catalyst tests were applied to design semi-continuous industrial applications at the pilot scale.

The benefits of the performed study are the development of new catalysts, capable of working even if added in small quantities and operating at relatively low pressure levels. This work allowed for the design of a cost-effective pilot plant for the selective catalytic hydrogenation of vegetable oils.

The estimation of the costs provides a return on the investment of 179%, which means in less than one year, the revenues of the hydrogenation plant cover the capital costs.

The prospects for the future of this study could be to extend the work to use exhausted vegetable oils. Besides the scientific interest, this further study could show the profitability of this process, and it is able to bring environmental benefits by reducing the impact of the disposal of used oils.

**Supplementary Materials:** The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/en16207201/s1, Figure S1: Adsorption and desorption curves of nitrogen of: (a) Cu5SiO<sub>2</sub>HP; (b) reduced Cu10SiO<sub>2</sub>HP; (c) Cu5SiO<sub>2</sub>AE; (d) reduced Cu10SiO<sub>2</sub>AE.; Figure S2: XPS survey data of: (a) Cu10SiO<sub>2</sub>HP; (b) reduced Cu10SiO<sub>2</sub>HPR; (c) Cu10SiO<sub>2</sub>AE; (d) reduced Cu10SiO<sub>2</sub>AER. Table S1: EDAX analysis for samples with 10% content of Cu, Oxygen was calculated stoichiometrically.

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