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ORIGINAL PAPER

Hydrogenation of Sunflower Oil over M/SiO_2 and M/Al_2O_3 (M = Ni, Pd, Pt, Co, Cu) Catalysts

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Abstract This work is aimed at evaluating the performance of several catalysts in the partial hydrogenation of sunflower oil. The catalysts are composed of noble (Pd and Pt) and base metals (Ni, Co and Cu), supported on both silica and alumina. The following order can be proposed for the effect of the metal on the hydrogenation activity: Pd > Pt > Ni > Co > Cu. At a target iodine value of 70 (a typical value for oleomargarine), the production of *trans* isomers is minimum for supported nickel catalysts (25.7–32.4 %, depending on the operating conditions). Regarding the effect of the support, Al_2O_3 allows for more active catalysts based on noble metals (Pd and Pt) and Co, the effect being much more pronounced for Pt. Binary mixtures of catalysts have been studied, in order to strike a balance between catalyst activity and product distribution. The results evidence that Pd/Al_2O_3–Co/SiO_2 mixture has a good balance between activity and selectivity, and leads to a very low production of *trans* isomers (11.8 %) and a moderate amount of saturated stearic acid (13.5 %). Consequently, the utilization of cobalt-based catalysts (or the addition of cobalt to other metallic catalysts) could be considered a promising alternative for the hydrogenation of edible oil.

Keywords Vegetable oil · Partial hydrogenation · Ni–Pd–Pt–Co–Cu · *trans* Isomers · Catalyst mixtures

Introduction

The partial hydrogenation of vegetable oils is of great importance in the production of frying oils, shortenings, margarines, industrial oils and greases. Hydrogenation leads to a reduction of color and odor and raises the melting point, resulting in a solid or semisolid product at room temperature. As a consequence of the hydrogenation process, the chemical stability of the product is effectively increased, which allows the product to be used as edible oil, as well as in industrial applications.

Although only *cis* isomers usually exist in untreated vegetable oils, during the hydrogenation process some double bonds are isomerized into the *trans* form. The excessive intake of *trans* fatty acids is associated with a higher risk of coronary heart disease. Dietary studies reveal a four to five-fold higher risk of *trans* fatty acids consumed, as compared to saturated fatty acids [1]. The European Union has recently considered the influence on health of *trans* isomers, and the European Commission was committed to submit a report on the presence of *trans* fats in foods, accompanied by a legislative frame if appropriate, by December 2014 [2].

In the hydrogenation process the composition and properties of the final product depend on various operating conditions, which affect mass and heat transfer, including catalyst concentration, agitation level, hydrogen pressure and temperature. Furthermore, the process is also sensitive to the architecture of the catalyst. Indeed, the mass transport limitations on hydrogen and unsaturated triglycerides to the active sites of the catalysts have a strong influence on both catalyst activity and selectivity. Thus, the isomerization reactions which result in the production of *trans* isomers can be influenced by the type of metal, the structure of the support and the metal-support interaction.

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Industrially, the partial hydrogenation of edible oil is carried out in semi-batch reactors using supported nickel catalysts. These catalysts require temperatures around 150–180 °C and pressures between 0.1 and 0.6 MPa [3]. Nickel catalysts have several advantages, including high activity, low cost and ease of separation from the processed oil. However, these catalysts produce a significant amount of *trans* and saturated fatty acids. In addition, traces of nickel remaining in the oil should be removed, due to toxicity and quality concerns.

Different metallic catalysts have been investigated as an alternative to nickel catalysts. Among them, noble metals have been extensively studied. Although the cost is an important drawback, their much higher activity and the possibility to be reused make noble metal catalysts a promising alternative. In this regard, palladium catalysts are more selective to *cis* isomers than nickel catalysts during the hydrogenation of polyunsaturated fatty acids [4]. Platinum has been found to be highly active and, in general, forms less *trans* isomers than nickel during hydrogenation [5]. Between both metals, it has been reported in the literature that the formation of *trans* isomers is lower for platinum catalysts, compared to palladium catalysts [4].

An alternative to noble metal-based catalysts is the use of formulations using less expensive base metals. Copper-based catalysts, although they possess lower activity than Ni catalysts, have long been known for displaying no activity towards monoenes. These catalysts exhibit an excellent ability to enrich the oil in oleic acid, whereas the formation of saturated stearic acid is very low [6]. Nevertheless, one drawback of copper catalysts is that traces of metal promote the autoxidation of fats [7]. Consequently, traces of metal remaining in the oil should be removed.

Cobalt-containing catalysts are widely used in hydrogen transfer reactions, the Fischer–Tropsch reaction being the most common application, in which cobalt catalysts are used in industrial scale. A cobalt-based catalyst has recently been used in the hydrogenation of vegetable oil for the production of liquid bio-chemicals [8]. Nevertheless, cobalt-based catalysts have been scarcely used in the hydrogenation of edible oil. Cobalt has also the disadvantage of being a pro-oxidant of fats [9].

Several authors have proposed the utilization of a mixture of catalysts, with the aim of improving the activity and selectivity of the catalytic material. Moulton *et al.* [10] used mixtures of copper and nickel catalysts to hydrogenate soybean oil, and found a ratio that provides a higher selectivity than nickel and a higher activity than copper, used separately. Wright *et al.* [11] reported that mixtures of ruthenium and nickel increase the activity and minimize the formation of *trans* isomers. The same authors studied the addition of nickel to a palladium catalyst, in order to improve the selectivity toward *cis* isomers.

Although there are studies in the literature on the influence of the type of catalyst, there is no comprehensive study concerning the performance (activity, selectivity and production of *trans* isomers) of several metallic catalysts (including noble and base metals) composed of Ni, Pd, Pt, Co and Cu, supported on silica and alumina, in the partial hydrogenation of sunflower oil. The specific objectives were: (1) the preparation and characterization of supported metallic catalysts; (2) the investigation of their activity and selectivity towards monoenes and saturated stearic acid; (3) the investigation of alternative strategies such as the use of mixtures of catalysts.

Materials and Methods

Catalyst Preparation

Two different types of supports were used: silica (Köstrosrob 1020) and γ-Al_2O_3 (Spheralite 511B, Procatalyse). The supports were crushed and sieved, in order to retain particles with a size of 17–80 μm.

Nickel catalysts were prepared by deposition–precipitation [12]. This method is based on the heterogeneous precipitation of nickel, using 100 mL of an aqueous solution of nickel nitrate [0.14 M $Ni(NO_3)_2{\cdot}6H_2O$, Fluka], 0.02 M nitric acid (Probus) and 0.42 M urea (Scharlau), slurried with silica or alumina (3 g). The slurry was shaken at 90 °C for 14 h in a rotary evaporator RE11 (Büchi). The precipitation was produced by the slow and homogeneous change in the pH from 4.6 to 5.5, induced by the thermal decomposition of urea. The precipitate was then allowed to cool at room temperature, filtered, washed and dried (110 °C, 14 h).

Supported palladium catalysts were prepared by diffusional impregnation [13]. Silica and alumina were impregnated with an aqueous solution of $PdCl_2$ (0.28 M, pH = 2, Fluka). The solution of $PdCl_2$ was prepared by dissolving palladium metal in aqua regia. This solution was then evaporated to dryness, and the precipitate was dissolved in an HCl solution (Panreac). The solution and the support were in contact for 20 min, using an impregnation ratio of 3 mL g^{-1} of support. The solvent was then slowly removed by heating at 60 °C in vacuum, and the solid was dried (110 °C, 10 h) and calcined (300 °C, 4 h).

Platinum catalysts were prepared following the incipient wetness technique [14]. Silica and alumina supports were impregnated with an aqueous solution of H_2PtCl_6 (Sigma Aldrich) under constant agitation. The volume of solution used was equal to the pore volume of the support. The solution concentration was that required to obtain the prefixed metal concentration. The solids were then dried (120 °C, 1 h) and calcined (300 °C, 4 h).

Supported cobalt catalysts were prepared following the ammonia method used by Barbier *et al.* [15]. 25 g of $Co(NO_3)_2\ 6H_2O$ (Probus) was added to 150 mL of water at room temperature and under agitation to prevent the oxidation of Co^{2+}. Afterwards, a solution of ammonia (30 wt %, Sigma Aldrich) was poured over the solution to produce the precipitation of $Co(OH)_2$. The precipitate was dissolved by an excess of ammonia (20 mL), and 10 g of support (silica or alumina) was added to the solution. After the solution reached an equilibrium pH value near 12, the system was stirred for 72 h. Finally, the solid was filtered, washed, dried (110 °C, 10 h) and calcined (400 °C, 4 h).

Copper catalysts were prepared by chemisorption-hydrolysis, following the method used by Boccuzzi *et al.* [16]. Ten grams of the support (silica or alumina) was added to a solution, prepared by adding NH_4OH (Sigma Aldrich) to a $Cu(NO_3)_2{\cdot}3H_2O$ solution (Sigma Aldrich) until a pH of 9. After 20 min of stirring, the slurry was diluted slowly in an ice bath at 0 °C, in order to allow the hydrolysis of the copper complex, as well as the deposition of the finely dispersed product. The solid was then separated by filtration, washed, dried (110 °C, 12 h) and calcined (300 °C, 4 h).

Before the hydrogenation process, all catalyst precursors were activated by reduction in a CHESA quartz tube furnace. First, samples were dried at 150 °C in a flow of pure hydrogen for 1 h to remove any trace of water. Then, temperature was raised up to the final reduction temperature. Samples were kept at the final temperature for a period of 6 h, in order to complete the reduction of the most stable fraction. The reduction temperature was established based on the results of temperature programmed reduction discussed below.

Catalyst Characterization

Samples of catalyst precursors were subjected to the temperature programmed reduction (TPR) technique, in order to determine the temperature interval at which the reduction process takes place. Measurements were performed using a Micromeritics AutoChem II 2920 apparatus, equipped with a thermal conductivity detector. Samples (20 mg) were heated from room temperature to 900 °C, at a heating rate of 5 °C min^{-1}, under a flow of 5 % H_2/Ar and at atmospheric pressure. Prior to the analysis, samples were subjected to a sweeping treatment with argon at 450 °C for 15 min.

The metal content of the catalysts was determined by inductively coupled plasma-atomic emission spectrometry analysis (Agilent 7700 X), after dissolving them in concentrated HNO_3. The textural properties (specific surface area, pore volume and pore diameter) of supports and catalysts were determined by nitrogen adsorption–desorption at 77 K in a Micromeritics ASAP 2010 equipment.

Hydrogenation Experiments

Experiments were performed using as feedstock a commercial refined sunflower oil (iodine value 138.1 ± 0.4) with the following composition in fatty acids: palmitic acid (16:0) 6.02 ± 0.12 %, stearic acid (18:0) 3.77 ± 0.08 %, oleic acid (18:1) 20.11 ± 0.37 %, linoleic acid (18:2) 69.76 ± 0.89 %, linolenic acid (18:3) 0.15 ± 0.02 % and arachidonic acid (20:4) 0.19 ± 0.03 %.

Hydrogenation experiments were carried out in a 300-mL stainless steel reactor, operated in a semi-continuous mode. The reactor was provided with four baffles to prevent vortex formation, thus allowing a suitable turbulence level. The reactor was heated using a PID controlled electric resistance attached to a Pt100 temperature sensor immersed in the liquid. A continuous flow of hydrogen was used, in excess of the stoichiometric amount, in order to obtain higher yield, as well as reproducible results.

In a typical hydrogenation run, 75 g of sunflower oil and the required amount of each catalyst (to yield a fixed metal to oil ratio) were charged into the reactor. After loading, the reactor was purged with nitrogen to ensure an oxygen free environment. The system was heated up to the reaction temperature while stirring, and then a flow of hydrogen was introduced. The reactor was purged for 15 s to eliminate nitrogen, and then pressure was increased up to the operation value. The time at which the operating pressure was reached was considered to be the initial time. During the hydrogenation process, samples of oil were collected through a sampling valve.

Refractive indices, measured at 60 °C using a refractometer (Abbé PZO-RL1), were used to monitor the progress of the hydrogenation reaction. A calibration curve was prepared to relate the refractive index to the iodine value (IV) of partially hydrogenated oils, measured by the Hanus method.

The fatty acid composition of oil samples was measured by gas chromatography. The reaction products were converted into their methyl esters and analysed in a 8700 Perkin-Elmer gas chromatograph, equipped with a flame ionization detector and split-splitless capillary inlet in a 50 m capillary column (Tracsil TR CN100, Tecnokroma). The injector and detector temperatures were 280 and 250 °C, respectively. Helium and hydrogen were used as carrier gases. After the oven temperature was kept constant at 80 °C for 6 min, temperature was raised up to 200 °C at a heating rate of 10 °C min^{-1}, and held for 20 min. The total amount of *trans* isomers was calculated as the sum of all C_{18} *trans* isomers.

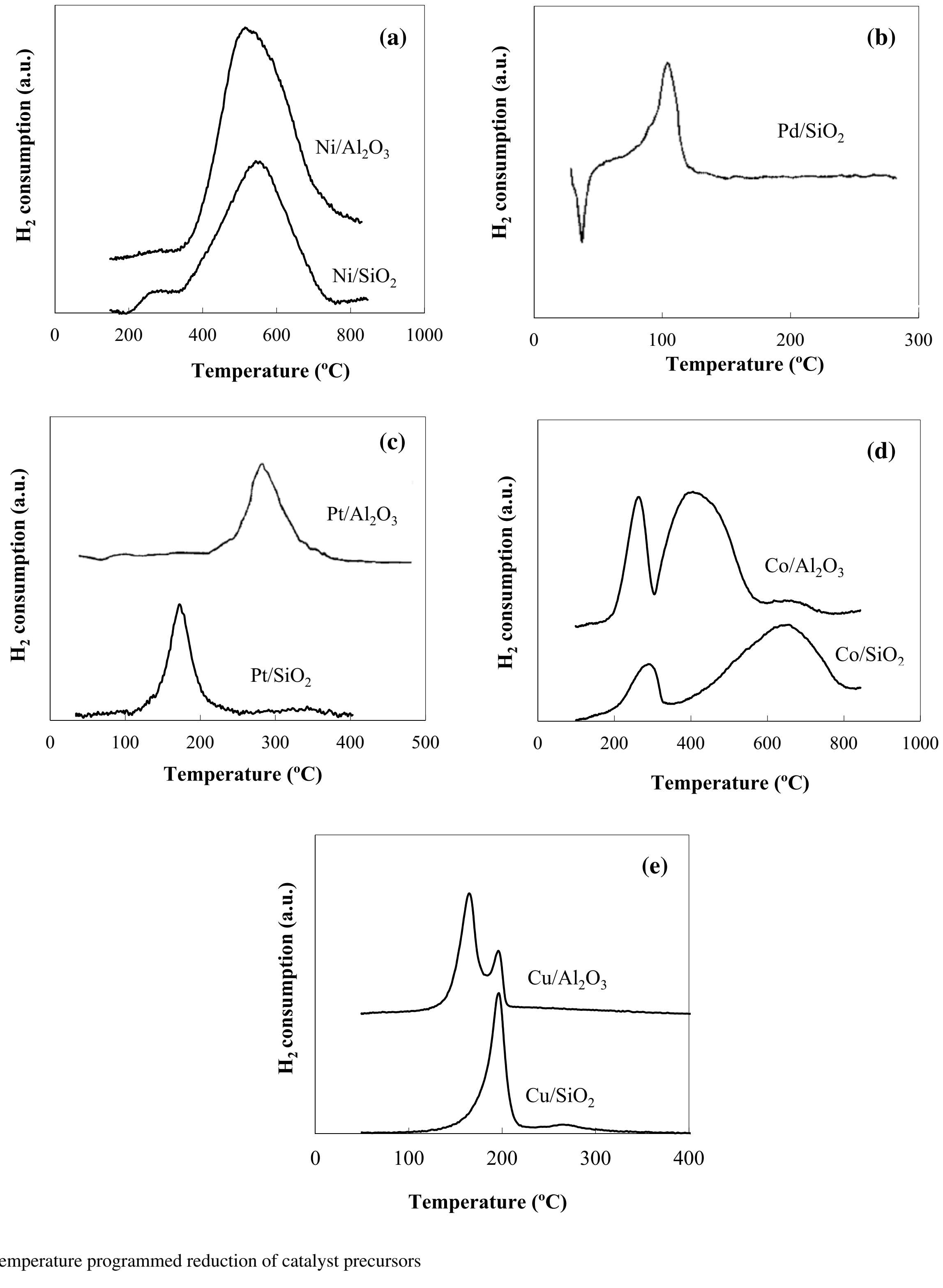

Fig. 1 Temperature programmed reduction of catalyst precursors

Table 1 Reduction temperature applied to each catalyst and criteria for the selection

Catalyst	Reduction *T* applied (°C)	Based on
Ni/SiO_2 and Ni/Al_2O_3	550	TPR (peak at 550 °C) [12, 23]
Pd/SiO_2 and Pd/Al_2O_3	300	TPR (peak at 120 °C) [4, 24]
Pt/SiO_2 and Pt/Al_2O_3	300	TPR (peaks at 180–280 °C) [4, 24]
Co/SiO_2 and Co/Al_2O_3	600	TPR (peaks at 400–650 °C) [20]
Cu/SiO_2 and Cu/Al_2O_3	320	TPR (peaks at 200–250 °C) [25]

Results and Discussion

Catalyst Characterization

Temperature-Programmed Reduction

Figure 1 displays the TPR profiles of catalyst precursors. Supported nickel catalysts exhibit a unique broad reduction peak with a maximum near 500 °C (Fig. 1a). This profile can be explained by the preparation method used. The hydrolysis of urea has the advantage of increasing the hydroxyl ion concentration, thus leading to a limited nucleation, which results in a homogeneous distribution of small particles over the support. The high temperatures required for both nickel catalysts evidence the presence of compounds of difficult reducibility. Nickel hydroxide has been reported to react with silica support to form nickel hydrosilicate, a highly dispersed phase [17]. When alumina is used as a support, the maximum of the reduction peak takes place at a slightly lower temperature. In this regard, although nickel hydroaluminate might also be formed, the formation of this phase would take place to a lesser extent, thus resulting in a weaker metal-support interaction.

The TPR profile of Pd/SiO_2 (Fig. 1b) has a different shape, with a negative peak at 50 °C and a positive hydrogen consumption around 120 °C. The consumption of hydrogen is due to the reduction of palladium oxide:

$$PdO + H_2 \rightarrow Pd + H_2O \quad (1)$$

Regarding the negative peak, it is known that palladium crystals can adsorb hydrogen at room temperature to form palladium hydride, PdH [18]. As the temperature is increased, this phase decomposes, resulting in the release of hydrogen.

The reduction of PdO supported on alumina takes place at room temperature. Due to the low reduction temperature required, hydrogen consumption cannot be observed in the TPR profile, since the apparatus cannot operate at such low temperatures.

Figure 1c shows the TPR profiles of platinum supported precursors. Pt/SiO_2 exhibits a peak at 180 °C and a very weak band between 200 and 350 °C. The peak at low temperature is attributed to the reduction of PtO_2 species. The band at higher temperature could be attributed to the reduction of oxy or hydroxychlorinated Pt species, which have a strong interaction with the support, probably due to the formation of a silicate [19]. Pt/Al_2O_3 catalyst shows a peak centered at 280 °C, attributed to the consumption of H_2 caused by the interaction between Pt oxide species and Al_2O_3 support.

The hydrogen consumption profiles of cobalt precursors are shown in Fig. 1d. Three regions of H_2 consumption can be identified for Co/Al_2O_3. The first peak, with a maximum near 250 °C, could be associated with the reduction of Co_3O_4 formed by calcination to CoO, whereas the peak at 400 °C is attributed to the reduction of CoO to metallic cobalt [20]. Moreover, Co/Al_2O_3 sample exhibits a very weak band at 650 °C, which could be ascribed to Co species that interact strongly with alumina support.

Co/SiO_2 sample exhibits two peaks, at 280 and 650 °C. The first peak could be related to the reduction of Co(III) to Co(II). Regarding the second peak, its shape (different from that of Co/Al_2O_3) and the separation between the two maxima, suggests that this peak could not only be attributed to the reduction of Co(II) to metallic cobalt. It is hypothesized that the last reduction peak appears as a consequence of the reduction of Co(II) and species of cobalt having different interaction strengths with silica support [21].

Figure 1e displays the TPR profiles of supported copper precursors. For both samples, the consumption of H_2 takes place at low temperature, between 150 and 300 °C. Cu/SiO_2 exhibits a well defined reduction peak with a maximum around 200 °C, attributed to the reduction of highly dispersed CuO particles to metallic copper. Furthermore, the Cu/SiO_2 sample shows a very weak and no clearly defined band at 250–300 °C. This hydrogen consumption could be related to the reduction of highly dispersed copper species and/or ions that are more difficult to reduce, since they have a strong interaction with the support.

The profile of Cu/Al_2O_3 has two peaks. The peak at high temperature is related to the reduction of Cu(II) species. The peak at low temperature region is assigned to highly dispersed copper species which are easy to reduce. These copper species might include Cu_2O oxide, isolated Cu^{2+} ions that interact strongly and weakly with alumina support and small two-dimensional or three-dimensional clusters [22].

The reduction temperature of the catalysts was established based on the TPR results, as well as on the preparation methods reported in the literature. Table 1 summarizes the reduction temperature used for each catalyst.

Table 2 Properties of supports and supported metallic catalysts

Catalyst	Metal (%)	S_{BET}^{a} (m^2 g^{-1})	V_p^b (cm^3 g^{-1})	D_p^c (Å)
Silica (SiO_2)	–	330.0	1.52	175.3
Alumina (Al_2O_3)	–	305.3	0.41	62.2
Ni/SiO_2	20.4	405.3	2.15	113.7
Ni/Al_2O_3	19.1	240.2	0.33	54.0
Pd/SiO_2	5.2	270.8	1.19	163.6
Pd/Al_2O_3	4.9	228.6	0.28	60.7
Pt/SiO_2	2.2	277.2	1.45	182.8
Pt/Al_2O_3	2.1	264.0	0.32	58.8
Co/SiO_2	35.4	194.3	0.64	136.2
Co/Al_2O_3	36.9	209.1	0.36	79.7
Cu/SiO_2	14.6	291.5	0.67	88.1
Cu/Al_2O_3	8.3	164.8	0.28	65.8

[a] Specific surface area (BET method)

[b] Pore volume (BJH method, adsorption branch)

[c] Pore diameter (BJH method, adsorption branch)

Textural Properties of Catalysts

Table 2 shows the properties of supports and supported metal catalysts: metal content, BET specific surface area, pore volume and average pore diameter.

It can be observed that, in general, the BET surface area of metallic catalysts is lower than that of the supports (SiO_2 or Al_2O_3). This effect could be attributed to the partial blockage of support pores due to the addition of the metal. Contrary to the general trend, the specific surface area of Ni/SiO_2 catalyst is 22.8 % higher than that of the support, which could be explained by the formation of porous structures of nickel hydrosilicate of high surface area. The effect of the support on the specific surface area depends on the type of metal. Pt and Co catalysts exhibit a similar BET surface area, irrespective of the support. On the contrary, Ni, Pd and Cu catalysts exhibit a higher surface area when silica is used as a support (68.7 % higher for Ni, 18.5 % for Pd and 76.9 % for Cu).

The pores of the catalyst must be large enough so that the active metal is accessible to triglyceride molecules. The oil molecular weight is about 890 g mol^{-1} and its diameter about 15 Å, considering a spherical molecule. The results of a previous study [26] suggest that a pore diameter three times larger than triglyceride molecular radii ensures an adequate diffusion through the pores of the catalyst and therefore the progress of the reaction. Surface area in the micropore range would not be available for the hydrogenation reaction. According to data in Table 2, the accessibility of the reactants inside the catalyst pores is not hindered.

Catalyst Activity

A comparative study of sunflower oil hydrogenation was performed. Due to the different activity of the catalysts, two series of experiments were carried out. The operating conditions are as follows: (a) 150 °C, 3.5 bar and a metal to oil ratio of 2.5×10^{-5} g_{metal} g_{oil}^{-1} for Pd and Pt catalysts; (b) 180 °C, 4.5 bar and a metal to oil ratio of 1.2×10^{-3} g_{metal} g_{oil}^{-1} for Co and Cu, as these catalysts possess a lower activity. For a better comparison, nickel-based catalysts were employed in both series of experiments, to be used as a reference.

Table 3 Percentage of *cis* and *trans* oleic acid and stearic acid for the indicated catalysts, corresponding to an IV of 70

Catalyst	*T* (°C)	*P* (bar)	Metal/oil ratio (g_{metal} g_{oil}^{-1})	Time to reach an IV = 70 (min)	Content of *cis*-C18:1 (%)	Content of *trans*-C18:1 (%)	Content of C18:0 (%)
Ni/SiO_2	150	3.5	2.5×10^{-5}	122	42.1	26.0	19.4
Ni/Al_2O_3	150	3.5	2.5×10^{-5}	125	43.4	25.7	14.6
Pd/SiO_2	150	3.5	2.5×10^{-5}	97	36.1	39.1	18.0
Pd/Al_2O_3	150	3.5	2.5×10^{-5}	49	35.7	44.7	16.3
Pt/SiO_2^a	150	3.5	2.6×10^{-5}	540	39.1	6.5	20.8
Pt/Al_2O_3	150	3.5	2.7×10^{-5}	102	37.7	33.0	21.8
Ni/SiO_2	180	4.5	1.2×10^{-3}	44	38.3	26.1	33.6
Ni/Al_2O_3	180	4.5	1.3×10^{-3}	67	43.0	32.4	12.4
Co/SiO_2	180	4.5	1.3×10^{-3}	119	34.8	32.4	8.3
Co/Al_2O_3	180	4.5	1.3×10^{-3}	83	39.1	44.2	7.9
Cu/SiO_2^b	180	4.5	1.2×10^{-3}	600	43.7	42.0	4.9
$Cu/Al_2O_3^c$	180	4.5	1.2×10^{-3}	630	40.2	32.4	4.9

[a] For an IV of 93

[b] For an IV of 73

[c] For an IV of 76

The hydrogenation activity of the catalysts was monitored by the decay of IV (Table 3). It was measured the time required to reach an IV of 70. This value was selected because: (1) it is a typical value for oleomargarine, the final product, and (2) it corresponds to the point at which the formation of stearic acid begins to be important.

The hydrogenation activity of the first set of catalysts decrease in the order: $Pd/Al_2O_3 > Pd/SiO_2 > Pt/Al_2O_3 > Ni/SiO_2 > Ni/Al_2O_3 \gg Pt/SiO_2$. Thus, the activity of Pd catalysts is higher than that of Ni catalysts. On the contrary, for the catalysts based on Pt, the activity depends to a great extent on the support. In fact, Pt/Al_2O_3 is more active than Ni catalysts, whereas Pt/SiO_2 exhibits the lowest hydrogenation activity. The activity of Pt/SiO_2 catalyst is much lower than expected, based on the activity of Pd metal and on its textural properties (the specific surface area of this catalyst is very similar to that of Pt/Al_2O_3). This behavior could be explained by the TPR profiles of both supported Pt catalysts. In fact, Pt/Al_2O_3 shows a well defined peak at 280 °C, ascribed to the interaction of platinum oxide species and the support, while this band is very weak for Pt/SiO_2. Thus, this interaction would hardly take place, thus resulting in a poorer dispersion of Pt.

Regarding the performance of the second group of catalysts, the hydrogenation activity of Cu catalysts was found to be very low, which is attributed to the low hydrogen adsorption ability of this metal. Co catalysts show a hydrogenation activity lower than that of Ni catalysts. Overall, these results are in good agreement with the order in hydrogenation activity proposed by Kitayama et al. [27]: Pd > Pt > Ni > Cu.

The influence of the support is different depending on the metal studied. Al_2O_3 allows for more active Pd, Pt and Co catalysts than SiO_2. The influence of the support is much more pronounced for supported Pt catalysts. In fact, Pt/SiO_2 catalyst has the lowest activity of all the catalysts studied. On the contrary, SiO_2 support results in Ni and Cu catalysts of higher activity.

Product Distribution

Figures 2 and 3 display the fatty acid composition profiles of the hydrogenation of sunflower oil with Ni, Pd and Pt catalysts, and Ni, Co and Cu catalysts, respectively.

The total conversion of linoleic acid was achieved at different reaction times, depending on the catalyst (i.e., 50 min for Pd/Al_2O_3 and 600 for Cu/SiO_2). Linoleic acid was not fully converted using Pt/SiO_2 and Cu/Al_2O_3 catalysts, due to their low hydrogenation activity. Regarding the level of oleic acid, it increases first, then levels off (reaching a value of 40–50 %) and subsequently decreases, except for the catalysts with very low activity. The monoenic *trans* fatty acid profiles exhibit a similar trend, with its maximum (very different in value, depending on the catalyst) achieved after that of *cis*-C18:1. In general, the stearic acid content remains low (at 5–7 %) up to a reaction time of 40–60 min and then steadily increases.

Figures 2 and 3 are useful as they give an overview of the performance of each catalyst over the whole reaction period. Nevertheless, it is essential to analyze the product distribution corresponding to a target IV, specially the amount of *trans* oleic acid and saturated stearic acid, which are of prime importance from the viewpoint of the quality of the final product. Table 3 shows the percentage of *cis* and *trans*-C18:1 and C18:0 for the selected IV level of 70.

Among the first group of catalysts (Ni, Pd and Pt), the highest percentage of *trans*-C18:1 is obtained with Pd, supported in either silica (39.1 %) or alumina (44.7 %), followed by Pt/Al_2O_3. The amount of *trans* isomers is the lowest (6.5 %) for Pt/SiO_2. Although this percentage has been obtained for an IV of 93 (after 9 h of reaction time, due to the low activity of this catalyst), for an IV of 70 a content of *trans* isomers lower than that of the other catalyst could be expected. The higher production of *trans*-C18:1 of Pd catalysts, compared to Pt catalysts has been previously reported in the literature [4], and is attributed to their higher activity, as well as to the formation of conjugated dienes on Pd catalyst surface. Numwong *et al*. [24] have recently reported the following order in the selectivity towards *trans* isomers in the partial hydrogenation of vegetable oil-derived fatty acid methyl esters, using metallic catalysts supported on silica: Pd > Ni > Pt. These authors attributed the low *trans* selectivity of Pt and Ni catalysts to the subsequent hydrogenation of the intermediate *trans*-monounsaturated to saturated compounds. Regarding the formation of stearic acid, the values range between 14.6 and 21.8 %, the highest values being for supported Pt catalysts.

Among Ni, Co and Cu catalysts, the highest amount of *trans* isomers is obtained with Co/Al_2O_3 (44.2 %), followed by Cu/SiO_2 (42.0 %). Ni/SiO_2 exhibits the lowest content of *trans*-C18:1 (26.1 %), whereas the other three catalysts result in the production of a similar amount. The production of stearic acid follows the order: Ni > Co > Cu. A very low amount of stearic acid (below 5 %) is produced using supported copper catalysts.

Mixtures of Catalysts

In order to strike a balance between the catalytic activity and the level of *trans* and saturated fatty acids, binary mixtures of catalysts were studied. Pd/Al_2O_3 was used in every mixture, since it provides the highest activity. The second catalyst was chosen on the basis of the production of the lowest amount of *trans*-C18:1: Pt/SiO_2, Cu/Al_2O_3, Co/SiO_2 and Ni/SiO_2.

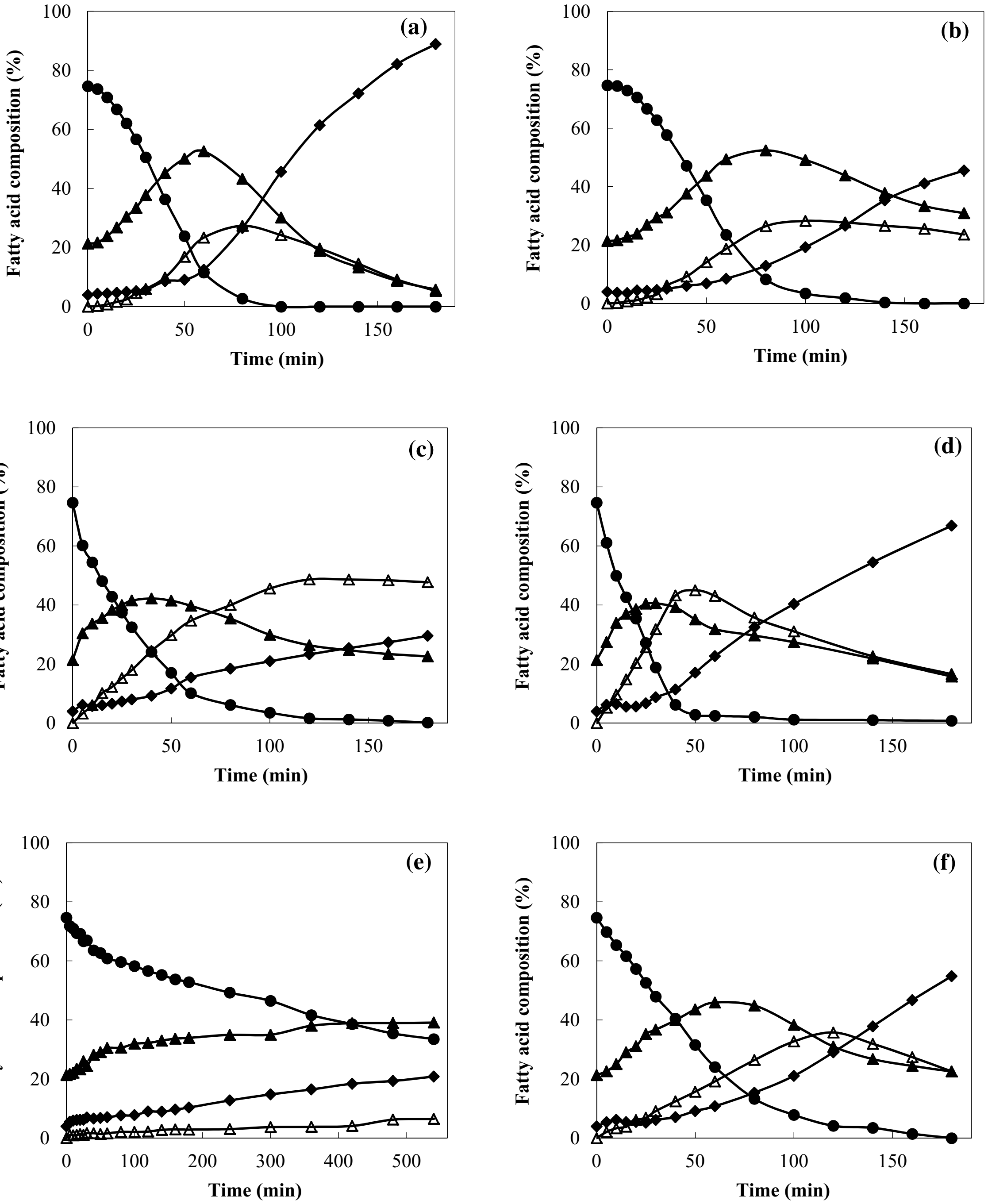

Fig. 2 Time course profiles of reactants and products (*circles*) C18:2; (*closed triangles*) C18:1 *cis*; (*open triangles*) C18:1 *trans*; (*diamonds*) C18:0; during the hydrogenation of sunflower oil: **a** Ni/SiO_2 catalyst; **b** Ni/Al_2O_3 catalyst; **c** Pd/SiO_2 catalyst; **d** Pd/Al_2O_3 catalyst; **e** Pt/SiO_2 catalyst; **f** Pt/Al_2O_3 catalyst. Reaction conditions: temperature 150 °C; H_2 pressure 3.5 bar

The hydrogenation of sunflower oil was carried out at 120 °C and 3.5 bar. These milder operating conditions were selected with the aim of minimizing the production of *trans* isomers and saturated stearic acid, while obtaining an acceptable level of activity, provided by Pd/Al_2O_3 catalyst.

The concentration of the catalyst in the oil was the same as that used when the catalysts were employed separately. The ratio between the content of palladium and the other metal is summarized in Table 4, as well as the time required to reach an IV = 70 and the content of *cis*, *trans* and saturated fatty acids.

According to the data of Table 4, under the operating conditions used, Pd/Al_2O_3 results in a much lower production of *trans* monoenes (24.1 *vs* 44.7 %), compared to the

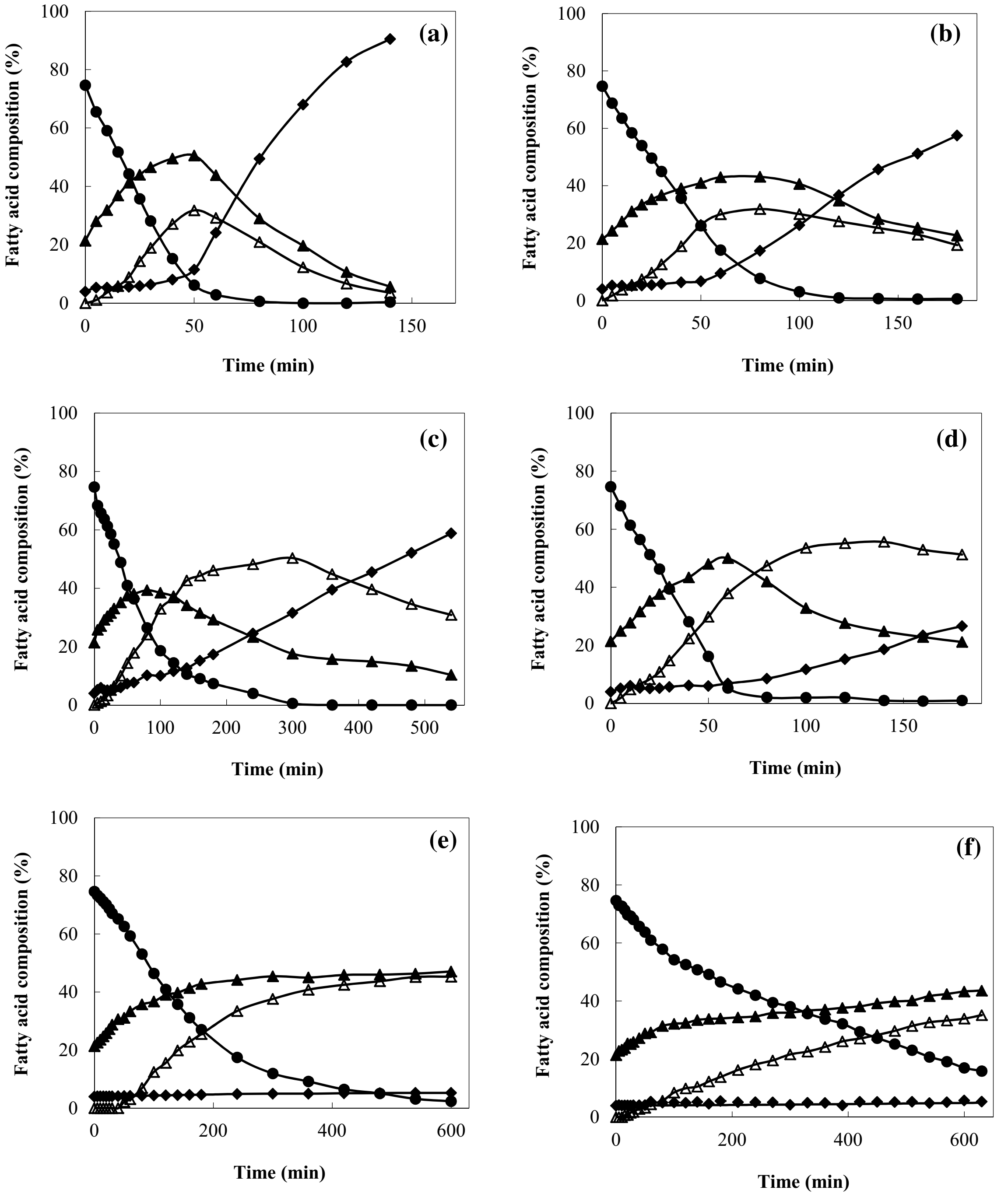

Fig. 3 Time course profiles of reactants and products (*circles*) C18:2; (*closed triangles*) C18:1 *cis*; (*open triangles*) C18:1 *trans*; (*diamonds*) C18:0; during the hydrogenation of sunflower oil: **a** Ni/SiO_2 catalyst; **b** Ni/Al_2O_3 catalyst; **c** Co/SiO_2 catalyst; **d** Co/Al_2O_3 catalyst; **e** Cu/SiO_2 catalyst; **f** Cu/Al_2O_3 catalyst. Reaction conditions: temperature 180 °C; H_2 pressure 4.5 bar

values obtained using a temperature of 150 °C (Table 3). The decrease in the production of stearic acid is less pronounced (11.8 *vs* 16.3 %).

Regarding the content of *trans*-C18:1 and stearic acid, two mixtures result in a slight variation (compared to Pd/Al_2O_3): Pd/Al_2O_3–Ni/SiO_2 and Pd/Al_2O_3–Pt/SiO_2. Although Ni/SiO_2 and Pt/SiO_2 lead to the production of low amounts of *trans* isomers (especially Pt/SiO_2), this effect cannot be observed when used in conjunction with Pd/Al_2O_3.

In contrast, two mixtures of catalysts provide a better product distribution. The addition of Cu/Al_2O_3 results in

Table 4 Percentage of *cis* and *trans* oleic acid and stearic acid for the indicated mixtures of catalysts, corresponding to an IV = 70

Catalyst	Pd/metal	Time to reach an IV = 70	Content of *cis*-C18:1 (%)	Content of *trans*-C18:1 (%)	Content of C18:0 (%)
Pd/Al_2O_3	–	170	45.2	24.1	11.8
Pd/Al_2O_3–Ni/SiO_2	1.19	105	44.8	25.6	11.6
Pd/Al_2O_3–Cu/Al_2O_3*	0.02	300	51.6	20.1	7.7
Pd/Al_2O_3–Co/SiO_2	0.02	98	56.3	11.8	13.5
Pd/Al_2O_3–Pt/SiO_2	0.96	102	45.5	24.2	11.3

* For an IV = 77.5

a decrease of 16.6 % in the production of *trans* monoenes (20.1 *vs* 24.1) and a reduction of 34.7 % in saturated stearic acid (7.7 *vs* 11.8 %). It should be noticed, nonetheless, that since this mixture of catalysts provide a much lower activity, the values correspond to an IV of 77.5.

Finally, Pd/Al_2O_3–Co/SiO_2 mixture results in a dramatic reduction of *trans* isomers (11.8 *vs* 24.1 %, a reduction of 51.0 %), whereas it leads to a slightly higher amount of saturated stearic acid (13.5 *vs* 11.8 %). This catalyst has a good balance between activity and selectivity, and provides the best product distribution of all the catalysts studied, both individually or in mixtures. Indeed, although Pt/SiO_2 used separately leads to a promising amount of *trans* isomers (6.5 % for an IV of 93), its low activity does not allow this catalyst to be considered suitable for the hydrogenation of sunflower oil.

Conclusions

The overall hydrogenation activity of the catalysts depends on both the type of metal and support. The following order can be proposed for the effect of the metal: Pd > Pt > Ni > Co > Cu. The influence of the support is different depending on the metal. Al_2O_3 allows for more active catalysts based on noble metals (Pd and Pt) and Co, the effect being much more pronounced for Pt. On the contrary, SiO_2 support results in catalysts based on Ni and Cu of higher activity. At a target IV of 70 (a typical value for oleomargarine), the production of *trans* isomers is minimum for Ni catalysts. On the contrary, the highest percentage of *trans*-C18:1 is obtained with Pd catalysts.

In order to strike a balance between the catalytic activity and product distribution, binary mixtures of catalysts have been studied. Among the mixtures studied, Pd/Al_2O_3–Co/SiO_2 results in a very low production of *trans* isomers (11.8 %), and a moderate amount of saturated stearic acid (13.5 %). This catalytic mixture has a good balance between activity and selectivity, and provides the best product distribution of all the catalysts studied. Consequently, from the standpoint of catalyst performance, the utilization of cobalt-based catalysts (or the addition of cobalt to other metallic catalysts), used in other hydrogenation processes, could be considered a promising alternative for the partial hydrogenation of vegetable oil. Further research is required to study the issue of autoxidation of fats (and thus, the economic feasibility), which is the main drawback of cobalt-based catalysts.

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