

Palladium supported catalysts for the selective hydrogenation of sunflower oil

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Abstract

Selective hydrogenation of ethyl esters of traditional sunflower oil (SOEE) was carried out at low temperature (40 °C) in ethanol as solvent in the presence of supported palladium catalysts. In the range of studied dispersions (12–55%), the SOEE hydrogenation reaction is insensitive to the size of the palladium particles deposited on silica, but the largest metallic particles enhance the C18:1 *cis*–*trans* isomerization. The use of various oxide supports (α -Al₂O₃, γ -Al₂O₃, TiO₂, MgO, ZnO, CeO₂, CeZrO₂) to deposit palladium does not allow to improve the selectivity of the reaction toward the *cis* C18:1 compared to Pd/SiO₂ catalysts. On the other hand, the modification of palladium by lead, introduced by surface redox reaction (catalytic reduction), promotes the selectivity in *cis* C18:1. In addition, this technique of preparation involves a moderate decrease of the palladium activity compared to a traditional method of successive impregnations. The introduction of amines in the reaction medium modifies the hydrogenating properties of the Pd/SiO₂ catalyst. According to the quantity and the nature of the added amine (aliphatic with linear or ramified chain and cyclic compounds), the catalytic activity can either be unchanged or inhibited. These evolutions result from a promoter electronic effect generated by the presence of the amine and from a poison geometric effect related to the adsorption of this nitrogen-containing compound on the palladium surface. Whatever the nature of the amine, it induces an increase of the selectivity toward the *cis* C18:1. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

The vegetable edible oils hydrogenation is a very important operation in the chemical industry. The main qualities of natural substances are their environment compatibility (low ecotoxicity, great biodegradability). Moreover, these resources are renewable. The industrial applications are as varied as pharmacy, cosmetics, plastics, detergents, lubricants, etc. The aim of this study is to produce lubricants. Oils used as lubricants have to remain liquid at ambient temperature and to be stable under oxygen atmosphere to avoid their polymerization [1]. Main unsaturated fatty acids in vegetable oils are linolenic acid (*cis*-9, *cis*-12, *cis*-15-octadecatrienoic

acid, C18:3), linoleic acid (*cis*-9, *cis*-12-octadecadienoic acid, C18:2) and oleic acid (*cis*-9-octadecenoic, C18:1). Their oxygen absorption rate is 800:100:1, respectively. Therefore, partial hydrogenation of rapeseed oil to the C18:1 acid should result in a strong stabilization over against oxygen. Moreover, the oleic acid C18:1 in the *cis* isomer form, contrary to the *trans* C18:1 and the totally saturated (stearic acid, C18:0) compounds, remains liquid at ambient temperature. However, a traditional sunflower oil can contain only 25–30% of C18:1 *cis* isomer, the main constituent being the *cis*-9, *cis*-12 C18:2. The selective hydrogenation of such vegetable oil must lead to a minimum of 80% toward *cis* oleic acid to correspond to the industrial needs. Currently, the catalyst used in the industrial hydrogenation process is a nickel catalyst deposited on a silica support [2–5]. Studies on the hydrogenation of different vegetable oils have been also

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undertaken on catalysts containing copper [6] or copper chromite [7]. Generally, these different catalysts require a reaction temperature above 150 °C and a high hydrogen pressure. Recently, we have studied the selective hydrogenation of ethyl esters of a traditional sunflower oil (SOEE) in the presence of monometallic catalysts containing noble metals (Pd, Pt, Ru) supported over silica, which allow to work under gentle conditions [8]. The activity decreases in the order Pd > Pt > Ru at 40 °C under 10 bar of hydrogen. However, the three metals are not selective in *cis* oleic isomer since *trans* oleic and stearic derivatives were produced in large amounts. In order to promote the selectivity toward the *cis* oleic isomer, noble metal can be modified by metallic additives or by addition of amines in the reaction medium. The effect of amines during the selective hydrogenation of unsaturated hydrocarbon compounds was the subject of many studies [9–16]. For example, it was shown that the addition of pyridine or quinoline allows to selectively hydrogenate the acetylenic compounds in ethylenic ones on palladium catalysts [17–23]. In the same way, the presence of amines allows to selectively obtain monoolefins starting from diolefins on catalysts containing palladium, nickel or cobalt [24,25]. These results are generally explained by a competition of adsorption between the amine and the hydrocarbon compounds and by a modification of the metal electronic properties resulting from an electron transfer from the free nitrogen doublet toward the metal phase.

Preliminary experiments concerning the addition of copper or lead to palladium, and the addition of amines in the reaction medium were performed [8]. The present work completes the previous paper on the selective hydrogenation of ethyl esters of traditional sunflower oil on supported palladium catalysts. We study the influence of the following parameters: the palladium particle size, the nature of the support, the addition of lead on palladium catalyst and the addition of various amines in the reaction medium during the SOEE hydrogenation on Pd/SiO₂ catalyst.

2. Experimental

2.1. Catalyst preparation

The various supports were ground and then sieved to retain particles with sizes between 0.10 and 0.04 mm. The monometallic Pd based catalysts were prepared either via cationic exchange of the support (SiO₂) by Pd(NH₃)₄(NO₃)₂ in basic medium (pH = 11) or via simple impregnation (Al₂O₃, TiO₂, MgO, ZnO, CeO₂, CeZrO₂) using the same Pd precursor. The monometallic catalysts were dried overnight at 120 °C, then calcined in flowing air at 300 °C for 4 h, and finally reduced under hydrogen flow at 400 °C for 4 h. The Pd/TiO₂ catalyst was reduced at 300 °C instead of 400 °C in order to avoid the SMSI effect. Bimetallic Pd–Pb catalysts were prepared by the surface redox reaction between

hydrogen activated on palladium particles and the lead precursor (Pb(CH₃COO)₂) dissolved in methanol (“catalytic reduction” method [26]). This preparation method of bimetallic catalysts is well known to induce a strong interaction between the two metals whatever the prepared bimetallic system [27–29]. A known amount of the pre-reduced palladium catalyst was introduced into a reactor under nitrogen and was activated at 300 °C for 1 h under hydrogen. Then the solution of the lead precursor in methanol, previously degassed under nitrogen flow, was introduced onto the catalyst at room temperature. After a 1 h reaction time under hydrogen bubbling, the solution was filtered out and the catalyst was dried overnight at 100 °C. Finally, the bimetallic catalysts were reduced under hydrogen flow at 300 °C for 2 h (2 °C/min heating rate). Using the same approach, a blank Pd catalyst over SiO₂, named “Pd₁ treated in CH₃OH/H₂” further in the text, was also prepared in a methanol solution without addition of the lead precursor.

2.2. Electron microscopy

Transmission electron microscopy (TEM) studies were performed on a Philips CM 120 instrument operating at 120 kV. The Pd/SiO₂ samples were ultrasonically dispersed in ethanol and the suspension was brought onto a copper grid with a carbon support film. The preparation of the grids was different for the catalysts supported onto TiO₂, MgO, CeO₂ and CeZrO₂ because of some contrast problems. These samples were embedded in a polymeric resin (spurr) and cut into a section as small as 40 nm with an ultramicrotome equipped with a diamond knife. Cuts were then deposited on an Al grid previously covered with a thin layer of carbon.

EDX microanalysis of palladium and lead was carried out in the nanoprobe mode. The diameter of the probe is 5.0–7.0 nm.

2.3. Metal accessibility

Metal accessibilities of catalysts were determined by chemisorption of hydrogen at 70 °C. The catalysts were first reduced under hydrogen at 400 °C (2 h), then evacuated at the same temperature under argon for 3 h. Hydrogen chemisorbs on palladium according to the stoichiometry H/Pd_s = 1. The particle size (*d*) was determined from the metal accessibility value (%*D*) according to Hugues et al. [30], which assimilated particles to cubes with one face in contact with the support. The equation is the following:

$$d(\text{Å}) = \frac{5 \times 10^6 M}{DS\rho} \quad (1)$$

with *M* is the atomic weight (g/mol), *S* the surface by mol of Pd metal (47,776 m²/mol) and *ρ* is the metal volumic weight (g/cm³).

2.4. Hydrogenation of sunflower oil

Classical refined sunflower oil (from VALAGRO, Poitiers) was transformed in presence of ethanol and sodium ethanolate, at 60 °C, into glycerol and ethyl esters. After the separation of the reaction products by decantation, the sunflower oil ethyl esters (SOEEs) were washed and dried at 110 °C for 3 h under vacuum. They were then purified on a molecular distillation apparatus at 120 °C ($P < 10^{-3}$ mbar) until a high purity near 98%. The hydrogenation of SOEE was performed in liquid phase in a stirred autoclave, at constant pressure of 10 bar and at low temperature (40 °C) according to an experimental procedure previously implemented at the laboratory [8]. A known amount of prereduced catalyst was immersed into 50 mL of solvent (ethanol) without exposure to air and introduced into the autoclave. Then a mixture of 75 mL of SOEE in 25 mL of solvent was poured into the autoclave and flushed with nitrogen. When the desired temperature was raised, 10 bar hydrogen pressure was introduced and the stirring was switched on (zero time for the reaction). In some experiments, amines were introduced directly in the reaction medium. Liquid samples were analyzed by VPC on a Varian 3400CX chromatograph equipped with a flame ionization detector and a capillary column DB-23 (J&W, 30 m, 0.25 mm i.d.) using nitrogen as carrier gas.

3. Results and discussion

Fig. 1 presents the reaction pathway of SOEE hydrogenation, with the various intermediates which can be observed.

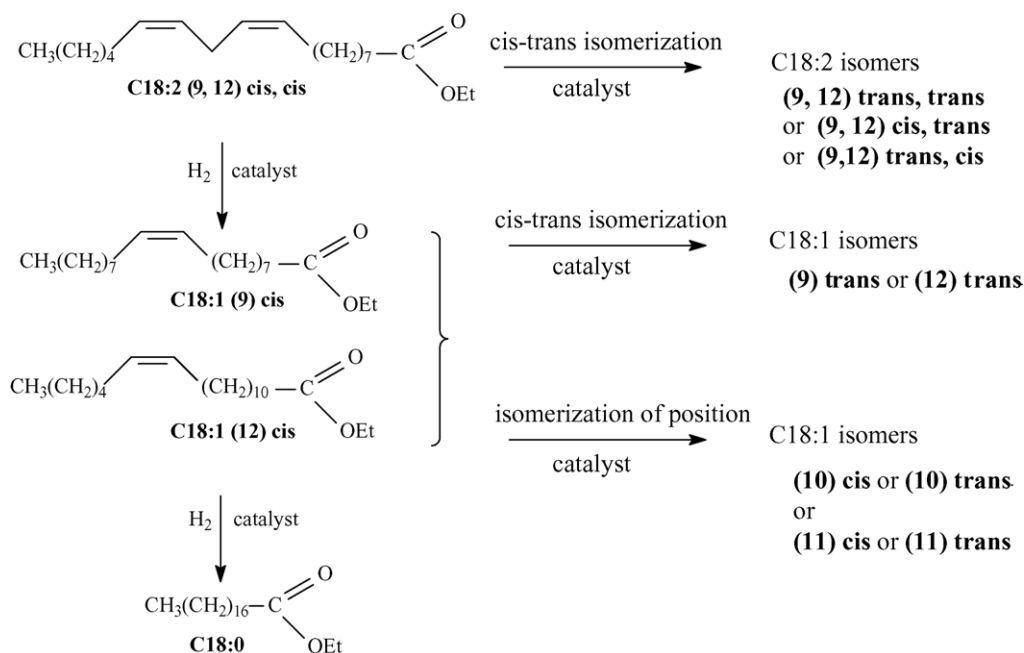


Fig. 1. Reaction pathway of SOEE hydrogenation.

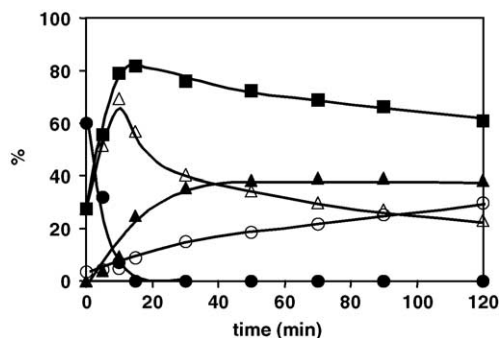


Fig. 2. SOEE hydrogenation vs. time at 40 °C over 1 wt.% Pd/SiO₂ catalyst ($m_{\text{catalyst}} = 122$ mg): (●) % C18:2; (■) % C18:1 (tot); (△) % *cis* C18:1; (▲) % *trans* C18:1; (○) % C18:0 (mol%).

It must be recalled that the aim of the study is to selectively hydrogenate C18:2 toward *cis* C18:1, avoiding the *cis*–*trans* isomerization and the complete hydrogenation to C18:0. It should be noticed that the C18:1 compounds include the various isomers of position of the C=C double bond (C=C in positions 9, 10, 11 or 12, Fig. 1). An example of the temporal percentage profiles of the various compounds is represented in Fig. 2. The reagent to be hydrogenated consists of a mixture of C18:0, C18:1 and C18:2 in the following initial proportions: C18:0, 3.72%; *cis*-9 C18:1, 27.49%; *cis*-9, *cis*-12 C18:2, 60.11%.

3.1. Particle size effect

In order to achieve a series of catalysts displaying various Pd particle sizes, two different strategies were followed: first, the Pd loading was increased from 0.3 to 1.5 wt.%.

Table 1

Main characteristics and TOF (C18:2 hydrogenation) of silica supported monometallic and bimetallic catalysts containing palladium

Pd _{wt.%} catalyst/SiO ₂	T _{calcination} , T _{reduction} (°C)	Metal ^a (wt.%)	d ^b (nm)	D ^c (%)	MC ^d (×10 ³ mol/L)	TOF C18:2 hydrogenation (×10 ¹⁹ mol/h)
Pd _{0.3}	300, 400	0.39	1.7 ^{**}	55	0.030	2.08
Pd ₁	300, 400	0.91	1.8 ^{**}	53	0.070	1.92
Pd _{1.5}	300, 400	1.45	2.0 ^{**}	47	0.037	2.25
Pd ₁ treated in CH ₃ OH/H ₂	–, 300	0.91	3.5 ^{**}	28	0.070	1.99
Pd ₁ treated in H ₂ O/H ₂	–, 500	0.91	7.8 ^{**}	12	0.070	2.12
Pd ₁ + 0.05 wt.% Pb	–, 300	0.91 (Pd), 0.04 (Pb)	3.8 [*]	–	0.070	–
Pd ₁ + 0.10 wt.% Pb	–, 300	0.91 (Pd), 0.07 (Pb)	4.0 [*]	–	0.070	–

^a Determined by ICP.^b Mean particle size deduced from electronic microscopy (*) or hydrogen chemisorption (**).^c Pd accessibility.^d MC: metallic concentration in the reaction medium during the SOEE hydrogenation.

The principal characteristics of the resulting catalysts are summarized in Table 1. Pd_{1.5}/SiO₂ presents slightly larger particle size (2.0 nm) than Pd_{0.3} and Pd₁/SiO₂, which are similar in size (mean diameter about 1.7–1.8 nm). The second strategy was a treatment of the Pd₁/SiO₂ catalyst under hydrogen atmosphere in a methanol or water solution. This treatment was suggested from previous results from our group, which show a sintering of the metallic particles under similar conditions on various monometallic catalysts containing Pd, Pt or Rh [28,29,31]. In our case, this treatment induces an increase of the particle size from 1.8 nm (Pd₁) to 3.5 nm (Pd₁ in methanol) and 7.8 nm (Pd₁ in water) (Table 1).

Fig. 3a gives the evolution of the C18:2 conversion as a function of time obtained on the five different monometallic catalysts. From these various curves, initial rates of

C18:2 hydrogenation were expressed as turnover frequencies (Table 1). Whatever the metallic particle size, the accessible atoms of the various Pd/SiO₂ catalysts seem to work at a comparable initial rate (about $(2.10 \pm 0.20) \times 10^{-19}$ mol/h). This observation suggests that the particle size in the range 1.7–7.8 nm does not have an effect on the intrinsic rate of the SOEE hydrogenation. Likewise, Fig. 3b shows no notable evolution concerning the C18:0 product. As for the *trans* C18:1 (Fig. 3c), it tends to increase for the Pd₁/SiO₂ catalyst treated in H₂O/H₂ medium, which presents the largest mean particle size of the Pd catalysts series (Table 1, $d = 7.8$ nm).

Consequently, the rate of hydrogenation of the SOEE is insensitive to the palladium particle size in the range 1.7–7.8 nm. However, larger particles should be avoided because they promote the *cis*–*trans* isomerization.

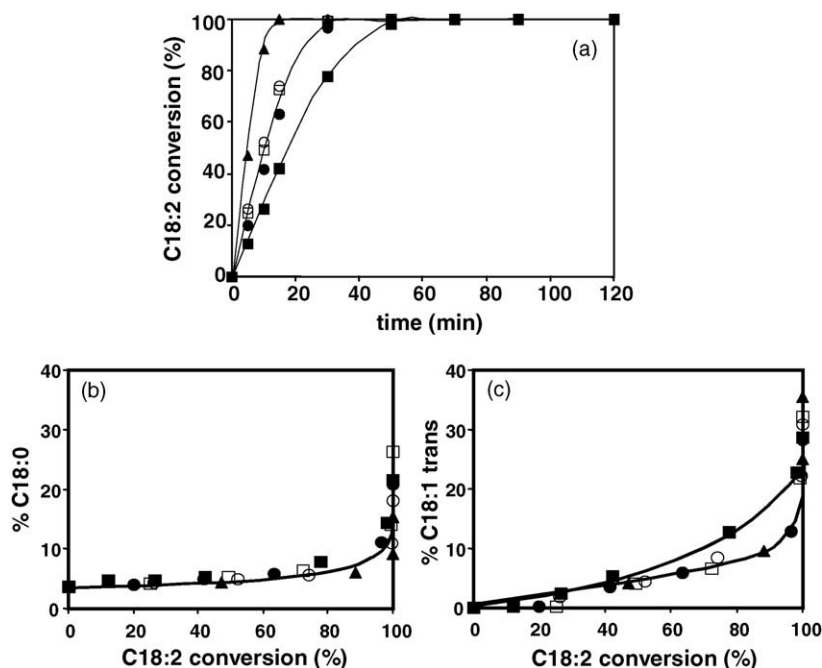


Fig. 3. SOEE hydrogenation on the various monometallic palladium/SiO₂ catalysts: (a) C18:2 conversion (%) vs. time, (b) C18:0 (%) and (c) *trans* C18:1 (%) vs. C18:2 conversion (mol%); (●) Pd_{0.3} catalyst; (▲) Pd₁ catalyst; (○) Pd_{1.5} catalyst; (□) Pd₁ treated in CH₃OH/H₂ catalyst; (■) Pd₁ treated in H₂O/H₂ catalyst (for each sample, $m_{\text{catalyst}} = 122$ mg except for Pd_{1.5} catalyst, $m_{\text{catalyst}} = 41$ mg).

Table 2
Main characteristics and TOF (C18:2 hydrogenation) of Pd catalysts supported on various oxides

Pd _{0.3} catalyst/support	Support surface area (m ² /g)	T _{calcination} , T _{reduction} (°C)	Metal ^a (wt.%)	d ^b (nm)	D ^c (%)	Accessible atom (×10 ⁻¹⁹ g _{cata})	TOF C18:2 hydrogenation (×10 ¹⁹ mol/h)
SiO ₂	200	300, 400	0.39	1.7**	55	1.21	2.08
α-Al ₂ O ₃ , SCS 9	9	300, 400	0.32	1.6**	59	1.07	3.52
γ _c -Al ₂ O ₃ GFS	215	300, 400	0.30	1.3**	70	1.18	3.70
TiO ₂	48	300, 300	0.38	2.0*	47	1.01	3.29
MgO	297	300, 400	0.30	2.4*	38	0.65	2.62
ZnO	40	300, 400	0.28	3.5**	26	0.41	3.80
CeO ₂	127	300, 400	0.30	3.6*	26	0.44	3.69
CeZrO ₂	87	300, 400	0.31	3.2*	29	0.51	3.35

^a Determined by ICP.

^b Mean particle size deduced from electronic microscopy (*) or hydrogen chemisorption (**).

^c Pd accessibility.

3.2. Support effect

The aim of the study was to examine the influence of the nature of the support on the catalytic properties of supported palladium for the SOEE hydrogenation. The amount of Pd was fixed at 0.3 wt.%. The main characteristics of the different catalysts are summarized in Table 2.

Fig. 4a and b represent the C18:2 conversion versus time during the SOEE hydrogenation on the various supported Pd_{0.3} catalysts. According to Fig. 4a and b, respectively, two tendencies become apparent concerning the activity in SOEE hydrogenation:

- The Pd_{0.3} catalysts supported on the two aluminas, as well as titanium oxide, present a conversion slightly higher than the Pd_{0.3}/SiO₂ catalyst.
- The Pd_{0.3} catalysts supported on magnesium oxide, zinc oxide, cerium oxide as well as cerium–zirconium, tend to be less active than the Pd_{0.3}/SiO₂ catalyst.

The reaction of SOEE hydrogenation being insensitive to the particle size in the 12–55% dispersion range, which includes the whole of studied catalysts, it is then appropriate to express the activities as turnover frequencies (Table 2). The results indicate that the support effect is really not significant despite the extremely variable specific surface areas, from 9 m²/g (α-Al₂O₃) to 297 m²/g (MgO), and the difference in acido-basic properties of the supports [32].

Fig. 4c–f represent the evolution of the C18:0 and *trans* C18:1 molar percentages, respectively, as a function of the C18:2 conversion during the SOEE hydrogenation on the various catalysts separated into two series according to their behavior compared to the Pd_{0.3}/SiO₂ system. The first series of catalysts (Fig. 4c and e) includes the Al₂O₃ supports and TiO₂. These samples present similar selectivities in C18:0 and *trans* C18:1. The second series of catalysts MgO, ZnO, CeO₂ and CeZrO₂ (Fig. 4d and f), shows more important amounts of C18:0 and C18:1 *trans* isomers, compared with the percentages obtained on the Pd_{0.3}/SiO₂ sample at iso-conversion of C18:2. These differences cannot be related to the structural properties of the supports nor to the size of the metallic particles. If we examine the classification of the ba-

slicity of the various oxides established by Martin and Duprez [32]: MgO ≫ CeO₂ > ZrO₂ > γ_c-Al₂O₃ > SiO₂, we observe that the catalysts producing higher amounts of C18:0 and *trans* C18:1 compounds (series 4d, 4f) are more basic than the alumina, silica and titanium oxide supports (series 4c, 4e). Nevertheless, the results cannot be explained only by this characteristic of the oxides because the more basic support (MgO) does not lead to higher percentages of C18:0 and *trans* C18:1 compared to a less basic support such as the cerium oxide for example.

In conclusion, this study shows that the use of various oxides to prepare supported palladium catalysts did not improve the selectivity of the reaction of C18:2 hydrogenation toward *cis* C18:1.

3.3. Modification of the palladium by lead addition

Two bimetallic Pd–Pb catalysts were prepared from the monometallic Pd₁/SiO₂ catalyst by catalytic reduction (Table 1). The blank catalyst “Pd₁ treated in CH₃OH/H₂” prepared under the same operating conditions, but in absence of the lead precursor, allows to estimate the influence of the preparation method of bimetallic catalysts by catalytic reduction (CR), on the hydrogenating properties of the Pd₁/SiO₂ catalyst. EDX microanalysis of Pd–Pb/SiO₂ catalysts reduced at 300 °C indicates that both metals are deposited into closed contact. The mean particle size of the Pd–Pb catalysts is approximately 50% larger than obtained for the parent catalyst (Table 1), indicating that some sintering is taking place during the preparation of bimetallic catalysts. Indeed, this phenomenon of sintering has been previously reported in the course of bimetallic catalyst preparation by catalytic reduction [28,33].

For comparison with the CR bimetallic catalysts, a 1 wt.% Pd–0.05 wt.% Pb/SiO₂ catalyst was also prepared by a traditional technique of successive impregnations (SI) using the same Pb(CH₃COO)₂ precursor. The blank and the bimetallic samples were reduced at 300 °C for 2 h. The comparison of the blank “Pd₁ treated in CH₃OH/H₂” and the CR Pd–Pb bimetallic catalysts indicates that the addition of lead involves a small decrease of the C18:2 conversion

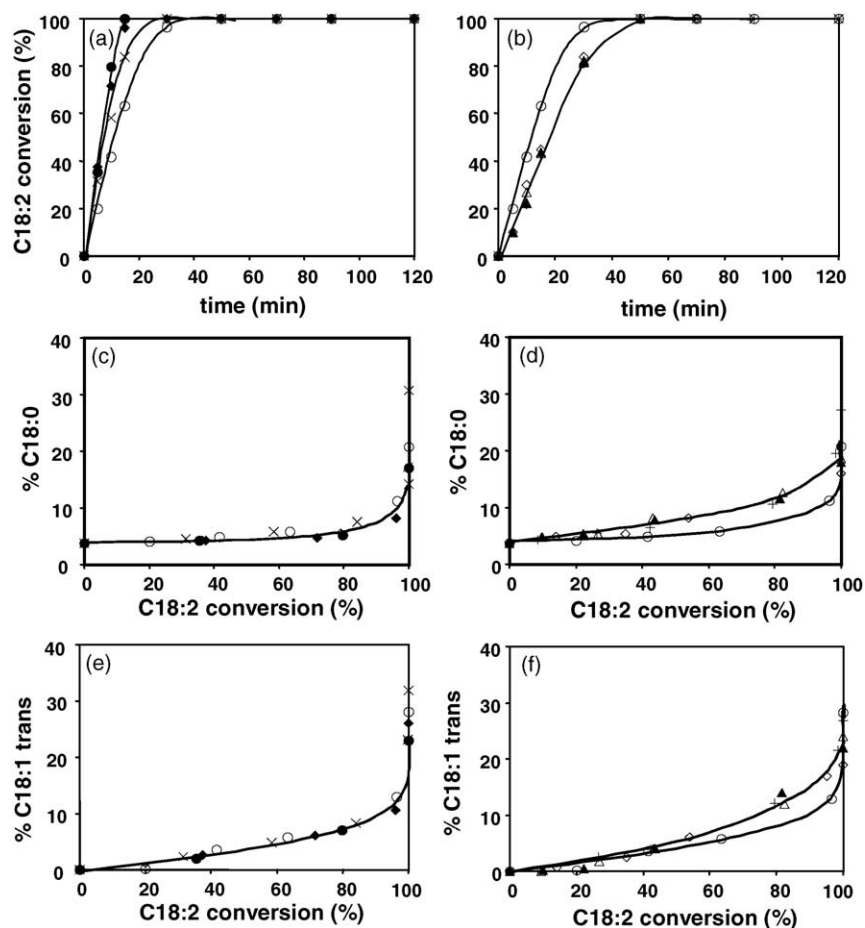


Fig. 4. SOEE hydrogenation on the monometallic Pd_{0.3} catalysts ($m_{\text{catalyst}} = 122$ mg) supported on various oxides: (a and b) C18:2 conversion (%) vs. time, (c and d) C18:0 (%) and (e and f) *trans* C18:1 (%) vs. C18:2 conversion (mol%); (○) SiO₂; (◆) α -Al₂O₃; (●) γ -Al₂O₃; (×) TiO₂; (+) MgO; (◇) ZnO; (▲) CeO₂; (△) CeZrO₂.

(Fig. 5a). The result can be explained by the deposit of inactive lead atoms on the surface of the palladium particles. This decrease is all the more significant as the content of the deposited lead is high (Fig. 5a). The deposit of a comparable lead content (0.05 wt.%) by the SI method led to a more severe poisoning of the catalyst activity. This phenomenon also means a strong interaction between the two metals introduced by successive impregnations. The different behaviors between the two modes of preparation can be explained by a selective deposit of lead on particular sites of palladium when this one is introduced by catalytic reduction. Similar results have been observed during the selective hydrogenation of isoprene on bimetallic catalysts PdFe/Al₂O₃ prepared by successive impregnations and by a surface controlled reaction [34]. Moreover, the addition of lead by both method of preparation does not influence the proportion in C18:0 (Fig. 5b) but decreases the formation of *trans* C18:1 isomers (Fig. 5c). Then, the addition of lead is beneficial to limit the C18:1 *cis-trans* isomerization during the SOEE hydrogenation on palladium. Furthermore, the hydrogenation rate of palladium is slightly inhibited when this inactive additive is introduced by catalytic reduction.

3.4. Addition of amines in the reaction medium

The effect of amine addition was studied on the Pd₁/SiO₂ catalyst. The different amines are listed in Table 3 with the introduced quantities and the pK_a value of their conjugated acid. The amine/Pd_{total} molar ratio is also specified in Table 3 for each experiment. The various amines, introduced directly in the reaction medium, are likely to be found in the hydrogenated oil after reaction. These compounds can be then eliminated by acidic hydrolysis. However, it should be specified again that the considered application is located in the nonfood field.

3.4.1. Addition of primary aliphatic amines

The hydrogenation tests were performed in the presence of methylamine and butylamine (Table 3, entries 1 and 2) in order to examine the influence of the length of the alkyl chain of the amine on the activity and selectivity of the Pd₁/SiO₂ catalyst. In addition, different amounts of these amines were introduced to observe the effect of their concentration on the reaction. Fig. 6a represents the C18:2 conversion in presence of methylamine as a function of time. From this figure, it can

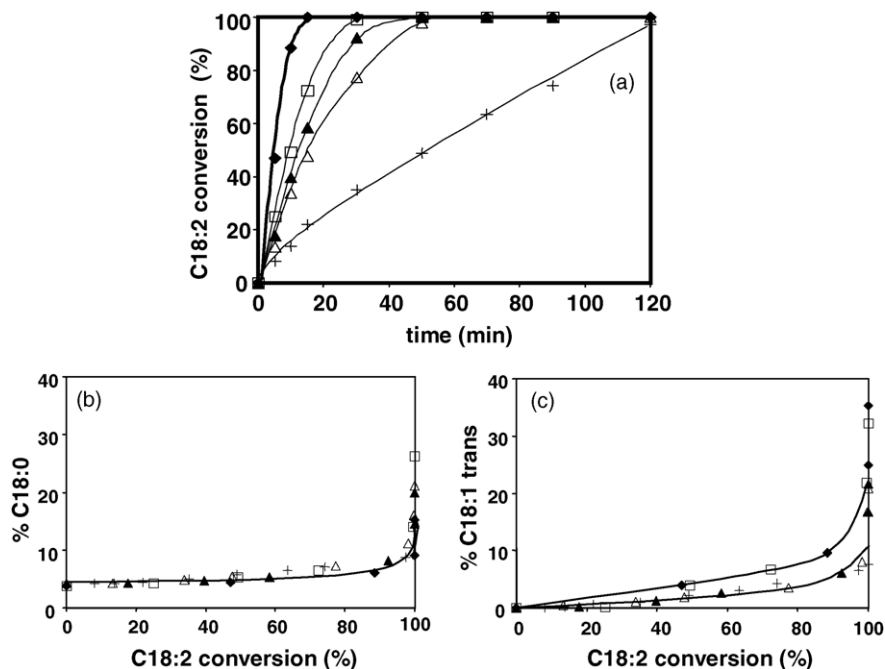


Fig. 5. SOEE hydrogenation on bimetallic Pd–Pb/SiO₂ catalysts ($m_{\text{catalyst}} = 122$ mg): (a) C18:2 conversion (%) vs. time, (b) C18:0 (%) and (c) *trans* C18:1 (%) vs. C18:2 conversion (mol%); (◆) Pd₁/SiO₂; (□) Pd₁ treated in CH₃OH/H₂; (▲) Pd₁–Pb_{0.04}/SiO₂ (CR); (△) Pd₁–Pb_{0.07}/SiO₂ (CR); (+) Pd₁–Pb_{0.05}/SiO₂ (SI).

be seen that the addition of methylamine strongly inhibits the activity of palladium, this effect being all the more significant as the quantity of methylamine is high. On the other hand, the introduction of this amine does not have any effect on the percentage of C18:0 (Fig. 6c). Moreover, Fig. 6e indicates that the presence of methylamine allows to decrease the formation of *trans* C18:1. However, the increase of the quantity of this amine does not induce a more significant drop in the formation of *trans* C18:1.

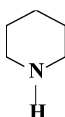

The same kind of experiments conducted in the presence of butylamine shows that even the addition of 0.40 mL of this amine (leading to an amine/Pd_{total} molar ratio comparable to the addition of 0.15 mL of methylamine, Table 3) does not induce such a strong deactivation of the Pd₁/SiO₂

catalyst (Fig. 6b). Moreover, in the case of the addition of small quantity of butylamine (0.15 mL), no deactivation is observed. Concerning the C18:0 (Fig. 6d) and *trans* C18:1 (Fig. 6f), these products present the same evolution in presence of methylamine or butylamine: no inhibition of the formation of C18:0 but a significant decrease of the *trans* C18:1.

In conclusion, addition of primary aliphatic amines in the reaction medium induces a more or less important deactivation according to the length of the chain of the amine and the introduced quantity. For a similar amine/Pd_{total} molar ratio, the methylamine deactivates more strongly the catalyst than the butylamine. The p*K*_a values of the conjugated acid of these two amines being comparable, this result can be explained by

Table 3

Quantities of introduced amines in the reaction medium during the SOEE hydrogenation on the Pd₁/SiO₂ catalyst, amine/Pd_{total} molar ratios and values of the p*K*_a of the conjugated acid of each amine

Entry	Amine	p <i>K</i> _a	Formula	Introduced volume (mL)	Amine/Pd _{total} molar ratio
1	Methylamine	10.65	H ₃ C–NH ₂	0.15, 0.30	377, 755
2	Butylamine	10.77	H ₃ C–(H ₂ C) ₃ –NH ₂	0.15, 0.25, 0.40	131, 217, 351
3	Triethylamine	10.70	H ₃ C–H ₂ C–N(CH ₂ –CH ₃) ₂	0.10, 0.20, 0.25, 0.60	62, 124, 155, 347
4	Piperidine	11.12		0.30, 0.60	264, 528
5	Pyridine	5.21		0.20, 0.70	215, 752

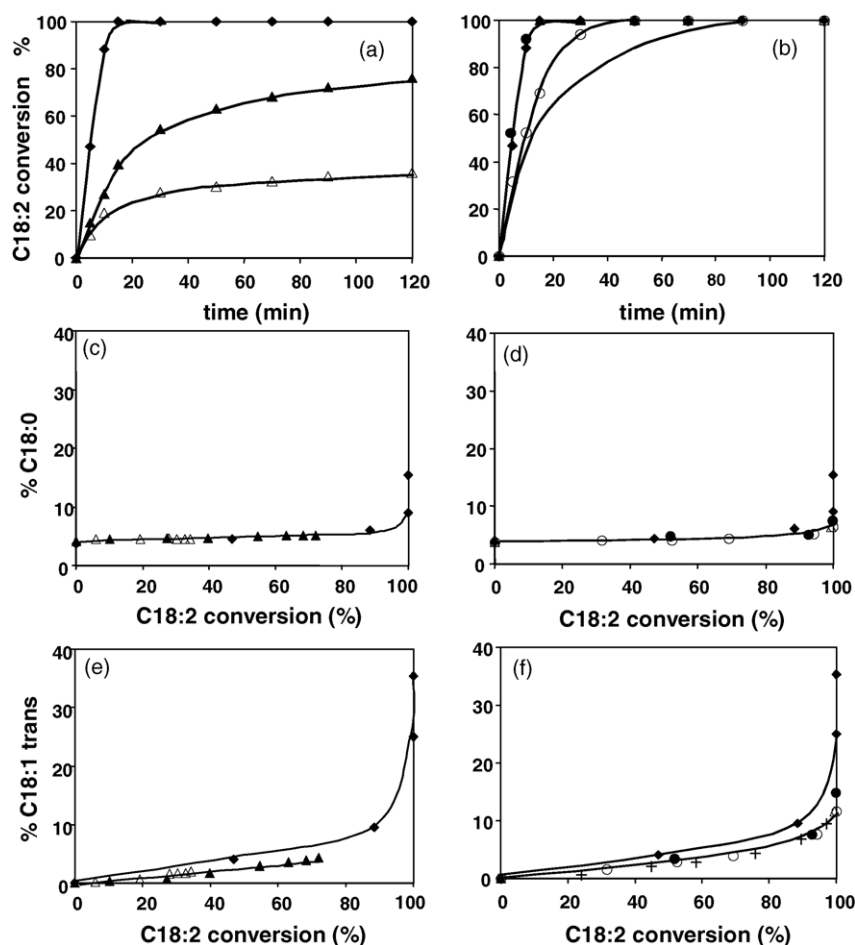


Fig. 6. SOEE hydrogenation on the Pd₁/SiO₂ catalyst in presence of primary amines: (a and b) C18:2 conversion (%) vs. time, (c and d) C18:0 (%) and (e and f) *trans* C18:1% vs. C18:2 conversion (mol%); (▲) 0.15 mL methylamine; (△) 0.30 mL methylamine; (●) 0.15 mL butylamine; (○) 0.25 mL butylamine; (+) 0.40 mL butylamine; (◆) without amine.

a higher coverage of the metallic phase by the methylamine because of its shorter carbonaceous chain. The more compact fitting of the methylamine on the surface of palladium particles would thus inhibit more strongly the adsorption of the C18:2 unsaturated ethyl ester. Concerning the selectivity of the reaction, the addition of these two amines has no effect on the formation of the C18:0 saturated ester, but allows to decrease the formation of the *trans* C18:1 compound.

3.4.2. Addition of tertiary aliphatic amines

In order to examine the assumption of the steric hindrance of the amines on the catalyst surface, the study was continued in the presence of a tertiary aliphatic amine, the triethylamine (Table 3, entry 3). The conversion of C18:2 in presence of different amounts of triethylamine is given in Fig. 7a. From this figure, it can be seen that contrary to the addition of methylamine or butylamine, the presence of triethylamine

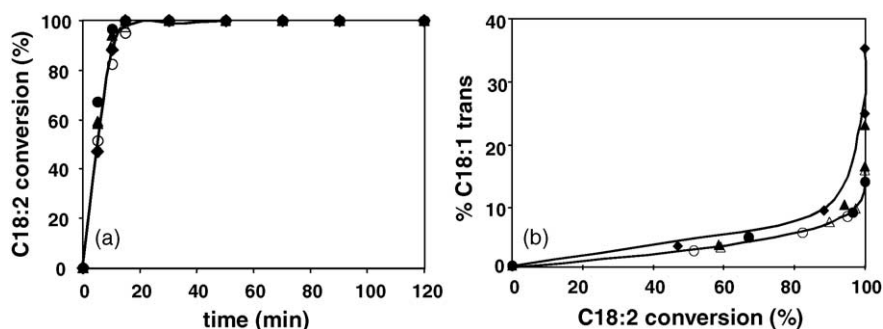


Fig. 7. SOEE hydrogenation on the Pd₁/SiO₂ catalyst in presence of different amounts of triethylamine: (a) C18:2 conversion (%) vs. time, (b) *trans* C18:1 (%) vs. C18:2 conversion (mol%); (▲) 0.10 mL; (○) 0.20 mL; (●) 0.25 mL; (△) 0.60 mL; (◆) without amine.

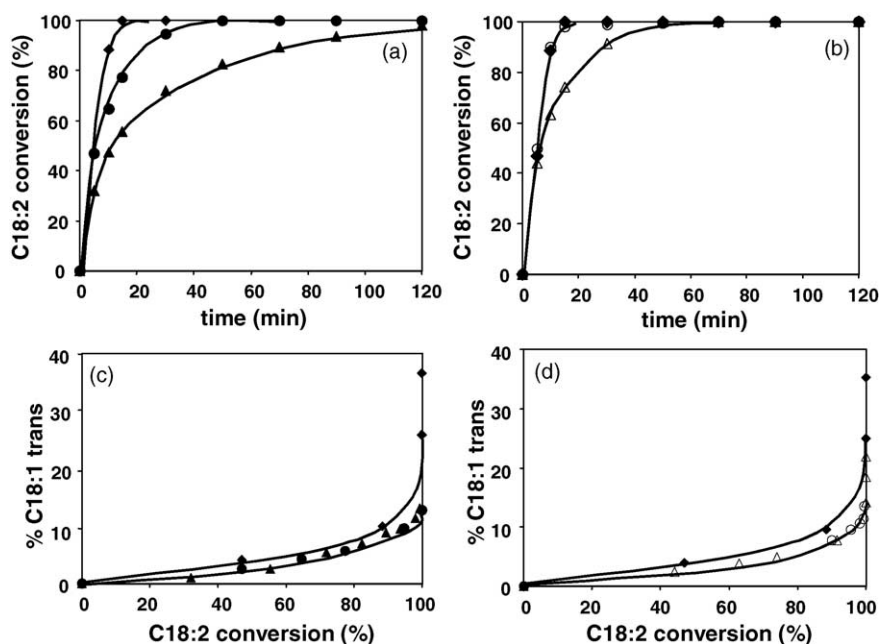


Fig. 8. SOEE hydrogenation on the Pd₁/SiO₂ catalyst in presence of cyclic amines: (a and b) C18:2 conversion (%) vs. time and (c and d) *trans* C18:1 (%) vs. C18:2 conversion (mol%); (●) 0.30 mL piperidine; (▲) 0.60 mL piperidine; (○) 0.20 mL pyridine; (△) 0.70 mL pyridine; (◆) without amine.

does not inhibit the C18:2 hydrogenation. Concerning the selectivity of the reaction, no evolution of the C18:0 was observed while the *trans* C18:1 decreases after addition of the triethylamine (Fig. 7b).

These results confirm that the effects observed on the hydrogenating activity of a Pd/SiO₂ catalyst depend on the nature of the aliphatic amine. For a comparable amine/Pd_{total} molar ratio, the inhibiting effect of the amine on the C18:2 conversion is all the more high as the hydrocarbon fragment of the amine is small: methylamine > butylamine > triethylamine. In addition, the p*K*_a value of the conjugated acid of these three amines being similar, these different behaviors can be explained by a lower coverage of palladium surface by the amine (amine/Pd_{surface} ratio) having the highest steric hindrance. The absence of inhibiting effect on the conversion of the C18:2 in the case of triethylamine probably results from a donor effect of nitrogen toward the metal (positive electronic effect) which compensates the loss of active surface related to the amine adsorption (negative geometric effect). So, the metallic surface which is accessible to the reagents decreases in the presence of amines but it would be more active because of a weaker adsorption of C18:2 resulting from the donor effect of the amine. Indeed, kinetic studies have shown a zero order for the hydrogenation of this ester meaning a strong adsorption on the metal [35]. This modification of the electronic properties of the metal also would explain the limited formation of *trans* C18:1. Beneficial effects of nitrogen containing compounds addition were already observed during the selective liquid phase hydrogenation of alkynes, explained by a ligand effect, which would decrease the complexation strength of the highly unsaturated hydrocarbons [9–11].

3.4.3. Addition of cyclic amines

The cyclic amines were often used as additives in the reaction medium during selective hydrogenations [13,14,17–23]. Two various cyclic amines are presented in this work, the piperidine and the pyridine. The introduced quantities are listed in Table 3, entries 4 and 5, respectively. The C18:2 conversions versus time on the Pd₁/SiO₂ catalyst are reported in Fig. 8a (piperidine) and b (pyridine). We can notice that the presence of cyclic amine involves a more or less important decrease of the catalyst activity. In particular, the pyridine does not deactivate the Pd₁/SiO₂ catalyst for a amine/Pd_{total} molar ratio = 215 (Fig. 6b, 0.20 mL introduced) whereas piperidine involves a drop of conversion for a comparable amine/Pd_{total} molar ratio (Fig. 6a, 0.30 mL introduced, molar ratio = 264). These differences could be explained by the weaker p*K*_a value of the conjugated acid of pyridine compared to piperidine and thus by a weaker adsorption of the former on the palladium surface.

Concerning the reaction products, the presence of the cyclic amines does not involve modifications on the formation of the C18:0 on the Pd₁/SiO₂ catalyst. On the other hand, the two cyclic amines induce a diminution of the *trans* C18:1 (Fig. 8c and d). These evolutions are similar with those previously observed in the case of the aliphatic amines.

4. Conclusion

The objective of this work was to selectively hydrogenate C18:2 ethyl esters of the sunflower oil (SOEE) toward C18:1 *cis* ethyl oleate on supported palladium catalysts, for a nonfood use such as lubricants. The influence of various

parameters related to the catalyst structure was evaluated in order to improve the selectivity of the reaction. In the range of studied dispersions (12–55%), the reaction of SOEE hydrogenation is insensitive to the size of the palladium particles deposited on silica. On the other hand, the largest metallic particles enhance the C18:1 *cis*–*trans* isomerization. In addition, the use of various oxides (α -Al₂O₃, γ -Al₂O₃, TiO₂, MgO, ZnO, CeO₂, CeZrO₂) to deposit palladium did not improve the selectivity of the reaction obtained in the presence of the Pd/SiO₂ catalyst. By opposite, some supports led to higher selectivities in *trans* C18:1. The modification of palladium by lead addition showed that this inactive deposit improves the selectivity in *cis* C18:1, the conversion being only slightly decreased when this additive is introduced by surface redox reaction (catalytic reduction). Finally, the introduction of amines modifies the hydrogenating properties of supported palladium catalyst. According to the quantity and the nature of the added amine (aliphatic with linear or ramified chain, cyclic compounds), the activity of the Pd/SiO₂ catalyst can either be unchanged or inhibited. These evolutions would result from a promoter electronic effect generated by the presence of the amine and from a poison geometric effect related to adsorption of this nitrogen-containing compound on the palladium surface. Whatever the nature of the amine, the selectivity in *cis* C18:1 is improved compared to the nonmodified monometallic Pd catalyst.

In conclusion, this study relating to the selective hydrogenation of ethyl ester of sunflower oil on palladium catalysts shows that it is difficult to be freed from the secondary reaction of *cis*–*trans* isomerization of the required compound (C18:1). All the results obtained in this work show that the best control of this selectivity was obtained by introduction of amines into the reaction medium.

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