Pd/Al$_2$O$_3$-cordierite and Pd/Al$_2$O$_3$-Fecralloy monolithic catalysts for the hydrogenation of sunflower oil

Jhon F. Sánchez M [a], Orlando J. González Bello [b,1], Mario Montes [b], Gabriela M. Tonetto [a,*], Daniel E. Damiani [a]

[a] PLAPIQUI (UNS-CONICET), Camino La Carrindanga Km 7, Bahía Blanca, CP 8000, CC 717, Argentina
[b] Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, UPV/EHU, Apdo. 1072, 20080 San Sebastián, Spain

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ABSTRACT

Monolithic catalysts were prepared using cordierite and Fecralloy as substrates, with Pd/Al$_2$O$_3$ catalyst deposited by a washcoating method. The samples were characterized and studied for the partial hydrogenation of sunflower oil at 373 K and 413 kPa.

In comparative tests, at equal operating conditions and conversion, the structured catalysts presented a lower *trans*-isomers formation than the powder catalyst.

After three consecutive tests, the ceramic monolith showed no change in activity or selectivity, whereas the metallic monolith showed a partial deactivation (10%), which is attributed to a loss of catalyst.

1. Introduction

The hydrogenation of edible oils has been carried out industrially since the beginning of the 20th century for increasing the fusion temperature and oxidation resistance. Besides the reduction, the isomerization of double bonds also takes place. The demand for lower *trans*-fatty acid levels in hydrogenated oils has led to different attempts to improve the hydrogenation process. A novel approach is the application of structured catalytic systems [1–3]. Their application would allow to eliminate some steps of the hydrogenation process. This could compensate for the higher costs of the catalyst if the operational problems posed by, among other aspects, the possibility of recovery and reuse of the catalyst are solved.

In recent years carbon coated monoliths have been used as catalyst supports in the hydrogenation of fatty acid methyl esters, showing that there exists a strong interplay between the carbon support properties and its performance in the Pd catalyzed selective hydrogenation of edible oils [2,3].

The present work studies the potential use of both monolithic systems, metallic and ceramic, in the partial hydrogenation of sunflower oil. Cordierite and Fecralloy substrates were coated with a Pd/Al$_2$O$_3$ catalyst, and the results compared to those obtained with a powder catalyst used in slurry.

2. Experimental

2.1. Catalyst preparation

The Pd/Al$_2$O$_3$ catalyst was prepared by the method of incipient wetness of a γ-Al$_2$O$_3$ support (Procatalyse, Spheralite 505, 257 m^2/g) with an aqueous solution of Pd(NO$_3$)$_2$ · 2H$_2$O (8.3 wt.% Pd, Johnson-Matthey). After impregnation, the catalyst was dried at 353 K for 2 h, and then calcined at 773 K for 2 h.

Cordierite (3SiO$_2$:2Al$_2$O$_3$:2MgO) with a honeycomb structure (400 cpsi) was used as ceramic substrate. Fecralloy, a ferritic stainless steel with high Al content (Goodfellow LS304496/4, 0.05 mm thick), was used as metallic substrate. Table 1 shows its chemical composition. Monoliths of 350 cpsi were prepared according to the method described in [4]. Then the samples were calcined at 1173 K for 22 h. Both monolithic catalysts were prepared as cylinders (14 mm diameter × 15 mm height).

Washcoating. The composition of the slurry was: 34 g catalyst, 23 g boehmite slurry (40% Al(OH)$_3$) and 43 g deionized water, while the pH was adjusted to 4 with a 0.5 M HNO$_3$ solution. The boehmite was used as binder [5].

* Corresponding author. Tel.: +54 291 4861700; fax: +54 291 4861600.
  E-mail address: gtonetto@plapiqui.edu.ar (G.M. Tonetto).
[1] Energy Unit, Department of Bioenergy, INASMET–TECNALIA, Mikeletegi Pasealekua, 2 - Parque Tecnológico, E–20009, San Sebastián, Spain.

Table 1
Chemical composition (wt.%) of the refractory steel Fecralloy®.

Fe	Cr	Al	Zr	Y
72.8	22.0	5.0	0.1	0.1

The monoliths were dipped in the catalytic slurry at 6 cm/min and maintained immersed for 15 s. They were then withdrawn at the same speed. The excess of slurry was eliminated by centrifugation. Then the monoliths were dried at 353 K for 2 h. This procedure was repeated until obtaining an approximate catalyst loading of 100 mg. Finally the samples were calcined at 773 K for 2 h.

The powder catalyst was obtained by drying at 353 K and further calcination at 773 K the corresponding colloidal slurry. This sample will be referred to as Pd/Al_2O_3. The same catalyst deposited on the metallic substrate will be referred to as FM, and on ceramic substrate as CM.

Boehmite was used as primer in the metallic substrates following the protocol described for washcoating. The samples were dried at 353 K and calcined at 823 K. The monoliths were then coated with the catalyst slurry. These samples are referred to as FM + P.

2.2. Catalyst characterization

The metallic content of the catalyst was determined by atomic absorption spectroscopy in a GBC AVANTA Σ spectrometer. The palladium particle size was determined by transmission electron microscopy (TEM) (JEOL 100 CX) operating at 100 kV.

The powder catalyst particle size distribution was evaluated by laser diffraction using a Mastersizer 2000 analyzer (Malvern Instrument).

The texture properties were studied by nitrogen adsorption isotherms at 77 K (Micromeritics ASAP 2020). The morphology and thickness of the catalyst layer deposited on the monolith substrates were analyzed by scanning electron microscope (SEM) (JEOL 35 CF).

The catalyst adhesion on the substrate was estimated by evaluating the weight loss of a catalyst-coated sample treated in a supersonic bath (Bandelin SONOREX 10P) at maximum frequency for 30 min [6].

The slurry viscosity was measured in a rotational viscosimeter (Haake VT500, NV geometry) at 298 K.

2.3. Catalysts evaluation

The hydrogenation experiments were carried out in semi batch 600 ml Parr reactor, which can be equipped with different stirrers as shown in Fig. 1. Chromatographic H_2 (AGA) and a commercial sunflower oil were used.

The reaction was studied at 373 K and 413 kPa, stirring at 800 rpm. The amount of catalyst used in all the tests was 200 mg (powder or supported on monolith). The catalyst was reduced *in situ* (373 K, 30 min), and then the oil was introduced into the reactor (previously deoxygenated). In the case of monolithic catalysts, three consecutive tests were performed (with no treatment or intermediate activation) in order to study the reuse of the samples.

The analytical studies were carried out chromatographically (AGILENT 4890D) using a flame ionization detector (FID), according to the AOCS Ce 1c-89 norm. A 100 m long SUPELCO 2560 capillary column, with a nominal diameter of 0.25 mm and a nominal film thickness of 0.20 mm, was used for the separation of the different compounds present in the samples. The iodine number was calcu-
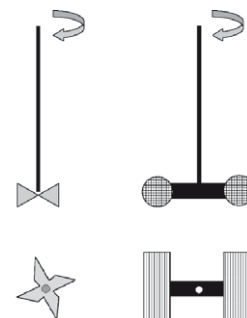

Fig. 1. Schematic views of the stirrers: (A) stirrer of inclined blades (used with the powder catalyst); (B) monolithic stirrer.

lated from the fatty acid composition following the AOCS Cd 1c-85 norm.

3. Results and discussion

3.1. Catalyst preparation

The metallic loading of the Pd/Al_2O_3 catalyst was 3.8 wt.%, and the specific surface area was 237 m^2/g. The powder sample presented an average particle size of 4.8 μm, and 90% of the total had a particle size smaller than 11.0 μm. The Pd metallic particle size determined by TEM was 3 nm. This powder catalyst was used to prepare the slurry (5.1 cp and pH = 3.1).

The Fecralloy substrate was thermally pretreated to induce the migration of aluminium from the bulk to the surface by atomic diffusion mechanism [7]. Under the oxidizing atmosphere, a rough layer of strongly adhered alumina whiskers (α-alumina, corundum) is formed, providing a high roughness to the metallic surface with a characteristic morphology (Fig. 2a) [8]. This alumina layer was used for anchoring the catalytic coating.

Table 2 presents the primer loading, the results of the adherence test and the surface area of the samples.

The catalyst loading reported in Table 2 for the metallic samples (FM + P and FM) was obtained after repeating the coating procedure 5 times. In the case of the ceramic samples, the coating was performed 3 times as a consequence of the capillarity phenomenon of cordierite porous (3–30 μm, 30–45% porosity [9]).

When analyzing the loss percentages, good levels of adherence in the FM and CM samples are found. Boehmite contains polymeric and dimeric aqueous ions $[Al(H_2O)_4OH]_2^{4+}$ bound between them by an Al–O–Al bond. These ions can react with the oxide of the catalytic material during the slurry preparation and the calcination of the coated monolith, to form chemical bonds that allow to improve the adhesion of the coating. As expected, the best adherence occurred in the samples with ceramic substrate.

When comparing the FM + P and FM samples, it is observed that the boehmite decreases the level of adherence of the catalyst layer to the substrate. The anchoring of the catalyst to the surface of the metallic substrate is the result of a combination of two factors: a chemical factor, related to the chemical compatibility between the catalyst (Pd/Al_2O_3 in this work) and the oxidized metal surface (alumina layer in the form of whiskers), and a physical factor, related to the roughness of the surface of the pretreated metallic substrate. The boehmite primer was used to increase the chemical bonding because alumina whiskers produced at high temperature present a low surface OH group density. However, as shown in Fig. 2b, the surface roughness of the primer-pretreated Fecralloy was dramatically reduced. Therefore, it can be concluded that the mechanical anchoring of the washcoating produced by the whiskers' morphology is more important than the additional chemical compatibility induced by the primer.
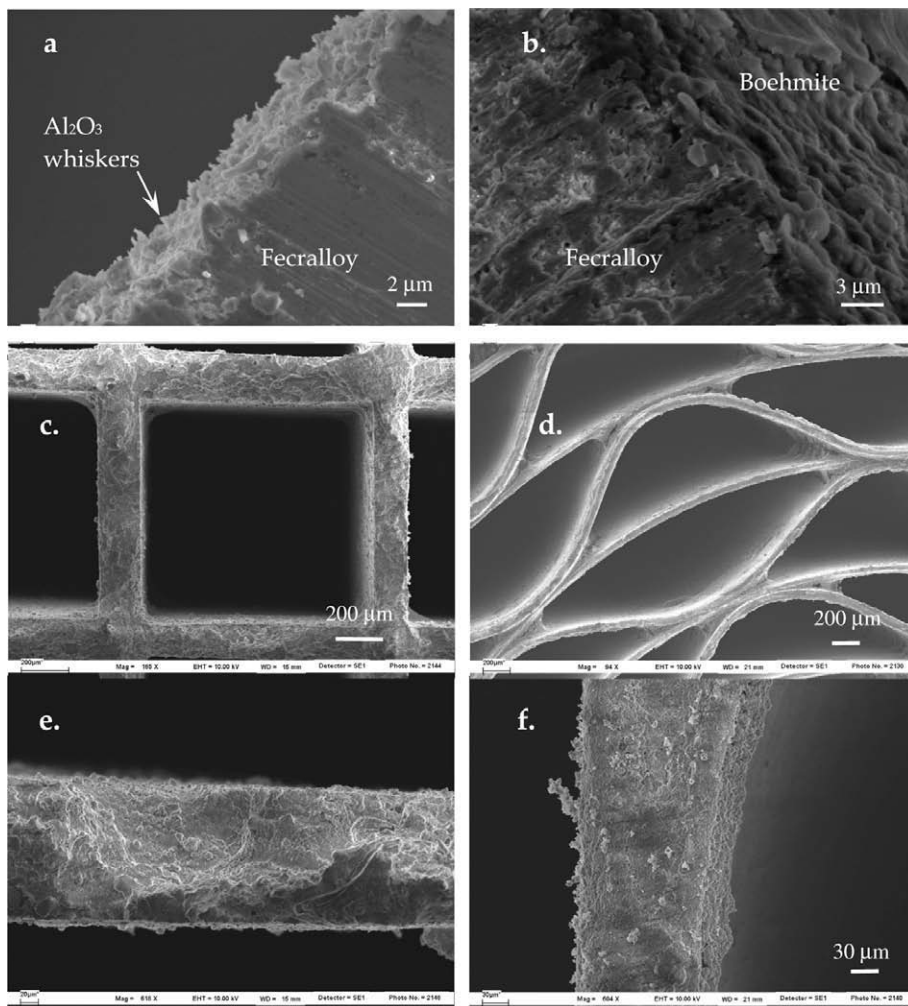
Fig. 2. SEM images. (a) Alumina whiskers on Fecraloy calcined at 900 °C for 22 h. (b) Boehmite (primer) on alumina whiskers. (c) CM. (d) FM. (e) CM (catalyst layer thickness ≈ 4 μm). (f) FM (catalyst layer thickness ≈ 30 μm).

Table 2
Characteristics of the monolithic catalysts.

Sample	Primer loading (mg)[*]	Catalyst loading (mg)[*]	BET (m²/monolith)	% Loss[**]
FM + P	7.2 ± 0.7	113.4 ± 6.5	20.8 ± 1.1	13.6 ± 5.7
FM		107.9 ± 1.9	19.1 ± 0.3	2.6 ± 1.1
CM		101.8 ± 2.8	18.7 ± 0.6	n.d.

n.d.: not detected.
[*] After calcination.
[**] % Loss of the catalyst (after ultrasonic treatment).

According to Fig. 2c the catalyst layer was homogenously dispersed in the channels of the ceramic monolith, whereas, in the metallic structure, the catalyst was located on all the exposed area of the channels, with the usual slight accumulation in the narrowest corners (see Fig. 2d).

Fig. 2e and f show the thickness of the catalyst layer in the different supports, being of approximately 4 μm for CM and 30 μm for the FM sample.

Given the above results, it could be deduced that the macropores present in the cordierite (and not in the metallic substrate) allow the anchoring of the powder catalyst. As a consequence, similar catalyst loadings are obtained after fewer washcoating steps, with better levels of adherence.

3.2. Catalytic activity

Fig. 3 shows the model proposed for the hydrogenation of sunflower oil (the concentration of the fatty acid C18:3 is very low), where the consecutive reactions of the unsaturated triglyceride and the *cis–trans* isomerization are considered. The dashed lines represent negligible reactions. The overall reaction comprises the consecutive saturation of *cis*-C18:2 to *cis*-C18:1 and its subsequent saturation to C18:0, as well as the isomerization of *cis*-C18:2 to *trans*-C18:2 taking place in parallel with the isomerization of *cis*-C18:1 to *trans*-C18:1. The reaction can also involve the hydrogenation of *trans*-C18:2 to *cis*-C18:1, and *trans*-C18:1 to C18:0.

Fig. 4 presents the double bond conversion on the Pd/Al₂O₃ catalyst and the CM and FM samples, for a reaction time of 2 h. The number after the dash indicates the sequence of use. A difference
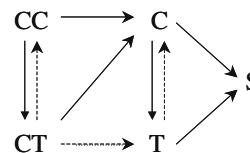
Fig. 3. Reaction scheme for the hydrogenation/isomerization of sunflower oil. References: CC: *cis*-C18:2, CT: *trans*-C18:2, C: *cis*-C18:1, T: *trans*-C18:1, S: C18:0.
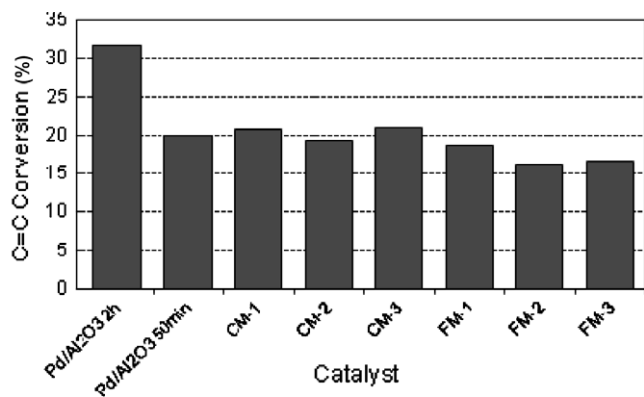
Fig. 4. Conversion C=C for the studied catalysts in the hydrogenation of sunflower oil at 373 K and 413 kPa, and reaction time 2 h (except in the case indicated). The number indicates the sequence of use.
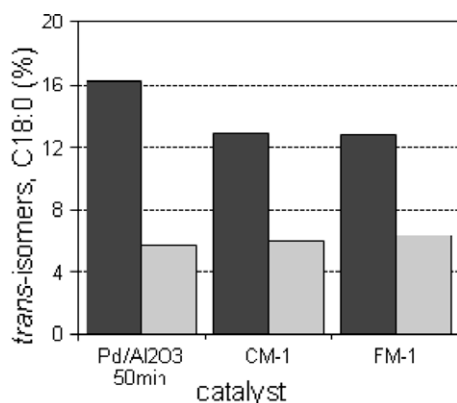

Fig. 5. Formation of *trans*-isomers and C18:0 for a C=C conversion of ~20%. References: ■ *trans*, ■ C18:0.

in activity can be observed for the powder sample (31.6%) and the monolithic samples: 20.9% for CM and 18.7% for FM. The powder catalyst reaches a conversion of 20% after 50 min. Given that the monolith samples were prepared with the same amount of the same Pd/Al_2O_3 catalyst, the difference in activity between powder and monolithic samples can be attributed to mass transfer phenomena and operation variables. Since this is a three-phase reaction, the diffusion processes are complex. The concentration of hydrogen in oil is very low (9.3 mol/m^3) and its diffusion through the catalyst pores to the active site is difficult.

The higher double bond conversion of Pd/Al_2O_3 sample could be attributed to the design of the stirrer and its effectiveness in the solubilization of H_2 in oil. The difference in activity for this reaction when operating with a stirrer of inclined blade or vertical blades (similar to the monolithic stirrer used in this work) was previously reported [10]. The first option will originate a pattern of axial flow, and the second one, a circular flow that does not favor mixing. It must also be mentioned that, when working in slurry conditions, the catalyst is dispersed in all the reactor, and thus it is more accessible to the limiting reactant (H_2) than when using a monolithic stirrer that concentrates the catalyst in a fraction of the total volume.

When consecutive tests for the same sample are compared, no variation in activity for the CM catalyst is observed. In the case of the FM sample, activity falls to 16.7% in the third test (a 10% decrease). Since both samples were studied under the same operating

conditions, poisoning or deactivation of the active site can be discarded. The loss of activity is a consequence of the detachment of the catalytic coating from the metallic substrate due to the high shear stress it is subjected to. In this respect, the values presented in Fig. 4 correlate with the results of the adherence test.

Fig. 5 shows the formation of *trans*-isomers and C18:0 compounds at 20% conversion. The selectivity to these two products is similar for the monolithic samples (12.8% towards *trans*-isomers and ~6% towards C18:0). The Pd/Al_2O_3 catalyst produced a similar amount of the saturated compound (5.6%), and a higher level of *trans*-fat (16.2%). Subsequent consecutive tests for CM and FM (not shown in the Figure) did not show significant variations regarding selectivity.

Such as the differences in activity was explained in terms of mass transfer in the gas–liquid interphase, selectivity is analyzed considering the mass transfer in the liquid–solid interphase. In the monolithic samples, the lower *trans*-isomers formation can be attributed to a better H_2/oil ratio on the active site [11]. The turbulent flow favors the transportation of Pd/Al_2O_3, but a different phenomenon occurs inside the monolith channels, where the flow is laminar. Moulijn et al. [12] report that there exists a segmented flux (Taylor flow) inside the capillary, where the gas and the liquid move as separate blocks in the channels. Between the gas bubble and the catalyst wall, a thin layer is formed through which the gas transfers to the active site very efficiently. This layer stays on the wall while the segmented flow moves through the channels.

4. Conclusion

Monolithic catalysts were prepared and characterized using Fecralloy and cordierite as substrate, on which Pd/Al_2O_3 was deposited by washcoating. The samples were studied for the partial hydrogenation of sunflower oil at 373 K y 413 kPa.

In comparative tests, at the same conversion and operating conditions, the structured catalysts presented a lower formation of *trans*-isomers than the Pd/Al_2O_3 powder.

After three consecutive hydrogenation tests, no change in activity and selectivity was observed for the ceramic monolith. On the other hand, the metallic monolith presented a partial deactivation (10%), attributed to the loss of catalytic material.

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