Partial hydrogenation of sunflower oil: Use of edible modifiers of the *cis/trans*-selectivity

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ABSTRACT

The partial hydrogenation of sunflower oil with minimum *trans*-isomer formation is studied, using a Pd/γ-alumina catalyst modified with promoters apt for human consumption: ethyl benzoate and magnesium glycinate. It was found that the hydrogenation rate diminishes with the additions of the modifiers.

Regarding the *cis/trans*-selectivity, significant differences were found: ethyl benzoate promoted the formation of *trans*-isomers, whereas magnesium glycinate diminished it. The results can be interpreted in terms of different effects: change in the electron density of palladium, which affects the relative adsorption strength of the reactant, intermediates and hydrogen, and a block of part of the surface by the modifiers. Theoretical calculations were performed to support this hypothesis.

1. Introduction

The hydrogenation of vegetable oils is an industrial process that allows turning vegetable oil into a solid and more stable substance. Concurrently with the hydrogenation of double bonds, geometrical and positional isomerizations take place. The *trans*-isomer formation was seen under a positive light for a long time, due to its higher fusion point relative to the *cis*-isomers naturally present in vegetable oils.

In recent years, however, it has been published that the intake of *trans*-fatty acids adversely affects blood lipid levels. Metabolic and epidemiologic studies confirm the potential role of *trans*-fatty acids in increasing the risk of coronary heart disease. Furthermore, on a per-gram basis, the negative health impact of *trans*-fatty acids appears to be stronger than that of saturated fatty acids [1–3].

Willett and co-workers [4] studied 80,082 women for 14 years. Their collected data provide strong evidence in support of the hypothesis that a higher dietary intake of saturated fat and *trans*-unsaturated fat is associated with an increased risk of coronary disease.

Recently, a significant and negative relationship was observed between birth length, weight and head circumference and the C18:1 (vide infra) *trans*-concentration in maternal plasma phospholipids in early pregnancy [5]. These results indicate that *trans*-fatty acids may compromise fetal development.

The Food and Drug Administration (FDA) ruled that, as from January 1, 2006, the nutrition labels for all conventional foods and supplements must indicate the content of *trans*-fatty acids [6].

Industrially, the process is carried out in semibatch reactors using nickel catalysts deposited on a silicate support. These catalysts require temperatures around 180 °C and pressures between 0.1 and 0.6 MPa. On the other hand, there are reports of this reaction studied on catalysts of palladium [7,8]. In these cases, smoother operation conditions are needed, because Pd is more active.

Previous experiments on the hydrogenation of vegetable oils carried out in our laboratory, include the study of palladium catalysts and their modification using Mo [9], V, Pb and K [10] with the purpose of promoting the *cis*-isomer selectivity.

Nevertheless, improvements are still needed in order to satisfy the new specifications of a lower *trans*-isomer concentration. This work presents the use of two edible compounds as modifiers of the *cis/trans*-selectivity. They were chosen for their electronic properties [11]: ethyl benzoate (as Lewis base) and magnesium glycinate (salt of an electropositive metal).

Ethyl benzoate (EtB, $C_9H_{10}O_2$, Fig. 1A) is an electron donor. It is a colorless liquid that is almost insoluble in water, but miscible with most organic solvents. Like many volatile esters, ethyl benzoate has a pleasant odor, being used as a component of some artificial fruit flavors.

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Nomenclature

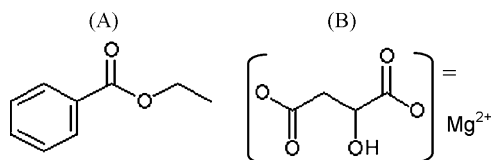|	
C16.0	palmitic acid
C18.1	*cis*-oleic acid
C18.1	*trans*-elaidic acid
C18:0	stearic acid
C18:1	oleic acid
C18:2	linoleic acid
C18:3	linolenic acid
C20.0	arachidic acid
C22.0	behenic acid

Fig. 1. (A) Ethyl benzoate and (B) magnesium glycinate.

Magnesium glycinate (GlyMg and $MgC_4H_4O_5$, Fig. 1B) is the salt of the ionized form of malic acid. Malic acid (hydroxybutanedioic acid) is a tart-tasting organic dicarboxylic acid present in many sour or tart foods. Apples contain malic acid, which contributes to the sourness of a green apple. Malic acid can make a wine taste tart, although the amount decreases with increasing fruit ripeness. As a food additive it is denoted by E296, and it is the source of extreme tartness in candies and potato chips.

There are previous works in the literature on the use of alkali metals as promoters of alumina and silica-supported palladium catalyst [12,13]. Prins and co-workers [12] explained the promoting effect on the silica-supported catalyst and the absence of a promoting effect on an alumina-supported Pd catalyst by proposing that the basic oxide additive must be close to or in contact with the Pd particles in order to be effective in the methanol synthesis. The rate enhancements for methanol formation of the metal oxides followed a volcano curve when plotted as a function of the metal ion electronegativity. Ca interacts strongly with the acidic sites of the alumina support. They proposed a selective location of the alkali oxide on kinks and corners of the Pd particle.

This work proposes the use of two edible modifiers of the selectivity, magnesium glycinate and ethyl benzoate, looking for a decrease in the *trans*-isomer formation during the partial hydrogenation of sunflower oil on a supported-Pd catalyst. Theoretical calculations are used in order to explain the experimental results.

2. Experimental

2.1. Catalyst preparation

The supported-Pd catalyst was prepared by wet impregnation. The support material was γ-Al_2O_3 (Condea, Puralox, 148 m²/g, average particle size: 211 μm). Prior to impregnation, the support was dried under a N_2 flow at 423 K for 2 h. The γ-Al_2O_3 support was impregnated with a solution of $Pd(Acac)_2$ (Acac = $C_5H_7O_2$) in toluene, at 298 K for 24 h. The concentration of the solution was adjusted to obtain a metal content of 1 wt%. After impregnation, the catalyst was dried in Ar at 423 K for 2 h, and then heated in chromatographic air at 773 K for 2 h.

The Pd–GlyMg/Al_2O_3 catalyst was prepared by impregnation. The Pd/Al_2O_3 sample was mixed with 8 ml of aqueous solution of magnesium glycinate (145 mg), at room temperature for 5 h under vigorous agitation. The resulting suspension was dried at 353 K in a vacuum oven in order to remove the water. The Pd–Mg/Al_2O_3 sample was obtained by calcination of Pd–GlyMg/Al_2O_3 catalyst in chromatographic air at 773 K for 4 h.

2.2. Catalysts characterization

The metal content was determined by atomic absorption spectroscopy (AAS).

Hydrogen chemisorption runs were carried out in a conventional pulse apparatus [14] at atmospheric pressure and 373 K. Prior to chemisorption, the catalysts were reduced "in situ" at 373 K in a H_2 flow. The fraction of exposed Pd was calculated assuming that one hydrogen atom is adsorbed per surface Pd metal atom.

2.3. Catalytic activity measurements

The hydrogenation tests were carried out in a semibatch microreactor of 9 ml. The oil used in the catalytic activity measurements was a refined, bleached, and deodorized commercial sunflower oil, which consists of a mixture of 5.7% C16:0; 3.9% C18:0; 1.5% C18:1*trans*; 38.8% C18:1*cis*; 46.5% C18:2*cis,cis*; 2.3% C18.2*cis,trans* and C18.2*trans,cis*; 0.3% C20:0; 0.7% C22:0; 0.3% C24:0 (where the first number represents the total carbon number of the acyl groups, and the second number represents the total number of double bonds).

The reactor was connected to a hydrogen (AGA grade chromatographic) source maintained at constant pressure. The catalytic tests were performed at 373 K and 413.5 kPa for 1 h, using 8 ml of refined sunflower oil. The catalyst weight was adjusted in order to maintain a 0.1-mg Pd/cm³ oil ratio for the various experiments. The stirring rate was 1400 rpm.

The catalyst was reduced at 373 K for 30 min, and dispersed in tristearin (glyceryl tristearate), forming a small pellet (150 mg) in order to preserve the reduced metal. The catalyst was then added to the reactor containing the sunflower oil, and the system purged to eliminate oxygen. Then the temperature was increased to 373 K. Finally, the pressure was increased in order to start the reaction.

In the tests using ethyl benzoate, the compound was added into the oil in a EtB:Pd_{total} molar ratio of 100 and 200. The operation procedure was above described and the catalyst used was Pd/Al_2O_3.

An Agilent 4890D gas chromatograph (GC) equipped with a flame ionization detector (FID) was used to identify the reaction products, following the procedures established by the AOCS Ce 1c-89 norm. A 60-m long SUPELCO 2380 capillary column, with a nominal diameter of 0.25 mm and a nominal film thickness of 0.20 μm was used for the separation of the different compounds present in the samples. The iodine number (IV) was calculated from the fatty acid composition following the AOCS Cd 1c-85 norm.

The IV measures the unsaturation of oils and fatty acids expressed in terms of the number of grams of iodine per 100 g of sample. Consequently, the calculation of the C=C conversion was performed as follows:

$$C{=}C \, conversion \, (\%) = \frac{(IV_0 - IV_f) \, 100}{IV_0}$$

where IV_0 is the iodine value of the original sunflower oil, and IV_f the corresponding value of the partially hydrogenated oil.

3. Theoretical methods

An ab initio calculation performed with Gaussian 98 software, B3LYP and G-321G as basis set was used to determine the charges on two different models: $Pd_2O_2H_4$ and $PdMgO_2H_4$ (Figs. 3 and 4). The Mulliken calculation method was used [15].

After this, the study of H_2 and reaction intermediate adsorption on both models was performed In this case, the MM2 software was used in the Chem3D 5.0 Ultra Package (Cambridge Soft) [15], with a Pd-atom set as square plane, and Mg modeled as a 2+ cation.

4. Results and discussion

4.1. Experimental results

Table 1 lists the catalysts and their metal content, and Pd dispersion.

Fig. 2 shows the C=C conversion, and the saturated compound (C18:0) and *trans*-fatty acid formation for a 1-h reaction. The *trans*-fatty acids include monounsaturated (C18.1*trans*) and polyunsaturated *trans*-fatty acids (C18.2*cis*,*trans*, C18.2*trans*,*cis* and C18.2*trans*,*trans*).

EtB is soluble in oil. It was added to the sunflower oil together with the Pd/Al$_2$O$_3$ catalyst. Fig. 2 shows a significant decrease in the hydrogenation activity when EtB was added (EtB-100 and EtB-200), compared to the reaction carried out without it: 11.9% and 8.7% versus 17.4% respectively.

This reduction was more significant at higher EtB concentrations. With regard to the selectivity, the addition of the modifier increased the *trans*-isomer formation. Surprisingly, the higher EtB concentration generated the same amount of *trans*-fatty acids, increasing the C18:0 production.

Magnesium glycinate is not soluble in organic solvents. Therefore it was loaded over the Pd/γ-Al$_2$O$_3$ catalyst to give the sample Pd–GlyMg/Al$_2$O$_3$. This sample was prepared in such a way as to reach a GlyMg:Pd$_{total}$ molar ratio of 200.

Part of the sample was calcinated in order to eliminate the organic component and leave only the Mg modifying the Pd. It was found that both Pd–Mg/Al$_2$O$_3$ and Pd–GlyMg/Al$_2$O$_3$ exhibited a low activity compared to the Pd/γ-Al$_2$O$_3$ catalyst (8.8% and 9.1% versus 17.4% respectively).

Table 2 shows the reaction time necessary for reaching a 10% C=C conversion and the corresponding *trans*-isomer and C18:0 formation. A lower *trans*-isomer production by the Pd–GlyMg/Al$_2$O$_3$

Table 1
Metallic contents of the catalysts.

Catalyst	Pd (wt%)	Mg (wt%)	Pd$_S$/Pd$_T$ (%)[a]
Pd/γ-Al$_2$O$_3$	0.78	0	62
Pd–GlyMg/γ-Al$_2$O$_3$	0.78	36	–
Pd–Mg/γ-Al$_2$O$_3$	0.78	36	17

[a] Pd dispersion, determined from H_2 chemisorption at 100 °C.
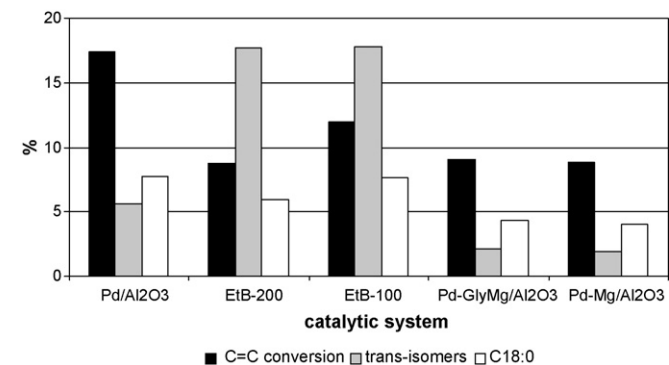
Fig. 2. Hydrogenation of sunflower oil: C=C conversion (%), *trans*-isomer and C18:0 formation (wt%). Operation conditions: $T = 373$ K, $P = 413.5$ kPa and reaction time = 1 h.

Table 2
Hydrogenation of sunflower oil: *trans*-isomers and C18:0 formation at 10% C=C conversion.

Catalytic system	Reaction time (min)	*trans*-Isomers (wt%)	C18:0 (wt%)
Pd/Al$_2$O$_3$	35.0	3.5	6
EtB-200[a]	69.0	20.3	6.2
EtB-100[b]	51.0	15.1	7.2
Pd–GlyMg/Al$_2$O$_3$	66.0	2.3	4.4
Pd–Mg/Al$_2$O$_3$	68.0	2.1	4.1

[a] Molar ratio EtB:Pd$_{total}$ = 200.
[b] Molar ratio EtB:Pd$_{total}$ = 100.

and Pd–Mg/Al$_2$O$_3$ samples (2.3% and 2.1%) was observed when compared to that of Pd/Al$_2$O$_3$ (3.5%). In contrast, the use of EtB increased the formation of *trans*-fatty acids (15.1% and 20.3% for the EtB:Pd$_{total}$ molar ratio of 100 and 200 respectively). It is interesting to note that EtB-200, Pd–GlyMg/Al$_2$O$_3$ and Pd–Mg/Al$_2$O$_3$ presented similar activities at a 1-h reaction time. These samples have an equal molar ratio of EtB:Pd$_{total}$, GlyMg:Pd$_{total}$ and MgO:Pd$_{total}$. The activity increased when the EtB concentration diminished.

It is possible that the deactivation is a consequence of the geometric effect of the modifier on the palladium. The Pd dispersion in the monometallic sample was 62%, whereas for the Pd–Mg/Al$_2$O$_3$ sample it was 17%. Therefore, the active sites that are accessible to the reactant diminish in the presence of the modifier.

In the case of the samples with Mg, it would be possible to postulate, based on numerous reports [16–20], that the exposed metallic surface is modified altering the adsorption strength of reactants and/or products.

Keane and co-workers [17] observed a reduction in the Pd 3d$_{5/2}$ binding energies compared with that of palladium bulk metal (334.4 eV versus 335.1 eV) in the reduced Pd/MgO catalyst. They indicated that the magnesia-supported palladium particles appear to be electron-rich as a result of a metal–support interaction where an electronic ligand effect is induced by the support. Indeed, Mojet et al. [18] and Kappers et al. [19] have reported that the use of magnesia as a support leads to the formation of small electron-rich supported-Pd and Pt particles.

Our group has accomplished a mechanistic study of *cis*/*trans*-isomerization and full hydrogenation of oleic acid over three Pd planes [22]. In addition to the well-known Horiuti–Polanyi mechanism, an adsorbed monoyne-mediated mechanism was considered. We will analyze the present results considering the effect of the modifiers in the both reaction intermediates, using theoretical calculation.

4.2. Theoretical results

Taking into account the best catalytic results of the Pd–GlyMg/γ-Al$_2$O$_3$ and Pd–Mg/γ-Al$_2$O$_3$ samples, two very simple theoretical models for the catalytic systems, Pd$_2$O$_2$H$_4$ and PdMgO$_2$H$_4$ respectively, were selected in order to simulate the effect of Mg on the adsorption of the reactants.

The hydrogenation of monoenes involves the production of saturated compounds and *cis*-*trans*-isomerization products, among other reactions. This was explained by the Horiuti–Polanyi mechanism, which considers the formation of a half-hydrogenated surface intermediate and its easy rotation [21,23]. If the hydrogen atom added to the adsorbed monoene to form the half-hydrogenated intermediate returns to the catalyst surface, the original *cis*-molecule is desorbed. On the other hand, if this H atom remains in the molecule and the original H is abstracted, a *cis*/*trans*-isomerization is observed and the *trans*-isomer is generated. If the half-hydrogenated intermediate takes a second hydrogen from
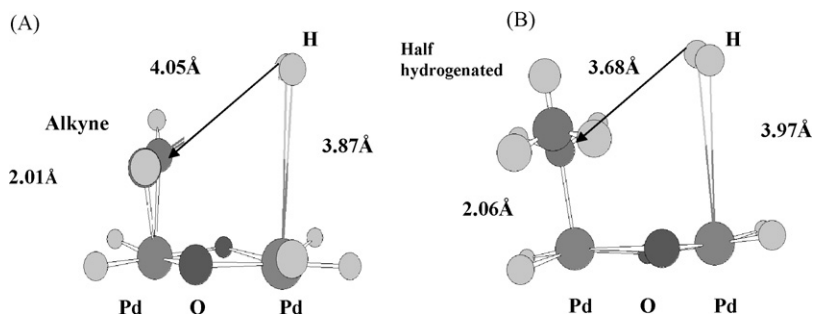
Fig. 3. Structural findings of alkyne (A) and half hydrogenated (B) models adsorbed on $Pd_2O_2H_4$.
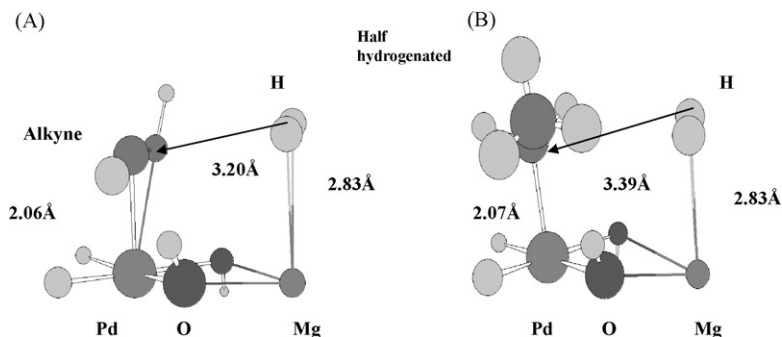

Fig. 4. Structural findings of alkyne (A) and half hydrogenated (B) models adsorbed on $PdMgO_2H_4$.

the surface, the desorption results in a completely hydrogenated molecule.

The *cis/trans*-isomerization of monoenes was also explained in terms of an abstraction-addition mechanism with a π-complex as intermediate [21,24]. This reaction mechanism involves the dehydrogenation of the precursor monoene molecule on the catalyst surface, forming an adsorbed monoyne intermediate. Then it is followed by a hydrogen addition. In this case, in order to produce the *trans*-species, the hydrogen must come from different sides of the adsorbed monoyne.

It is extremely important to point out that no alkynes are detected in the triglyceride hydrogenation. This species is proposed to remain on the surface, strongly adsorbed if hydrogen is absent, or reacted to monoene (*cis* or *trans*) when hydrogen is present.

Figs. 3 and 4 show the $Pd_2O_2H_4$ and $PdMgO_2H_4$ models, respectively. The structural findings are represented in the schemes. Figs. 3 and 4A represent the adsorbed monoyne structure (as HCCH) on Pd, whereas Figs. 3 and 4B correspond to the half hydrogenated species (as CH_3CH_2) on the Horiuti–Polanyi mechanism.

From the Gaussian 98 results, palladium changed the charge from +0.258 to +0.658 with a Mg^{2+} bond through an O bridge ($Pd_2O_2H_4$ and $PdMgO_2H_4$ are compared). This result is consistent with those reported by Mojet et al. [18] and Kappers et al. [19].

The H_2–Mg bond length was approximately 1 Å shorter than the H_2–Pd bond length (2.83 Å versus ~3.9 Å respectively). What is more, the distance between H_2 and the half hydrogenated/monoyne species adsorbed on Pd was also shorter when Mg is present (3.68–4.05 Å up to 3.39–3.20 Å), as shown in Figs. 3 and 4.

For the $Pd_2O_2H_4$ model, the C–Pd distance in the half hydrogenated species was 2.06 Å, whereas the distance of Pd to the centroid of the C–C bond in the alkyne species was 2.01 Å. When Mg^{2+} was present, the distances were 2.074 and 2.06 Å, respectively.

This theoretical result is parallel to the experimental observation made by Price and co-worker [20]. These authors investigated the behavior of K-doped Pd/Al_2O_3 catalysts for selective acetylene hydrogenation. They found a reduction in the strength of the adsorption of hydrocarbons, which may be caused by an increased

electron density on Pd particles. Pd would then have a low propensity to share electrons with adsorbed hydrocarbons.

These preliminary results support the idea of a hydrogenation of an adsorbed monoyne-intermediate with "on the same side" hydrogen (not dissociated molecular hydrogen), promoted by the presence of MgO close to Pd, as an explanation of the decrease in the *trans*-isomers selectivity in the case of $Pd–GlyMg/Al_2O_3$ and $Pd–Mg/Al_2O_3$ catalysts.

Nevertheless, in the case of ethyl benzoate as modifier, the effect was opposite to that desired. This can be due to (a) the destabilization of the monoyne intermediate due to the presence of ethyl benzoate, (b) the repulsive interaction of the monoyne intermediate with the electron-rich Pd particles and (c) the electron transfer to Pd (by ethyl benzoate) that polarizes even more the Pd–H bond, facilitating the surface hydrogen dissociation and resulting in a higher formation of C18:0.

5. Conclusions

The effect of the addition of edible modifiers (EtB and GlyMg) to Pd/Al_2O_3 catalysts for the hydrogenation of sunflower oil was studied. It was found a decrease in the hydrogenation activity when either modifier was added. Regarding the *cis/trans*-selectivity, significant differences were found: ethyl benzoate promoted the formation of *trans*-isomers, whereas the magnesium glycinate diminished it. The results can be interpreted in terms of different effects: change in the electron density of palladium, which affects the relative adsorption strength (of the reactant, intermediates and hydrogen), and a block of part of the surface by the modifiers. Theoretical calculations were performed, which support this hypothesis.

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