

Research Article

Selective Electrocatalytic Hydrogenation of Linolenic Acid on Pd/Al₂O₃ and Pd-Co/Al₂O₃ Catalysts

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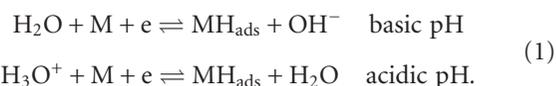
Electrochemical hydrogenation of linolenic acid as a model for polyunsaturated acids was studied on Pd and Pd/Al₂O₃ catalysts in acidic and alkaline media. The results are presented in terms of number of double bonds in the polyunsaturated fatty acid and interpreted in terms of the adsorption capacity of the catalysts in these media. The highest hydrogenation yield was obtained with Pd/Al₂O₃ at pH 13, in good correlation with the adsorption power of linolenic acid and its first hydrogenation product, linoleic acid, measured in this solution. A preliminary electrochemical hydrogenation study was conducted on Pd/Al₂O₃ catalyst containing Co, in the optimum electrolysis conditions, showing a cooperative effect of the noble metals regarding the *cis/trans* selectivity with preferential formation of *cis*-oriented monounsaturated compound. All the products were characterized by gas chromatography after derivatization of the samples; fifteen *cis-trans* isomers of monounsaturated fatty acid which could be identified are presented here.

1. Introduction

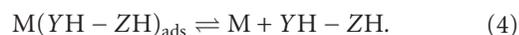
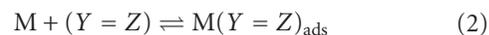
Catalytic hydrogenation (CH) of vegetable oil is one of the processes used since the beginning of the 20th century in order to transform oils in the food industry [1, 2]. This process converts some double bonds in the unsaturated fatty acids contained in oils into single bonds in the presence of a metal catalyst. The hydrogenation rate is one of the parameters determining the physical and chemical properties of the oil [3]. A few years ago, *trans* and saturated fats have been shown to be harmful for the organism [3–5] whereas monounsaturated fatty acids seem to be able to reduce the bad cholesterol in the blood [6]. Although CH shows many advantages for conversion of fatty acids, there is still unwanted formation of *trans* isomers during the process, mainly when nickel catalysts are used [3, 7] because of isomerization or migration of double bonds [8–16]. Recently, Pintauro and coworkers showed that electrocatalytic hydrogenation (ECH) carried out with noble metals leads to less *trans* fat production [7, 17] and to more monounsaturated compounds, a promising outcome for practical use although

the process is still not usable commercially. ECH studies have also been performed on supported metallic catalysts in order to increase the hydrogenation output, in particular by reducing the *cis* to *trans* isomerization rate [18]. The ECH process uses H atoms produced by the reduction of water on the working electrode and adsorbed on its surface (1)–(7). The hydrogenation of the double bond is then complete (3) and cannot lead to isomerization or migration reactions.

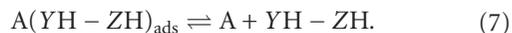
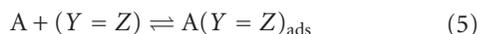
H atoms production on the metal M (Volmer reactions):



Reactions on the metal M (adsorption, hydrogenation, desorption) [19] where $Y = Z$ represents the unsaturated bond and $YH-ZH$ the saturated one

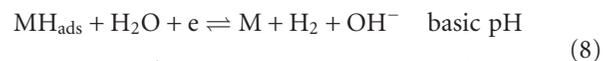


Reactions on the support A (adsorption, hydrogenation, and desorption) [20]:

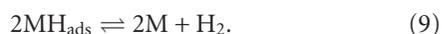


Competing H_2 production reactions:

Heyrovsky reactions



Tafel reactions



In this paper, we present studies of the ECH of linolenic acid, chosen as a model fatty acid. Catalysts made of nanoaggregates of Pd used either directly, or deposited on an Al_2O_3 support, were explored and the crucial role of the pH in the ECH mechanism involving adsorption phenomena was observed. The influence of a cooperative effect from a second metal on the support was also tested in an attempt to allow of the *cis/trans* selectivity and enhance the formation of monounsaturated oleic acid. Characterization of the multiple hydrogenation reaction products is very difficult and two approaches were considered here. First of all, the rate of conversion was determined as a function of the number of double bonds hydrogenated. Linolenic acid, having three double bonds, can be converted to double unsaturated, monounsaturated, or saturated fatty acids (Figure 1). Secondly, we tried to determine the position of the double bond(s) and their *cis* or *trans* orientation. In all the cases, gas chromatography (GC) techniques coupled to either mass spectrometry (MS) or to a flame ionization detector (FID) was used to characterize the products. The samples had to be derivatized in order to become more volatile or to allow an usable fragmentation in the MS detector (Figures 1(a) and 1(b)). Some isomers of the monounsaturated fatty acid could also be easily identified by comparison with the literature [21].

2. Experimental

Note 1. The polyunsaturated acids are denominated by the symbol Cx:y where x is the number of carbon atoms in the molecule and y the number of double bonds contained in the chain. The isomers of the fatty acids are denominated by the symbol $\mathbf{a}\Delta\mathbf{b}$, where \mathbf{a} is the orientation of the double bond (“*c*” for *cis* or “*t*” for *trans*) and \mathbf{b} its position. For example, linolenic acid, which contains three double bonds of *cis* configuration at the 6, 9, and 12 positions, would be referred to as $\text{C18:3 } c\Delta6, c\Delta9, c\Delta12$ (Figure 1).

2.1. Chemicals. Acid standards (linolenic acid ~70% + linoleic acid ~25% + oleic acid ~5%, linolenic 99%, linoleic 99%, oleic 99%, and stearic 99%) were purchased from Fluka

and used as received. Ethyl alcohol (anhydrous), high purity water (from a Milli-Q Unit), glacial acetic acid (Caledon, HPLC grade), NaOH solution (10 M), and NaCl (EMD) were used to prepare the electrolytes whereas the HPLC eluents were prepared with HPLC grade ethanol and water (Fisher Scientific). Reticulated vitreous carbon (RVC, 100 pores per inch) from Electrolytica Inc. was used as cathode; commercial 10% (w/w) Pd-alumina, powder, reduced (Aldrich) and finely divided Pd (1.1–2.0 μm APS, Alpha Aesar) were used as catalysts in the present study. Cobalt wire (diameter = 0.1 mm, 99.995% Alpha Aesar) was used to make the metallic deposition. For the analysis, palmitic acid (Aldrich) was used as internal standard. Extractions of the acids were performed using HCl (VWR), hexane and heptane (Fisher Scientific). Derivatizations were performed with trimethylsilyldiazomethane, dimethyl disulfide, iodine, sodium thiosulfate, 2-amino-2-methylpropanol, and diethylether/isohexane (Aldrich).

2.2. Pd/Al₂O₃ and Pd-Co/Al₂O₃ Catalysts. Pd/Al₂O₃ and Pd-Co/Al₂O₃ catalysts were prepared by physical evaporation according to reference [22]. The specific conditions were 150 mg of 0.25 mm diameter Pd wire (Aldrich 99.9%) and 20 mg of 0.1 mm diameter Co wire (Alfa Aesar, 99.995%) for 1 g of alumina (Alfa Aesar, aluminium oxide, activated, neutral, γ , 99.9%, metal basis, 40 μm APS powder, SA 200 $\text{m}^2 \cdot \text{g}^{-1}$). Catalysts characterization was done by atomic absorption on a Perkin Elmer Analyst 100 apparatus. Pd was analysed with a 244.8 nm Pd lamp, slit of 0.2 nm, (Perkin Elmer) at 30 mA and a $\text{C}_2\text{H}_2/\text{N}_2\text{O}$ flam. Co was analysed with a 240.7 nm Co lamp, slit of 0.2 nm, (Perkin Elmer) at 30 mA and a $\text{C}_2\text{H}_2/\text{air}$ flam

2.3. Electrolysis. All electrolyses were conducted at ambient pressure and temperature in a two-compartment circulating cell, detailed elsewhere [23]. The cell is equipped with a variable flow chemical pump (Fisher Scientific) connected to the cell by a PVC tube. The flow rate is maintained at 1072 mL/min, and the circulation of the solution is upward through the cathode. The cathode is a cylindrical piece of reticulated vitreous carbon (RVC) (100 ppi) purchased from Electrolytica Inc. with diameter = 23 mm, width = 13 mm and geometrical surface area = 1770 mm^2 . To maximize the forced electrolyte flow through the RVC/catalyst system, the electrochemical cell is used as a punch to cut an electrode disk in the RVC, forcing a close press-fit tolerance. A carbon rod inserted into the RVC provides the mechanical support and electrical contact for the cathode; this support was coated with a thermoretractable polymer to prevent electrolytic processes on this conductor. The platinum mesh counter electrode (i.e., the anode) is introduced into a glass tube with an external diameter of 15 mm that was inserted into the cell from above. A Nafion 117 membrane is fixed at the lower end of the tube with a stopper thread to ensure the separation of the anodic compartment from the rest of the cell. The cathodic compartment was filled with 39 mL of 0.05 M NaCl supporting electrolyte ($\text{CH}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$ 70/30 solution) containing 200 mg of the catalytic powder. The pH was previously adjusted to 5 with glacial acetic acid

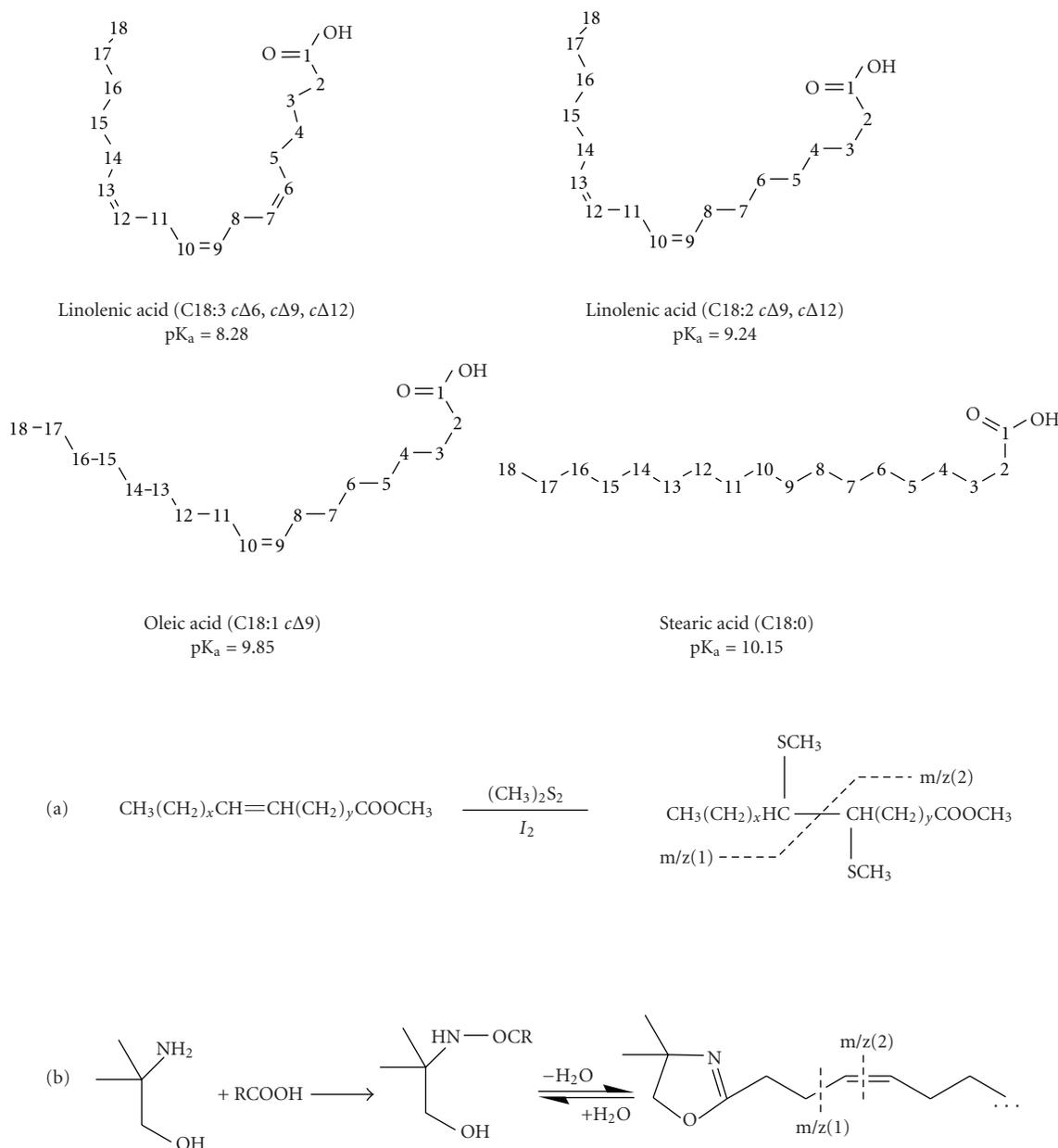


FIGURE 1: Linolenic acid and some of its hydrogenation products [10]. Derivatization mechanism of (a) methyl esters into DMDS and (b) fatty acids into DMOX, and MS fragmentation of the products. m/z(1) and (2) refer to the values given in Table 2.

or to 13 with 10 M NaOH. The catalyst (10% Pd-alumina, finely divided Pd or Pd-Co-alumina) was added to the cathodic compartment solution and dynamically circulated through the RVC cathode. The anodic compartment was filled with the same electrolyte. All electrolyses were carried out under galvanostatic conditions ($I = 20 \text{ mA}$) using an Agilent galvanostat/potentiostat (model 6634 B). The coulombic charge (Q) used for conditioning or for reaction can be converted into time (t) by the following equation:

$$t(s) = \frac{Q(C)}{I(A)}. \quad (10)$$

All the experiments presented in this paper have been stopped after 120 C, that is, after 100 minutes of reaction. The RVC cathode was polarized under constant current (20 mA), the corresponding total charge being equal to 50 C. The coulombmeter was reset after polarization; linolenic acid (70%) was added in the cathodic compartment (with final concentration of pure linoleic acid being $3.143 \times 10^{-3} \text{ M}$) and a 0.5 mL aliquot of this mixed solution was immediately removed as a reference sample (0 C). During the ECH reaction, aliquots of 0.5 mL were withdrawn from the catholyte after every 20 C up to 120 C and treated as described in the next section.

Note 2. As the starting material contains 70% of linolenic acid and 30% of linoleic and oleic acids, initial concentrations determined at 0 °C by GC take into account the presence of all the molecules.

2.4. Aliquots Treatment, Quantification, and Characterization. Fatty acids are usually analyzed by GC as methyl ester derivatives [21], but their mass spectra may not always contain ions indicative of structural features; the positions of double bonds in the aliphatic chain, for example, cannot be determined unequivocally. Two methods were then employed to quantify the ECH reaction products.

First, a fast derivatization method transforming the acids into esters enabled us to characterize the products depending on the number of double bonds they contained. These results allowed us to determine the percentage of C18:3, C18:2, C18:1, and C18:0 in solution.

The second method allowed us to analyze the C18:1 isomers in terms of the position of the double bond along the aliphatic chain. In one reaction, DMDS (dimethyl disulfide) derivatives were prepared from the last aliquot (120 °C) containing mainly C18:1 (Figure 1(a)). In the other, DMOX (4,4-dimethyloxazoline) derivatives were formed in order to better identify the various C18:1 isomers (Figure 1(b)).

2.4.1. Methyl Esters for Fast Analysis. An external standard (palmitic acid 0.1 mg/mL in ethanol/water 70/30) was added to the 0.5 mL aliquot and the solution was acidified with 1.0 N HCl. The products were then extracted with hexane, and the organic phase dried on anhydrous MgSO₄, before esterification with a small amount of trimethylsilyldiazomethane (2.0 M in ether).

The methyl esters were finally injected to a Hewlett Packard 5890 series II GC-MS equipped with a 5971A mass selective detector and an automatic injector. An Alltech capillary column At-Silar (30 m × 0.25 μm × 0.25 mm ID) was used. Method parameters were as following: 250 °C (injector temperature), 280 °C (detector temperature) and 180 °C (oven temperature) during 15 min, in SIM mode. Helium was used as carrier gas under a 0.9 mL/min flow rate and the split ratio was fixed to 50:1. A standard solution containing 20% of esters of linolenic, oleic, stearic, and palmitic acids (K108 FAME mix, Mandel) was injected to allow us to quantify the products concentrations.

2.4.2. DMDS Derivatives [24]. One milligram of the methyl esters produced for preliminary analysis were dissolved in 0.2 mL of dimethyl disulfide and 0.05 mL of iodine (60 mg/mL in ether) was added. The mixture was stirred during 24 hours and then, 5 mL of hexane added. Sodium thiosulfate (0.1 N) was used to wash the solution and the organic extract was then dried on anhydrous sodium sulfate and evaporated. The sample was diluted in hexane and 1 μL was injected in the column of a Fisons MSD800 GC-MS operated in electronic impact ionization mode. The column used was a CP-Sil 88 Chrompack (100 m × 0.20 μm × 0.25 mm ID). The GC conditions included helium as carrier gas at 1.0 mL min⁻¹ in constant flow mode, an initial temperature 100 °C for 1 min, 4 °C min⁻¹ gradient up to

230 °C, followed by an isothermal period of 60 min. The temperature of the injector was set at 250 °C. The MS operating conditions were the following: ion source and transfer line temperatures were 200 and 250 °C, respectively. The electron energy was 70 eV and the emission current was set to 250 μA.

2.4.3. DMOX Derivatives [25]. Two hundred fifty milligram of 2-amino-2-methylpropanol was added to 2 mg fatty acids samples. The flasks were placed under a nitrogen atmosphere and heated to 190 °C overnight. Then, the solutions were cooled and washed with water, 5 mL diethylether/isohexane (1:1) and finally once again with 5 mL of water. If necessary, KCl could be added to break the emulsion. The organic phases were transferred into separate flasks and the aqueous phases were extracted again with 2 mL of organic solvent. Three milliliter of distilled water were added to the total organic phases and after decantation; the organic phases were dried over anhydrous sodium sulfate by stirring during one hour. Then, the extracts were purified on a 3 cm sodium sulfate column and rinsed with 3 mL of isohexane. The extracts were washed with 2 mL of isohexane in the column and the final organic phases were evaporated under nitrogen.

The samples were diluted in isohexane and 1 μL aliquots were injected on the column of a Fisons MSD800 GC-MS equipped with DB-Wax column (100 m × 0.25 μm × 0.25 mm ID). Method parameters were as following: 170 °C during 10 min, then 1 °C/min until 200 °C, this temperature being maintained for 45 min.

2.5. Henry Law Constants (k_H). The chromatographic curves were recorded using an Agilent 1100 series HPLC equipped with a diode array detector (G1315B). The dead volume, τ₀, was determined by injecting 10 μL of deuterium oxide, D₂O. The mobile phases were ethanol/water 70/30 solutions with pH fixed to 5 or 13 with CH₃COOH or NaOH, respectively. The flow rate was 1.00 mL/min. The columns (15 cm) were filled with Pd/Al₂O₃ or finely divided Pd that were used as received and had an average particle size of 45 μm. The parameters used to determine the dynamic adsorption isotherms were collected from the HPLC elution chromatogram and the Henry constants were calculated from the well known isotherm:

$$Q_e = k_H \cdot C_e, \quad (11)$$

where Q_e is the quantity adsorbed onto the support, k_H is the Henry constant and C_e is the concentration of molecules in solution at equilibrium, following a previously reported methodology [26, 27].

3. Results and Discussion

All the samples were esterified in order to obtain compounds more volatile than the corresponding fatty acids. They were analyzed by GC, with a MS (for qualitative characterization) or a FID (for quantitative characterization) detector. Thus, for all the results reported here, the names of the acids or of their corresponding esters are used indifferently as they correspond to the same starting molecule.

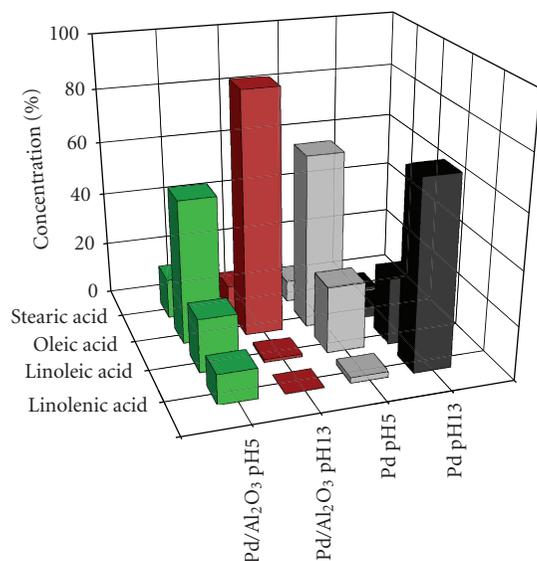


FIGURE 2: Distribution of products of the ECH of linolenic acid with different catalysts after passage of $38 \text{ C} \cdot \text{mmol}^{-1}$.

It is noteworthy that CH results obtained in the literature and ECH results presented herein can be compared in terms of reaction time as the polarization charge can be converted into time. In our experiments, reaction times typically used are around 100 minutes, which are usually shorter than for the CH reaction. As far as the reusability of the catalyst is concerned, the efficiency of the powder has been tested 6 times without any changes in the results. However, the turnover rate of our catalysts has not yet been measured.

The desired electrochemical hydrogenation product is the monounsaturated acid, that is, oleic acid, because it has been shown that it is the least harmful for the human organism [6]. Moreover, it has been demonstrated that the ultimate product of ECH, that is, the totally saturated stearic acid, is strongly detrimental for human beings [4, 28].

Our electrocatalytic hydrogenation experiments conducted in ethanol/water 70:30 media on different catalysts and at two different pHs showed interesting results.

As far as the formation rate of the final desired product (i.e., oleic acid) is concerned, Figure 2 shows that the best results were obtained with Pd/Al₂O₃ at pH 13. Indeed, for the same charge passed (120 C), these conditions provide the highest yield of oleic acid after quasicomplete conversion of linolenic acid. Besides, we notice that there is also a good yield of oleic acid with use of the Pd catalyst at pH 5 although there remain large quantities of linoleic acid. Pd/Al₂O₃ at pH 5 provides a good distribution of products whereas Pd at pH 13 is totally ineffective for linolenic acid conversion. As the ECH mechanism depends on the adsorption of the target molecule (2) and (5), the adsorption of the different fatty acids involved in this study on the several supports at pH 5 and 13 (Table 1) was investigated.

It is important to note that the molecules exist in solution as acids, or as their conjugated bases, depending on the pH. Figure 1 presents the pK_a of the starting acids in water; it

TABLE 1: Henry constants of linolenic, linoleic, oleic, and stearic acids in ethanol/water 70/30 at different pH (13 and 5) on different supports (Pd/Al₂O₃ and Pd) given in mL · m⁻² (± 0.0001).

Acid	Pd pH 13	Pd pH 5	Pd/Al ₂ O ₃ pH 13	Pd/Al ₂ O ₃ pH 5
Linolenic	0.0004	0.0012	0.0074	0.0591
Linoleic	0.0004	0.0013	0.0076	0.0311
Oleic	0.0002	0.0013	0.0371	0.0176
Stearic	0.0002	0.0008	0.0338	0.0157

TABLE 2: Identification of the different C18:1 isomers by GC-MS. Cis and trans orientations were determined by comparison with commercial standards.

Peak number	m/z (1)	m/z (2)	Attribution
DMDS			
1	189	201	<i>t</i> Δ7
2	173	217	<i>t</i> Δ9
3	159	231	<i>t</i> Δ10
4	145	245	<i>t</i> Δ11
5	189	201	<i>c</i> Δ7
6	131	259	<i>t</i> Δ12
7	173	217	<i>c</i> Δ9
8	159	231	<i>c</i> Δ10
9	145; 117	245; 273	<i>c</i> Δ11 and <i>t</i> Δ13
10	131	259	<i>c</i> Δ12
11	117	273	<i>c</i> Δ13
12	103	287	<i>c</i> Δ14
13	—	—	Unknown*
14	—	—	Unknown*
DMOX			
1	—	—	Unknown*
2	—	—	Unknown*
3	182	194	<i>t</i> Δ8
4	196; 210; 224	208; 222; 236	<i>t</i> Δ9, <i>t</i> Δ10, <i>t</i> Δ11, and <i>c</i> Δ10
5	196	208	<i>c</i> Δ9
6	224	236	<i>c</i> Δ11
7	238	250	<i>t</i> Δ12
8	238	250	<i>c</i> Δ12
9	252	264	<i>t</i> Δ13
10	280	292	<i>t</i> Δ15
11	—	—	Unknown*
12	—	—	Unknown*
13	—	—	Unknown*
14	—	—	Unknown*
15	—	—	Unknown*

* Unknown products are not fatty acids.

must be taken into account that the pK_a values in ethanol would be slightly higher. It is concluded that all of the molecules are present as acids at pH 5 and as conjugated bases (i.e., in a dissociated form) at pH 13. It must then be taken into account that the acid or its conjugated base may

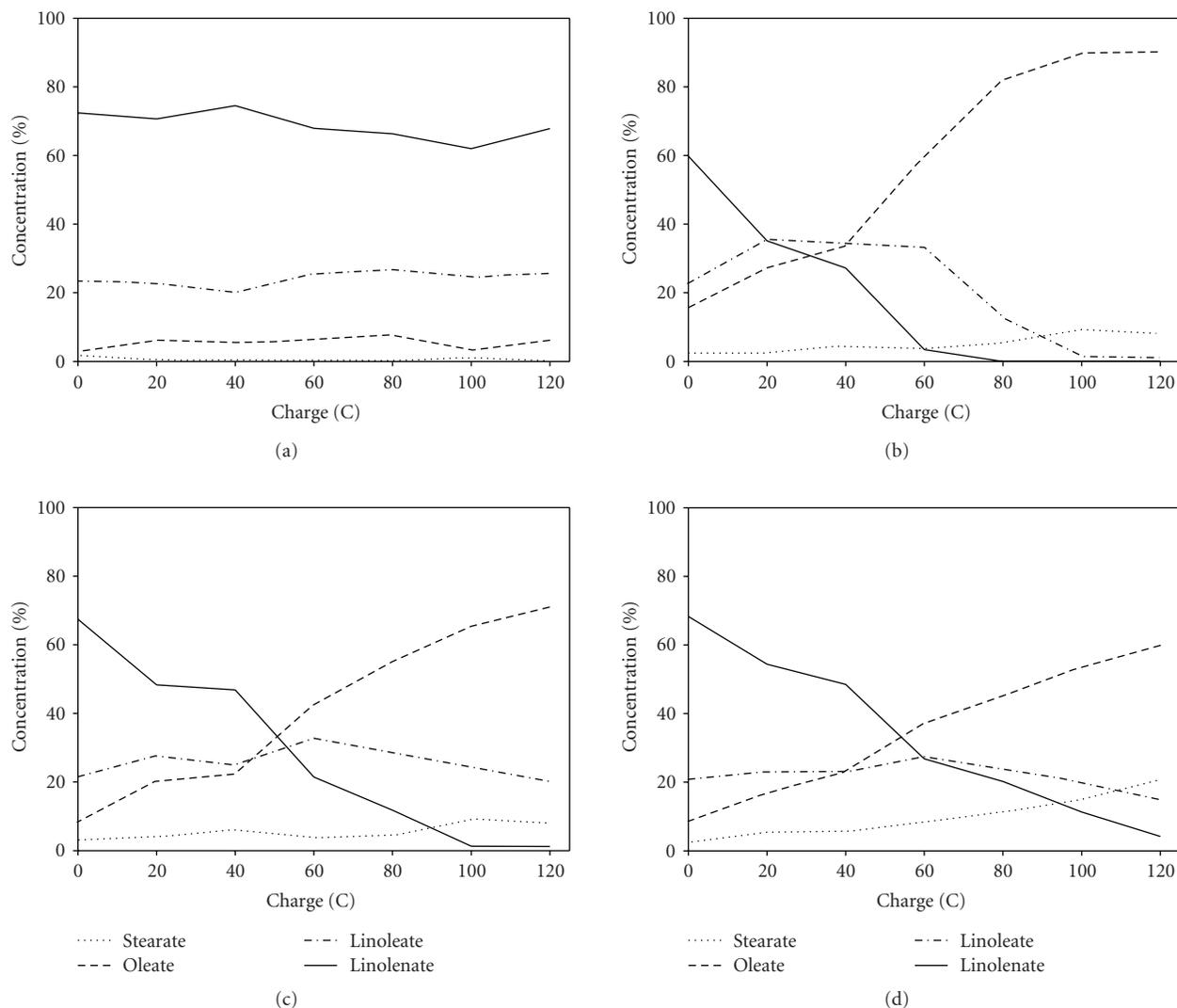


FIGURE 3: Distribution of products of the ECH of linolenic acid as a function of charge consumed on (a) Pd in ethanol/water 70 : 30, pH 13 (b) Pd/Al₂O₃ in ethanol/water 70 : 30, pH 13 (c) Pd in ethanol/water 70 : 30, pH 5 (d) Pd/Al₂O₃ in ethanol/water 70 : 30, pH 5.

follow different adsorption mechanisms. In particular it is known that some molecules can be weakly adsorbed on metal catalysts [23]. In any case, the adsorption measurements were carried out in the same conditions as the ECH experiments, so Henry's constants (Table 1) were used to interpret ECH results.

First, it can be noticed that the least active medium, that is, Pd at pH 13, shows the smallest Henry's constant for the initial product indicating that linolenic acid is not adsorbed strongly enough to be transformed totally into linoleic acid. For this intermediate product, the Henry's constant is the same ($0.0004 \text{ mL} \cdot \text{m}^{-2}$) as for linolenic acid suggesting the subsequent hydrogenation reactions may be unrealizable. Secondly, for Pd/Al₂O₃ at pH 5, we can see that the Henry's constant of linolenic acid ($0.0591 \text{ mL} \cdot \text{m}^{-2}$) is very high compared to the values for the other conditions. This result indicates that linolenic acid is adsorbed strongly on the support and deactivates the catalyst by covering it

with the starting molecules. Thus, the conversion of linolenic acid cannot be completed. Third, we can notice that in the case of Pd at pH 5, the conversion of linolenic acid is not as good as for Pd/Al₂O₃ at pH 13, probably because the Henry's constant of the starting molecule ($0.0012 \text{ mL} \cdot \text{m}^{-2}$) is not high enough. Finally, the best medium, that is, Pd/Al₂O₃ at pH 13, shows an intermediate Henry's constant for linolenic ($0.0074 \text{ mL} \cdot \text{m}^{-2}$) and linoleic ($0.0076 \text{ mL} \cdot \text{m}^{-2}$) acids.

As these results have been taken after 120 C, it is interesting to examine the kinetics of the ECH process. Unsurprisingly, ECH on Pd at pH 13 (Figure 3(a)) presents almost no formation of any reaction product. For ECH on Pd/Al₂O₃ at pH 13 (Figure 3(b)) and on Pd at pH 5 (Figure 3(c)), differences in the kinetics of the reaction can be noticed. Although the quantity of stearic acid remains constant, the conversion of linolenic acid is faster on Pd/Al₂O₃ at pH 13 than on Pd at pH 5. The total conversion occurs at 80 C in the first case whereas in the second, it takes

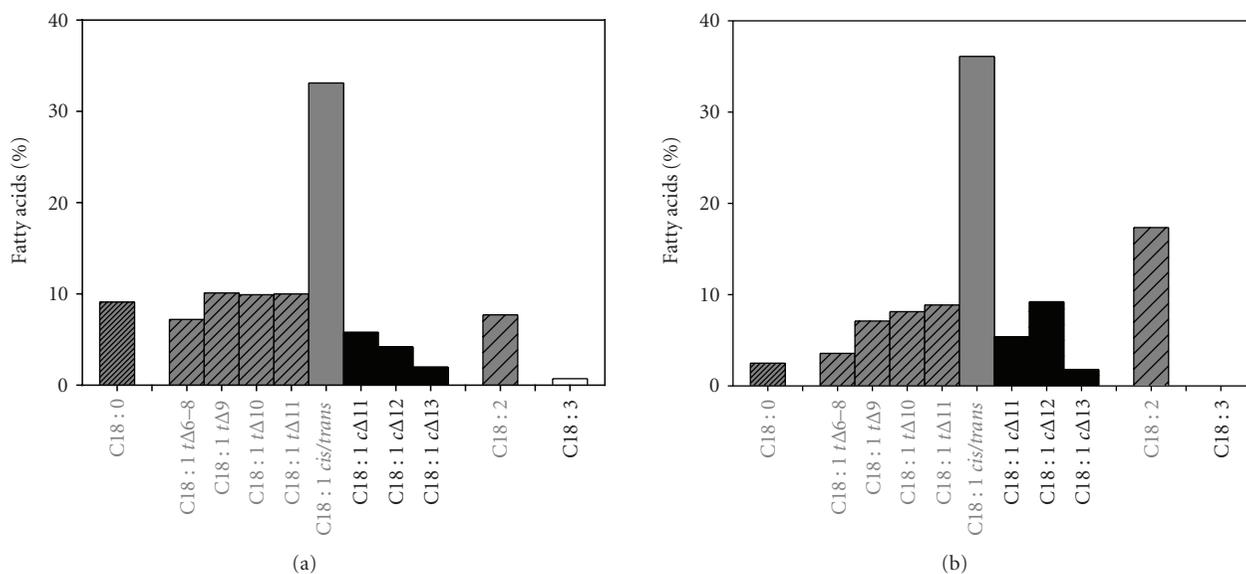


FIGURE 4: Distribution of the products of ECH of linolenic acid after passage of 120 C on (a) Pd/Al₂O₃ 5% (b) Pd-Co/Al₂O₃ 5%.

100 C to hydrogenate all the linolenic acid. We can even see that at 80 C, the yield of oleic acid is much higher and that of linoleic acid less important with Pd/Al₂O₃ at pH 13, than with Pd at pH 5 whereas the yield of stearic acid remains constant. Obviously, ECH of linolenic acid on Pd/Al₂O₃ at pH 13 is more effective than that on Pd at pH 5. Finally, the electrocatalytic process performed on Pd/Al₂O₃ at pH 5 (Figure 3(d)) appears less interesting as the conversion of linolenic acid is slower than on Pd/Al₂O₃ at pH 13 and than on Pd at pH 5 and because there is formation of higher quantities of unwanted stearic acid.

As expected, the adsorption of any of the fatty acids is favored on the supported catalyst independently of the pH value (Table 1). Indeed, it has been demonstrated elsewhere [23, 27] that alumina supports increase the adsorption of organic molecules. In fact, in the case of acidic pH, there is presence of acetic acid that has been shown to be chemically bonded to Al₂O₃ [23] which can favor the fatty acids adsorption. Moreover, Table 1 shows that the highest adsorption for all the molecules occurs in this medium. In the case of alkaline pH, CH₃COOH has been added to the medium in order to verify its effect on ECH efficiency and no effect on hydrogenation rates has been detected. Beside that, the ECH media contains 70% ethanol which has pK_a of 15.9 and which may be adsorbed on the Al₂O₃ surface in the same way independently of the pH value. This can then promote adsorption of the fatty acids.

If we now consider only the influence of pH for each of the catalysts, we can notice that the acid forms of the molecules are more strongly adsorbed than their conjugated bases. This may be due to a better solubility of the acid form in the medium (ethanol/water 70:30) as compared with the ionic conjugated base form. Nevertheless, in the case of Pd/Al₂O₃ at pH 5, this adsorption becomes too strong to allow a necessary desorption of the hydrogenated molecule (7).

Beside the number of unsaturated bonds contained in the fatty acids, it is very important to know and to control the position and the *cis/trans* orientation of the double bond in oleic acid. To realize this type of characterization, it is necessary to derivatize the fatty acids into DMDS (dimethyl disulfide) or DMOX (4,4-dimethyloxazoline) derivatives (Figures 1(a) and 1(b)). The typical fragmentation masses of these derivatives observed by MS allow determining precisely the position of the double bond [21]. Indeed, cleavage occurs between the carbon atoms that originally constituted the double bond to yield two characteristic ionic fragments, that is, which contain the terminal methyl part of the molecule in the case of DMDS and the oxazoline part for DMOX. Then, by comparison with the commercial standards, it was possible to determine their *cis* or *trans* orientation. Using the MS spectra corresponding to each peak, the position of the double bond has been attributed for each of them (Table 2). This experiment allowed us to ascribe eight *trans* isomers and seven *cis* isomers. It is remarkable that the two types of analyses allowed us to identify different isomers. Indeed, only DMDS analysis showed *t* $\Delta 7$, *c* $\Delta 7$, *c* $\Delta 13$, and *c* $\Delta 14$ isomers whereas *t* $\Delta 8$ and *t* $\Delta 15$ isomers were only observed with DMOX analysis. All the other isomers were detected in both analyses. For measurements of concentration of the *cis/trans* isomers of fatty acids, we used GC-FID which is a better method for quantitative determination. It has been shown that hydrogenation of fatty acids on precious metal catalysts produces oils containing less than 8% *trans* fatty acids [2], including C18:2 and C18:1 compounds. For CH of linoleic acid on Pd/Al₂O₃, a *cis/trans* distribution near to 1:1 has been reported for C18:1 compounds [29]. Although the reaction conditions of ECH are different than for CH (in situ generation of H₂, room temperature and pressure, solvent), better results were obtained in our conditions than reported by Kitayama et al. [29] as far as the yields of *cis*-C18:1 $\Delta 11$, 12, and 13 are concerned. Indeed, the distribution of C18:1

isomers formed by ECH of linolenic acid on Pd/Al₂O₃ at pH 13 shown in Figure 4(a) is 5.9% of C18:1 *c*Δ11, 4.2% of C18:1 *c*Δ12, and 2% of C18:1 *c*Δ13 versus 1.1%, 3.6%, and 0.4%, respectively, in this paper. However, distribution of *trans*-C18:1 Δ9, 10, and 11 reveals worse results for ECH than for CH. Although four *trans* isomers and three *cis* isomers have been identified in our work, one can notice that there is still about 33.1% of the C18:1 isomers that were not clearly attributed to *cis* or *trans* orientation. However, the enhancement of the selectivity of the ECH reaction for *cis* bonds formation was studied by experiments with a new home-made catalyst, Pd-Co/Al₂O₃ in the best conditions determined, that is, pH 13. It has been shown previously that the Co-promoted Pd catalyst increases the reaction efficiency [30, 31]. This catalyst was made by evaporation of cobalt on Pd/Al₂O₃ powders. Figure 4(b) shows that C18:1 *cis* compounds are favored versus the *trans* ones. Although the C18:2 and C18:1 yields are higher using the Co-doped catalyst, it is remarkable that the yield of unwanted C18:0 is highly diminished and that all the initial linolenic acid is consumed. On one hand, it may be interesting to find out a method to identify all the *cis* compounds in order to know their exact yield at a chosen charge. However, at the moment, all the isomers standards are not commercially available. On the other hand, we could use a total *trans* determination method (using infra-red method for example [32–35] in order to be able to determine the total *cis* content. Nevertheless, the preliminary experiments carried out with Pd-Co/Al₂O₃ electrodes demonstrated the cooperative effect of the two metals in the catalytic activity for selective ECH of linolenic acid into *cis*-oleic acid.

4. Conclusion

In conclusion, it has been established that the best ECH conditions to obtain monounsaturated fatty acids from linolenic acid is Pd/Al₂O₃ at pH 13. The results are correlated to the adsorption isotherms measurements. In order to enhance the formation of *cis*-oriented double bond for oleic acid, we demonstrated the effectiveness of the cooperative effect induced by the presence of cobalt using a new home-made catalyst, Pd-Co/Al₂O₃. Fifteen *cis-trans* isomers of the monounsaturated C18:1 fatty acid could be identified by GC-MS.

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