Experimental study of the deactivation of Pd on anodized aluminum monoliths during the partial hydrogenation of vegetable oil

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HIGHLIGHTS

- Deactivation of $Pd/Al_2O_3/Al$ catalyst in the partial hydrogenation of sunflower oil.
- Catalysts were widely characterized in order to understand the deactivation behavior.
- Loss in activity was proportional to decreasing percentage metal exposed.
- Fouling with reaction residues over Pd surface.

GRAPHICAL ABSTRACT
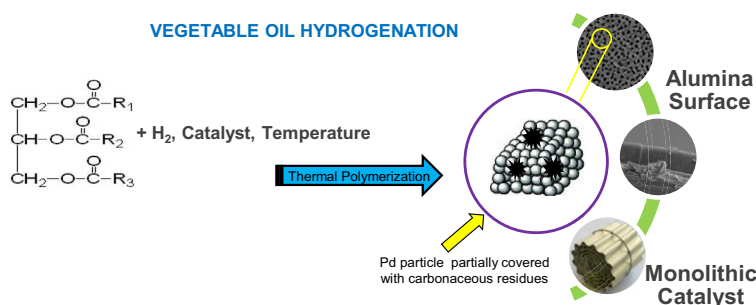
ABSTRACT

Partial hydrogenation of sunflower oil was studied over $Pd/Al_2O_3/Al$ catalysts in a monolithic stirred reactor. The catalyst showed similar or even better activity and selectivity than conventional Pd/Al_2O_3 catalysts. However, in consecutive runs, a continuous decreasing activity was observed. In order to understand the deactivation phenomena, fresh and spent catalysts were characterized using temperature programmed reduction, N_2 adsorption isotherms, dynamic H_2 chemisorption, transmission electron microscopy (TEM), atomic absorption spectroscopy, inductively coupled plasma spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy, ultrasound adherence tests, and X-ray photoelectron spectroscopy. Furthermore, an extensive number of catalytic tests under different operating conditions were carried out. The loss in activity was proportional to the reduction in metal dispersion. The decrease in Pd dispersion was due to the coverage of the Pd surface. The deactivation occurred due to fouling with reaction residues most probably coming from polymerization and/or cross-linking reactions. The catalysts can be regenerated ex situ using a careful desorption–washing–calcination process, although this requires further research because the temperatures required are too high for Al.

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1. Introduction

Vegetable oils are a sustainable source food, energy and feedstocks for a high variety of product [1,2]. The hydrogenation of vegetable oils as well as the manufacture of many specialty and fine chemical products is currently done in a three phase slurry batch reactor using mostly Ni as a catalyst. In the case of vegetable oils, hydrogenation is intended to improve physical and chemical properties required by the food production industry. When non edible oils are considered as alternative lubricants or fuels, their resistance to oxidation is improved by partial hydrogenation [3,4]. The research in hydrogenation catalysts is a field in continuous advance, especially with palladium due to its performance [5–7].

Oil hydrogenation is a well established process but the use of slurry catalysts presents some drawbacks like the catalysts-oil separation at the end of the reaction where part of the catalyst is

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lost. Besides, hydrogenated oil requires a bleaching step in order to remove metal traces from the product. Filtration and bleaching steps could represent up to 20% of total operation costs [8].

An important step in overcoming these difficulties was taken by Moulijn and coworkers who introduced the use of monolithic catalysts in liquid phase reactions [9]. Using structured catalysts like monoliths facilitates product recovery by elimination of the filtration step which helps in lowering operational costs [10]. This could in principle make affordable the use of more active but expensive noble metal catalysts that could result in running the reaction at much lower temperature leading to energy savings. This concept is taken today at the scale of microreactors [11].

Another important aspect to be considered is that a high percentage of the noble metal used in catalyst formulation can be recovered and used in new catalysts preparation. On the other hand, only around 10% of the Ni financial value can be recovered by selling the spent catalyst [12].

In a recent paper [13] we discussed the use of metallic monoliths in oil hydrogenation reactions. These monoliths present important advantages over ceramic monoliths since their preparation is cheap and affordable in small quantities, they have a better thermal conductivity, they present thinner wall thickness allowing a greater flow area, have a higher mechanical resistance, and allow a greater flexibility in the design [14,15]. Aluminum results an interesting substrate to prepare metallic monoliths since anodization of its surface generates a strongly adhered layer of alumina onto which the active metal could by incorporated. Thus, a structured catalyst with the advantages of a metal monolith and with a layer that is resistant and compatible with the active phase is obtained [4].

Our results showed that these structures can be a good alternative as structured catalysts in the reaction of partial hydrogenation of sunflower oil, intended to simplify the industrial process. The monolithic $Pd/Al_2O_3/Al$ catalysts showed to be active, with a 50% C=C conversion in 30 min. When consecutive tests were performed, a loss of activity was observed, decreasing 80% in the sixth test, which were attributed to the presence of residues. Boger et al. [16] observed similar behavior using a palladium based monoliths. Regeneration of spent monolith was also studied, but no suitable solvent or method was found at this point of the research [13].

Deactivation of conventional supported palladium catalysts in edible hydrogenation was previously studied [17]. Edvardsson and coworkers, though dealing with Pd on alumina catalysts worked with a different catalytic system. They used conventional supported catalysts while in the present work we studied structured catalysts with Pd supported on an alumina support generated in situ. On the other hand, Edvardsson et al. impregnated alumina with Pd nitrite that is known that leads to larger metallic particles. In this work, Pd acetylacetonate is used as the source of Pd. This means that the paper by Edvardsson and coworkers though very valuable does not represent the whole picture in oil hydrogenation catalysts poisoning by carbonaceous residues and the present paper contributes to enlarge the understanding of the studied phenomena. We provide a deeper insight into the deactivation–regeneration process of aluminum monolith supported Pd catalyst in a monolithic stirrer reactor.

2. Experimental and methods

2.1. Catalyst preparation and characterization

Anodized aluminum monoliths were prepared as reported in [13]. The metallic samples were loaded with Pd by wet impregnation with a $Pd(C_5H_7O_2)_2$ solution in toluene. The monoliths were calcined at 773 K for 2 h. The catalysts were characterized by XRD, N_2 adsorption isotherm, ICP, IR, SEM, TEM, TPR, H_2 chemisorption [13] and XPS.

Textural properties were studied by N_2 adsorption–desorption isotherms at 77 K in a Micromeritics ASAP 2020 apparatus between 0.1 and 0.995 mmHg with a home-made cell that allows complete monolith analyzing. Before analysis, the monoliths were degassed for 2 h at 423 K in vacuum. The morphology and thickness of the catalyst layer deposited on the monolith substrates was analyzed by scanning electron microscope (SEM) (JEOL 35 CF) operating at 15 keV. The Pd particle size distribution was also determined by transmission electron microscopy (TEM) (JEOL 100 CX) operating at 100 keV. The Pd catalysts were ground and dispersed onto holey carbon-coated Cu grids for direct observation.

The Pd content of the catalyst was determined by atomic absorption spectroscopy in a GBC AVANTA spectrometer. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were recorded in a Nicolet 6700 FT-IR spectrometer in the 4000–400 cm^{-1} region. The spectra were recorded with a 4 cm^{-1} resolution and 64 scans using a high-sensitivity mercury cadmium telluride (MCT-A) detector. Silicon carbide disks (Si-Carb) were used to sample the surface layer of the monolith. A clean Si-Carb paper was used for the background.

The amount of alumina generated during anodization was determined by means of gravimetry. It was calculated from the weight difference of the anodized sheet before and after the chemical treatment which dissolved selectively the alumina layer. The dissolution process was carried out at 358 K for 20 min using a 0.5 M phosphoric acid and 0.2 M chromic acid solution.

Hydrogen chemisorption runs were carried out in a conventional pulse apparatus [18] at atmospheric pressure and 373 K. The corresponding furnace were the sample is placed was modified to allow the use of a special cell of low dead volume containing a monolith of the same dimensions of those used in reaction experiments. Prior to chemisorption, the monoliths were reduced in situ at 563 K in flowing H_2. The fraction of exposed Pd was calculated assuming that one hydrogen atom is adsorbed per surface Pd metal atom.

The mechanical stability of the catalysts was tested in ultrasound adherence tests. Monoliths samples previously carefully weighted were exposed to an ultrasound test immersed in a sulfuric ether bath during 30 min at maximum power. Once finished the test the monoliths were washed with distilled water, dried in an oven and weighted again in order to detect possible loss of catalytic material. For these experiments a Cole-Palmer model 8892 ultrasonic cleaner was used.

Temperature programmed reduction (TPR) experiments were performed in the conventional pulse apparatus described above used in the TPR mode. Before reduction, the monolith was oxidized in flowing chromatographic air at 573 K for 1 h, and purged and cooled in Ar. A mixture of 5% H_2 in Ar flow was then passed through the sample, and the temperature was raised from 223 to 623 K at a heating rate of 10 K min^{-1}. Hydrogen consumption due to the reduction process was followed by processing the response of a thermal conductivity detector.

Fresh and used $Pd/Al_2O_3/Al$ monoliths were examined by XPS. Small portions of the monoliths were analyzed using a multitechnique Specs instrument equipped with a dual Mg/Al X-ray source and a hemispherical Phoibos 150 analyzer operated in the fix transmission analyzer mode (FAT). Spectra were obtained operating the Mg anode at 200 W and using energy steps of 30 eV. The pressure was maintained at 2×10^{-8} mbar during the whole experiment. Samples were evacuated at least 12 h before the taking the spectra. The binding energy values were corrected for loading effects using signal 1s C at 284.6 eV as a reference.

Cleaning and calcining of deactivated catalysts was done in the following way: A monolith sample (0.00168 $kg_{Pd,exp}$ m^{-3}) exposed

Table 1
Composition of the commercial sunflower oil used in the catalytic tests.

Fatty acids	wt.%
Palmitic, C16:0	5.9
Stearic, C18:0	3.4
Oleic, *cis*-C18:1	39.5
Linoleic, *cis-cis*-C18:2	49.1
Araquidic, C20:0	0.3
Linolenic, *cis-cis-cis*-C18:3	0.2
Behenic, C22:0	0.7
Total *trans* isomers	<1.0

to ten consecutive reactions lasting 60 min each, at 373 K, 414 kPa, 1400 rpm (Set 1) washed with trichloroethylene at 353 K and calcined with chromatographic air 12 h at 773 K.

Ultrasonic cleaning of used monolith was done as follows: the monolith was placed in a ultrasonic bath immersed in trichloroethylene at 343 K during 10 min, then washed with acetone at 303 K during 5 min and finally dried at room temperature during 24 h.

2.2. Catalytic tests

The monolithic catalysts were used in the partial hydrogenation of sunflower oil at 373 K, 413 kPa and an agitation rate of 1400 rpm, studying the performance of the catalyst in consecutive tests with and without intermediate treatments between experiments.

The hydrogenation reactions were carried out in a 600 cm^3 Parr® reactor operated in semi-continuous mode. The monoliths were arranged in the axis of the stirrer.

The Pd/Al$_2$O$_3$/Al catalyst was reduced in situ (373 K, 30 min), and then the oil was introduced into the reactor (previously deoxygenated). When reaction temperature was reached, the H$_2$ pressure was increased to start the reaction.

Chromatographic H$_2$ (AGA, 99.9999% purity) and a commercial sunflower oil were used. The composition of the sunflower oil is shown in Table 1. The mass of the Pd catalyst used in all the tests was 2 mg Pd/kg oil. In a set of tests, a commercial Ni/SiO$_2$ catalyst (Pricat 9910: 22% Ni, 4% SiO$_2$ dispersed in hydrogenated edible fats) was used as scavenger, while the rest of the operation conditions remained constant.

2.3. Analytical procedures

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, which allows to monitor the reaction progress, was calculated from the fatty acid composition following the AOCS Cd 1c-85 norm. The double bond shift is not considered here.

3. Results

Preliminary results of our laboratory on catalyst deactivation were already published [19]. The present paper is intended to get a better understanding of the deactivation phenomena in order to include it in the reactor modeling for more accurate predictions.

In a single run, the Pd/Al$_2$O$_3$/Al monolithic catalyst showed similar or even better activity and selectivity than conventional Pd/Al$_2$O$_3$ catalysts and Pd/cordierite monolithic catalysts [20]. However, in consecutive runs without any catalyst pretreatment between each experiment, a continuous activity decline is observed
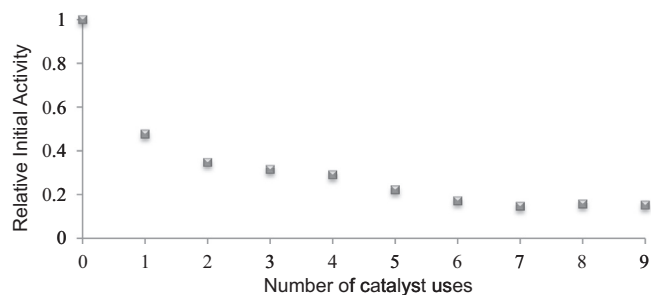

Fig. 1. Relative initial activity as a function of the number of times the catalyst is used in the semibatch hydrogenation reaction.

Table 2
Ultrasound adherence test results.

Sample	Initial weight [g]	Final weight [g]	Weight loss [%]
1	1.08637	1.08640	0
2	1.08591	1.08598	0
3	1.10481	1.10476	0

Table 3
BET surface area results of unused and used monoliths (Set 1).

Monolith	BET area [m^2 g^{-1}]
Unused	6.3
Washed	5
Washed and calcined	6.3

without changes in selectivity. This behavior is represented in Fig. 1.

The following are the potential causes of catalyst deactivation that were considered in order to explain the facts: thermal effects, active site poisoning by adsorption of minor components present in the oil, loss of support structure, pore blockage, sintering and active site fouling by carbonaceous compounds. In order to detect the possible cause of the observed deactivation, a number of complementary experiments were carried out that are described below.

3.1. Collapse of catalytic support

Table 2 shows the results of the adherence test of the physical stability of the catalytic support for three different samples. These allowed the conclusion that loss of catalyst support is not the cause of the observed catalyst deactivation with time.

3.2. Pore structure blockage or collapse

After cleaning and calcining treatment the specific surface area of the used monolith was measured. The results are given in Table 3 in comparison with reference data of unused monoliths. It is evident from the data that the morphological properties of the monolith remain unaltered after its repeated use in reaction. Therefore, this hypothesis is not relevant for explaining the observed deactivation.

3.3. Loss of active metal

Temperature programmed reduction experiments were done in order to detect possible changes in the total amount of active metal after several cycles of reaction. Fig. 2 shows the TPR profiles of two monolithic catalysts, one fresh, not exposed to the reaction, and a
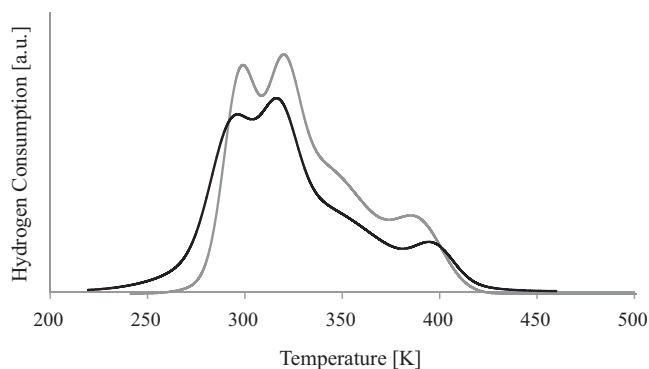
Fig. 2. TPR profiles. Ref.: fresh catalysts (gray), used catalyst (black).

Table 4
Percentage metal exposed of fresh and used monolithic catalysts.

Monolith	Percentage metal exposed [%]
Fresh	35
Used	5.6

second one used in ten consecutive 60 min hydrogenation reactions (Set 1). In both cases the metal loading was 0.00168 $kg_{Pd,exp}$ m^{-3}.

The area under the curves was numerically determined resulting 32 Arbitrary Units in the case of the fresh catalyst and 27.2 AU for the used one. Since both monoliths belong to the same set they have the same catalytic characteristics, therefore direct comparison is allowed. Although a small fraction of the metal is apparently not available, this is not enough to explain the actual catalyst deactivation. The small temperature shifts of the TPR signals maxima are not significant and they are not assigned to any particular effect.

3.4. Change in the percentage metal exposed

Dynamic hydrogen chemisorption experiments were performed aiming to detect changes in the percentage metal exposed during catalyst use. Results obtained on fresh monolith and on a monolith exposed to ten consecutive reaction cycles (Set 1) are presented in Table 4.

It can be observed that the fraction of exposed Pd atoms dramatically fell after prolonged exposure of the catalysts to cycles of reaction. This result could be due either to palladium particles sintering or to particles covered by products originated during the operation of the reactor, probably polymers. Transmission Electron Microscopy results allow the authors to rule out the former hypothesis. Fresh and used monolith micrographs are given in Figs. 3 and 4, respectively. The palladium particle size distribution (volume–area average diameter, D_{va}) for both, fresh and use monolith is given in Fig. 5. D_{va} is usually compared to percentage metal exposed measured by chemisorption and it is defined as:

$$D_{va} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2}$$

where n_i means the (number-based) frequency of occurrence of particles in size class i, having a mean diameter d_i.

Pd diameters were 4.9 and 5.6 nm for fresh and used monoliths. They indicate that the metal particle size remain unaltered after been exposed to ten consecutive cycles of reaction. Considering
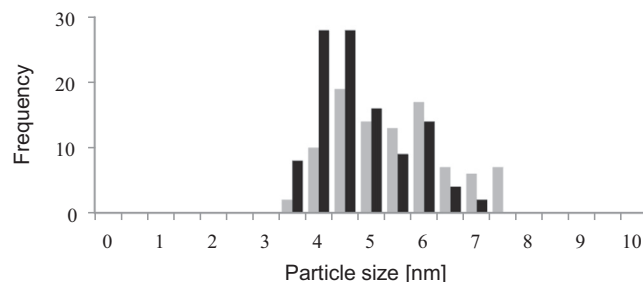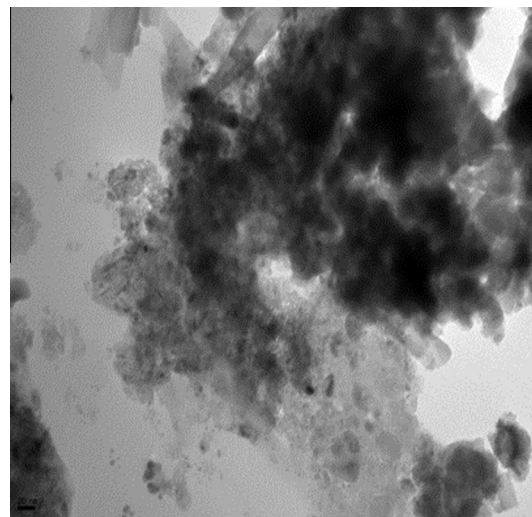

Fig. 3. TEM image. Fresh monolith.
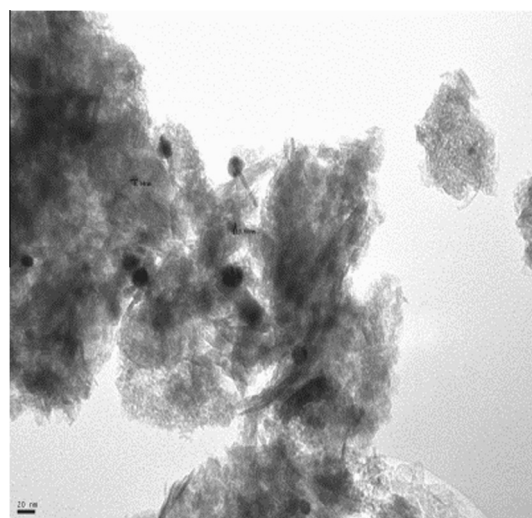

Fig. 4. TEM image. Used monolith.

Fig. 5. Palladium particle size distribution (volume–area average diameter) from TEM data. Fresh monolith (black), used monolith (gray).

the precision of measurements and the calibration of the microscope amplification, error is estimated to be 10%.

Based on the present results it is possible to state that the metal particle size did not change in a significant manner. Therefore, it is not linked to the observed deactivation. The marked drop in percentage metal exposed as determined by hydrogen chemisorption

Table 5

Sulfur and phosphor content in the commercial oil used in the present paper.

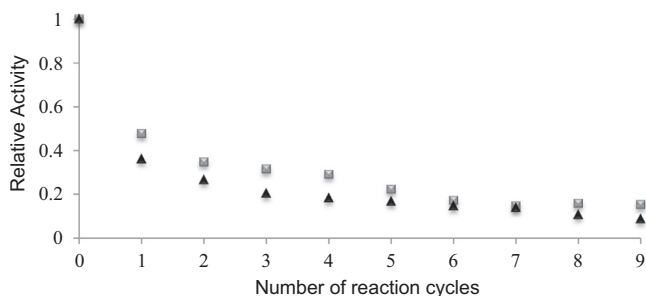| Sample	Sulfur [ppm]	Phosphor [ppm]
Commercial oil Lot 1	0.088	1.31
Commercial oil Lot 2	0.065	0.71

Fig. 6. Sets of consecutive reactions. Ref.: (▲) Ni:Pd molar ratio = 0, (■) Ni:Pd molar ratio = 100. Reaction temperature 373 K. Pd loading: 0.00168 kg m^{-3}.

Table 6

Main products distribution of triolein hydrogenation in consecutive reactions.

	C18:0 [%]	C18:1 [%]	C18:2 [%]	C16:0 [%]	C22:0 [%]
Initial	5.8	82.7	7.2	3.5	0.8
Reaction 1	15.2	78.9	1.6	3.5	0.8
Reaction 2	12.9	79.9	2.9	3.5	0.8
Reaction 3	11.6	78	6.1	3.5	0.8

could be assigned to the presence of polymeric residues adsorbed on the metal particles surface, as already advanced.

3.5. Adsorption of minor components present in the oil

It has been previously suggested that sulfur and phosphorous compounds present in the oil are strongly adsorbed on the surface of the active metal through electron donation [21].

Abraham and deMan [22] studied this type of chemicals and concluded that volatile sulfur compounds are the main cause of catalyst deactivation in the hydrogenation process. Irandoust et al. [23] reviewed data on poisoning during the oil hydrogenation and investigated several compounds that poison the reaction as well as the role of the poison in the adsorption of the reactants.

Table 5 shows the level of sulfur and phosphor detected in the oil batches used in the present paper. The results indicate that it is negligible from the deactivation point of view.

In order to detect whether the catalyst deactivation is due to the presence of minor components in the oil, two sets of ten consecutive reactions (Set 1 and Set 2) were carried out adding a Ni catalyst to the reaction media in one of them (Set 2), as scavenger of sulfur and phosphor compounds [24]. A commercial Ni/SiO$_2$ (Pricat 9910) catalyst was used for that purpose.

An additional experiment (not shown) was done in which the reaction was carried out at 373 K using a nickel catalyst only, under the same conditions than in the main experiment. It proved that at those conditions Ni is almost inactive for oil hydrogenation. Fig. 6 shows the activity profiles determined during the experiments.

This result suggests that poisoning of the active site by minor oil components (phospholipids [25] or sulfur [22]) is possible to some extent, although it does not fully explain the observed deactivation phenomenon. The presence of Ni in high concentration related to Pd (Ni:Pd = 100) can hardly avoid the observed deactivation of
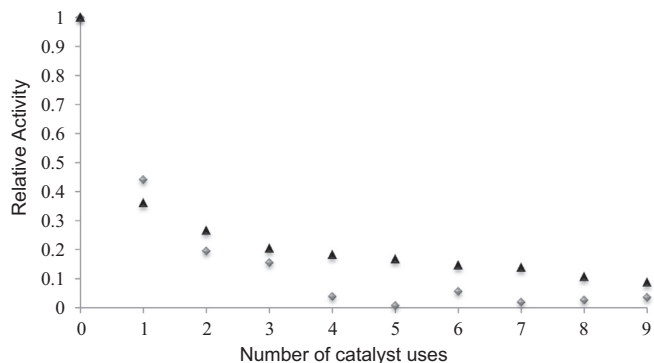

Fig. 7. Sunflower oil hydrogenation at different temperatures. Ref.: (▲) 373 K; 0.00168 kg$_{Pd,exp}$ m^{-3}; Ni:Pd molar ratio = 0, (♦) 353 K; 0.00168 kg$_{Pd,exp}$ m^{-3}; Ni:Pd molar ratio = 100.

the Pd/Al$_2$O$_3$/Al catalyst. Even higher Ni:Pd ratios (Ni:Pd = 3000) do not improve the activity level.

Three additional consecutive reactions at the same conditions were done at 373 K using triolein (Sigma, 97%) as reactant instead of sunflower oil because it is free of impurities usually found in oil. The results are presented in Table 6.

A similar deactivation pattern is observed, therefore it cannot be associated to impurities in the oil to be processed.

3.6. Temperature effect on deactivation

In order to test the possibility that deactivation could be induced by thermal effects, two sets of ten consecutive reactions were carried out at two different temperatures (Set 1 and Set 3). The results are given in Fig. 7.

Even though the activity level was low, deactivation was evident also at 353 K. Therefore, it is evident that the reaction that generates the deposits is important even though the reaction temperature is lower than in the main set of experiments.

3.7. Carbonaceous residues formation

With the purpose in mind of testing the hypothesis that polymers formed during the reaction might be linked to the deactivation process Set 1 of reactions described above was compared to a new set of ten consecutive reactions, Set 4. In this one the monolithic catalyst was washed after each reaction with trichloroethylene followed by a calcination step using a procedure already described. The outcome of the comparative test is presented in Fig. 8.

It is evident from the data that cleaning the catalyst after the reaction cannot recover the initial activity although some improvement is obtained. This could indicate the presence of very resilient carbonaceous residues, hard to remove even with the severe treatment used.

Fresh and used monoliths in Set 1 comprising ten consecutive reactions were analyzed by FTIR. The corresponding spectra are given in Fig. 9. The sample named "washed" corresponds to a monolith used in the reaction which was washed in an ultrasonic as described above. On the other hand the sample named "calcined" refers to monoliths used in reaction washed as before but calcined al 773 K in chromatographic air for 24 h.

The main infrared signals present near 3000 cm^{-1} are due to C—H stretching and those at 1460 cm^{-1} and 1380 cm^{-1} correspond to C—H deformation. Bands at 1750 and 1250 cm^{-1} are assigned to C=O and C—O groups respectively. Functional C=O groups are responsible for the band at 1460 cm^{-1} while that at 970 cm^{-1}
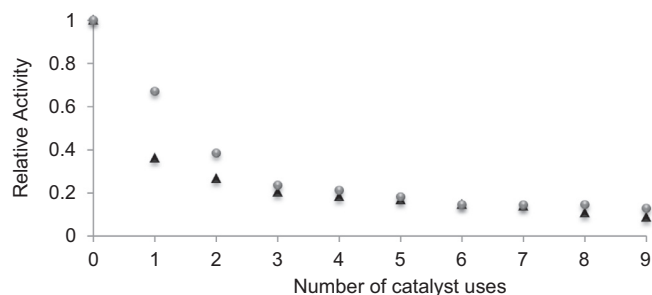
Fig. 8. Activity in consecutive reactions with and without catalyst cleaning procedures. Ref.: (▲) Set 1, (●) Set 4.

Fig. 9. FTIR spectra of different monoliths. Ref.: fresh (light gray), washed (black), washed and calcined (dark gray).

corresponds to trans olefins. *cis* olefins originate infrared bands at 3008 and 1655 cm^{-1}. The wide and intense band at 3500 cm^{-1} is characteristic of the stretching of OH associated to water content in the solid [13]. Signals below 1000 cm^{-1} are attributed to Al—O vibrations from the Al$_2$O$_3$ support. The bands centered at 1547 cm^{-1} and 1465 cm^{-1} indicate the presence of oxalate anions [26]. These bands are due to the symmetric and antisymmetric stretching of carboxylate anions and the difference between their wavelengths suggests a bidentate bridge coordination of the oxalate groups and the Al cations [27,28].

It can be seen that washing followed by calcination lead to a decrease in the intensity of the bands at 3000 cm^{-1}, 1460 cm^{-1} and 1380 cm^{-1}, associated to the vibration modes of the C—H bond. This could indicate the presence of carbonaceous residues hard to eliminate, even after that strong cleaning treatment.

Table 7 shows the XPS results obtained for a fresh monolith and for a monolith used in ten consecutive reactions at 373 K under the operational conditions already described for Set 1.

It is clear from data in Table 7 that there is no evidence of binding energy shifts for all the elements analyzed. Base on these results it is possible to conclude that no changes in the interactions between the catalyst constituents were produced upon exposure to the reaction.

The ratio of the XPS signals of the main components of the catalyst measured in the fresh and used samples are presented in Table 8. The Al/O ratio is practically the same in both cases and corresponds to the stoichiometry of Al$_2$O$_3$. On the other hand, the Pd/Al ratio decreases for the used catalyst and this can be the consequence of a strong sintering (already discarded) or to a partial coverage of the noble metal surface.

1s C spectra of fresh and used catalyst were curve fitted using three individual components (data not shown) that represent adventitious carbon (C—C, Peak I), carbon present in alcohol or ether groups (C—OH or C—O—C, peak II) and carboxylic or ester groups (O—C=O, peak III) [29]. Table 9 shows XPS analysis of the carbon oxide species on fresh and used catalysis.

Contributions from peak II (C—OH or C—O—C) and peak III (O—C=O) in the used catalysts are significantly greater than those in the fresh catalyst, which can be explained by the deposition of carbonaceous residues. These carbonaceous species could be formed in the thermal polymerization reaction [30]. These data follow the trend presented by Liu and coworkers [31], although the intensity is not as high as in these author's case probably because in our study the samples were washed and calcined prior to be studied by XPS.

As already mentioned in the Introduction, aluminum monoliths present several advantages compared to cordierite monoliths. However its fusion temperature (933 K) makes difficult its use in reactions requiring high temperature operation. Similarly a high temperature cleaning treatment could be detrimental to aluminum morphological stability in monolithic catalysts. For that reason
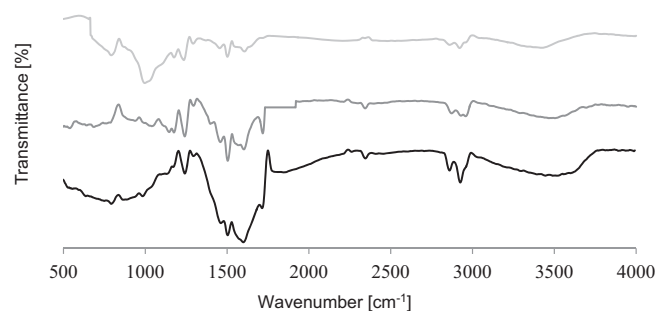
Table 7
XPS results for fresh and used monoliths.

	Fresh monolith	Used monolith
Region	Position	Position
C 1s	284.6	284.6
O 1s	531.0	531.3
Al 2p	74.1	74.3
Pd 3d5/2	336.8	336.4

Table 8
XPS signal ratio between main surface components in the catalyst.

Ratio	Fresh monolith	Used monolith
Al/O	0.616	0.607
Pd/Al	0.00909	0.00236

Table 9
XPS analysis of various carbon oxide species on fresh and used catalysts.

Species		Binding energy (eV)	Atomic composition (%)[a]	
			Fresh catalyst	Used catalyst
Peak I	Adventitious (C—C)	284.6	80.3	75.3
Peak II	Alcohol or ether (C—OH or C—O—C)	286.7–287.0	9.0	9.7
Peak III	Carboxyl or ester (O—C=O)	289.3–289.4	10.7	15.0

[a] Refers to the surface atomic concentration on the total of C found.

complementary regeneration experiments were done using a commercial Pd/Al$_2$O$_3$ catalyst (ICI 38-6, egg-shell, 0.037 Pd wt%, 8.79 m^2 g^{-1}, 100 A pore radius, 0.0217 cm^3 g^{-1} pore volume, 0.2 percentage metal exposed). The reaction was run at 473 K using the catalyst pellets arranged as in a Carberry-type reactor.

Similarly to previous observations for monolithic aluminum catalysts, a progressive deactivation was found for the commercial Pd/Al$_2$O$_3$ catalyst as long as it was exposed to consecutive reactions. The different methodologies used for activity recovery indicate that the most probable cause of deactivation is the strong fouling caused by products generated during the reaction.

After the reaction, the catalyst was washed with trichloroethylene (W) following the procedure described above. After it, the catalyst was heated at 623 K in nitrogen during 24 h (WN) and finally calcined at 923 K in chromatographic air for 7 h (WNC). FTIR analysis after each step of the regeneration procedure were done and are given in Fig. 10.
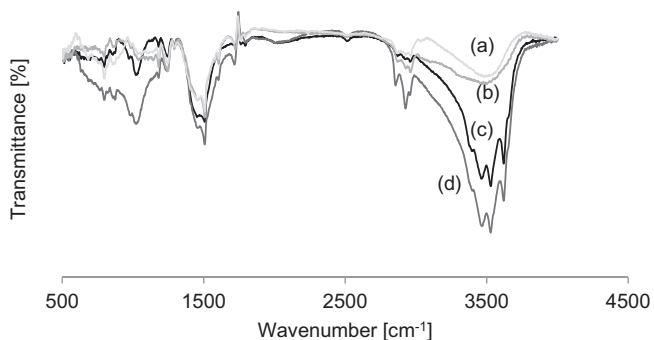
Fig. 10. FTIR spectra of ICI 38-6. Reference: WNC (a), WN (b), fresh (c) and W (d).

The FTIR analysis indicates that the signals associated to the presence of carbonaceous residues onto the catalyst surface practically disappear and return to their original state after the regeneration procedure. This result indicates that these residues could be thermally decomposed although relative high temperatures are required.

Ping et al. [32] studied the deactivation of supported Pd catalysts in the decarboxylation of fatty acid reaction. The authors exposed the used catalysts to a cleaning sequence at 353 K during 12 h. In this case the results indicate that the catalysts recover their surface area, porosity and (contrary to the present case) the metal exposed area. However, FTIR spectra are similar to those presented here and similarly, after the cleaning procedure the bands assigned to organic compounds (C—H at 3000 cm^{-1}, C—O at 1250 cm^{-1} and C=O at 1750 cm^{-1}) decrease significantly.

It is evident then that high temperature treatments allow the removal of carbonaceous deposits present on the catalysts surface although they have the potential to affect the catalyst performance.

The possible source of these carbonaceous deposits is the reaction media itself. It is known that vegetable oil has the inherent ability to polymerize (cross link) to form a solid insoluble film which, in automotive terminology, is often referred to as varnish or gum. This characteristic is a disadvantage if the oil is intended to be used as a fuel. Cross linking occurs in all three dimensions resulting in a hard insoluble varnish. Unsaturated triglycerides are highly reactive molecules in the presence of oxygen. Cross linking occurs in all three dimensions resulting in a hard insoluble varnish. Although oxygen is not present in our reaction media, heating the oil in the absence of air will also cause molecules to polymerize. Catalysts can play a major role in speeding up polymerization. These catalysts are commonly called "driers" in the paint and varnish industry. Metal ions which act as catalysts included lead, cobalt, manganese, iron, zinc, aluminum, vanadium, copper, nickel and chromium. As little as 0.005% of some of these ions is all that is required in paints to fully catalyze the drying process [33].

Additional experiments were done running the reaction system under the same conditions of pressure, temperature and time replacing but using nitrogen instead of hydrogen. Regardless the hydrogenation reaction was not possible the monolithic catalyst was deactivated as before. This is taken as an evidence that the reaction products responsible for the observed deactivation are produced in a secondary reaction most probably a cross linking reaction of the unsaturated triglycerides.

4. Conclusions

The deactivation observed during sunflower oil hydrogenation using Pd/Al$_2$O$_3$/Al monoliths is due to fouling with reaction resi-

dues most probably coming from polymerization and/or crosslinking reactions. The catalysts can be regenerated ex situ using a careful desorption–washing–calcinations process although this requires further work since the temperatures required are too high for Al. An adequate selection of Pd loading could result in a longer sequence of runs retarding the moment to take the catalyst out of the reactor for regeneration. The poisoning of the metal particles is by blocking the access to the active sites. Therefore the surface to volume ratio is an important factor since having more surface area should result in a catalyst less prone to total deactivation compared to catalyst having the same metal content in low surface area to volume ratio particles, when exposed to the same proportion of poison. Besides, increasing Pd loading could result in longer activity periods and the problem will be one of costs minimization.

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