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High performance monolithic catalysts for hydrogenation reactions

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Abstract

The performances of two different monolithic catalysts are compared in the selective hydrogenation of fatty acid methyl esters (FAMEs). The monolith samples were a classical square channel cordierite and one modified with α-Al_2O_3 blocking the macroporosity of the cordierite and rounding the channel cross section. On both samples a carbon layer was applied by carbonization of a polyfurfuryl alcohol coating obtained by dipcoating. The carbon was oxidized to create anchoring sites for ion exchange with a tetraamminepalladium(II) nitrate solution resulting in a carbon supported Pd catalyst. The rounded channels yielded an even carbon layer, whereas in the square channels an uneven carbon distribution resulted and penetration in the wall. The rounded channel shows a superior performance compared to the square channel sample in the partial hydrogenation of FAMEs, evidenced by the much lower formation of *trans* double bonds at similar hydrogenation levels of the double bonds. This is ascribed to the much shorter diffusion distances of the reactants and products.

Keywords: Carbon-coated monolith; Catalyst; Hydrogenation; FAME; Selectivity; Palladium

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1. Introduction

Monolithic catalyst supports are an attractive option for conventional carriers in heterogeneous catalysts and particularly in industrial hydrogenation reactions. Thus, new generations of monolithic catalyst structures are being developed. In contrast to traditional monolithic supports, like cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) with a macroporous wall structure in which sometimes an ineffective catalytic active phase can be deposited, the idea of monolithic catalyst structures with inaccessible walls and uniform round channels are pushed strongly forward. For this proposal α-Al_2O_3 is an interesting first coating because of its very low surface area and price.

In this way, short and uniform diffusion lengths are created, the potential of plug flow behaviour in so-called Taylor flow mode of gas and liquid through monolith channels is obtained and a better utilization of the active phase is achieved [1,2]. Overall, the catalytic performance (activity, selectivity and catalyst life) can be improved.

On the other hand, monolithic catalysts supports have to be chemically inert against reactants and products, for this reason they are coated with different inorganic and/or organic phases depending on the reaction that will be used.

Carbon is a good coating and catalytic support. The surface of carbon is relatively inert, the chemical surface properties of the carbon may be changed easily and carbon is stable in non-oxidizing acidic and alkaline media. The morphological properties of carbon, like surface area and pore size distribution, which are very important in adsorption process, can be also advantageous in order to increase the dispersion of catalyst (metal) [3].

Vegetable oils are mainly composed of complex mixtures of fatty acid esters in triglyceride form, usually of different degrees of unsaturation. The aim of their partial hydrogenation is a certain reduction in the amount polyunsaturates, with as little formation of saturates or *trans* fats. In recent years, the negative health effects of *trans* fats have received increasing attention and are considered to be even more detrimental than saturated fats [4]. As a consequence there is growing interest in new hydrogenation processes that reduce the amount of *trans* fats formed. This is an illustrative example why research continues in

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developing monolith catalysts or monolith catalytic reactors to enhance selectivities, catalytic activity and catalyst life [5]. In this way, the most important steps are: to enhance exposure of the catalytic metal to the reactants (high catalytic activity) and to avoid the undesired products (high selectivity).

The major emphasis of this work is the preparation of these high performance monolithic catalysts. To meet this target well defined coatings of support structures and active phases have been developed and demonstrated in a selective hydrogenation of fatty acid methyl esters (FAMEs).

2. Experimental

Cordierite monolithic substrates have been coated with an α-Al_2O_3 layer using a dipcoating method, in order to block the macroporosity and to prevent deposition of catalytic material in the wall of this monolith substrate. The monolithic substrates had square cells, a cells density of 62 cells cm^{-2} (400 cpsi), a wall thickness of 0.18 mm, a length of 5 cm and a diameter of 1 cm. The particle size of the α-Al_2O_3 used range between 0.35 and 0.39 μm, and its BET surface area is 9 $m^2\,g^{-1}$. This preparation method consists in dipping the cordierite monolith into a α-Al_2O_3/water suspension (70 wt% of solid, pH 3). The excess of suspension in the channels is removed by flushing with a controlled air flow, the monolith is dried rotating at room temperature. Finally, the monoliths were heated to 1273 K with the rate 2 K min^{-1} and calcined at this temperature for 4 h in order to avoid cracks.

In a second step, a carbon layer of uniform thickness has been formed on the α-Al_2O_3 layer, which serves as a support for the active catalytic phase. The method consists of the thermal decomposition of a polyfurfuryl alcohol (PFA) coating obtained by dipcoating the α-Al_2O_3-coated monolith into the liquid polymer (Hüttenes-Albertus 1114140) that is subsequently cured and carbonized. The carbonization process was carried out at 623 K for 30 min in N_2 flow with a heat rate of 2 K min^{-1}. This carbon layer also was formed with the above-mentioned method, directly on cordierite monolithic substrates without α-Al_2O_3 layer.

The carbon layer was activated at 573 K for 2 h in air flow and secondly oxidized with a solution of H_2O_2 9.8 M for 24 h at room temperature to create anchoring sites for metal deposition. After this process, the monoliths (catalytic supports) were washed several times with demineralized water.

The catalyst was deposited on the monoliths by impregnation in an aqueous solution of tetraamminepalladium(II) nitrate 0.01 M. A 10 pH value of the solution was used to promote electrostatic interaction between the oxygen surface groups of the carbon and the palladium complex. After this process, the monolithic catalysts were carefully washed with demineralized water. Both the impregnation method and the liquid phase oxidation treatment were carried out in a glass set-up especially designed for the treatments of monoliths in a liquid phase, where the liquid ($\sim$50 ml) is forced by internal recycling through the channels of the monoliths. The monolithic catalyst prepared on the cordierite monolithic substrate that was coated firstly with an α-Al_2O_3 layer and secondly with a carbon layer, is referred to, hereafter, as high performance monolithic catalyst (HPMC). The abbreviation MC is referred hereafter to the monolithic catalyst prepared on the cordierite monolithic substrate coated only with a carbon layer.

The different steps followed in the preparation of the catalytic support were studied with a Philips XL-20 scanning electron microscope using the samples sputtered with gold. The textural surface properties of the catalytic support were determined by physical adsorption of N_2 and CO_2 at 77 and 273 K, respectively, using a Quantachrome Autosorb-6B. The chemical surface properties were characterized by temperature programmed desorption (TPD), by heating the samples to 1273 K in He flow at a heating rate of 20 K min^{-1} and using a thermocube model quadrupole mass spectrometer (Balzers) to record the amount of evolved gases as a function of temperature. The Pd loading of the monolithic catalysts (HPMC and MC) was analyzed by neutron activation analysis (NAA) using a germanium semiconductor as detector. Pd-dispersion on the catalytic support was analyzed by CO-chemisorption performed at 313 K on the Quantachrome Autosorb-1C and assuming a CO:Pd = 1:1 stoichiometry, and Pd particle sizes were calculated from Pd-dispersion data. Prior to the characterization by CO-chemisorption as well as the catalytic activity measurements, the catalysts were pre-treated at 573 K in a H_2 flow for 2 h.

Both, HPMC and MC samples were tested in the reaction of hydrogenation of the fatty acid methyl esters of sunflower oil. Experiments were carried out in a 300 ml autoclave, which was equipped with a Screw Impelled Stirrer (SISR) [5]. The stirrer speed was 1600 rpm, H_2 pressure was kept at 2.0 MPa and the temperature was 373 K. Pure FAMEs were used. Samples were taken at regular intervals and stored for later analysis. The composition of the sunflower oil FAME is given in Table 2. The GC-analysis of the reaction products was carried out at 443 K with a 50 m × 0.25 mm × 0.2 mm CP-Sil 88 (Cyanopropyl Polysiloxane) fused silica column and a flame ionisation detector (523 K) and helium as carrier gas (150 kPa, 0.45 ml min^{-1}). A split ratio of approximately 1:200 was used. Samples of pure FAME were diluted with heptane prior to injection.

The different *trans* and *cis* isomers of the reactants were identified using the AOCS Official Method Ce 1f-96 [6]. The conversion is defined as the fraction of the carbon–carbon double bonds that have been hydrogenated with respect to the original amount of this kind of double bonds. '*Monoene*' is referred to, hereafter, as the total amount of *trans* and *cis* mono-unsaturate esters in the product, '*trans*' is referred to, hereafter, as the total amount of *trans* carbon–carbon double bonds in the product. Poly-unsaturated esters containing at

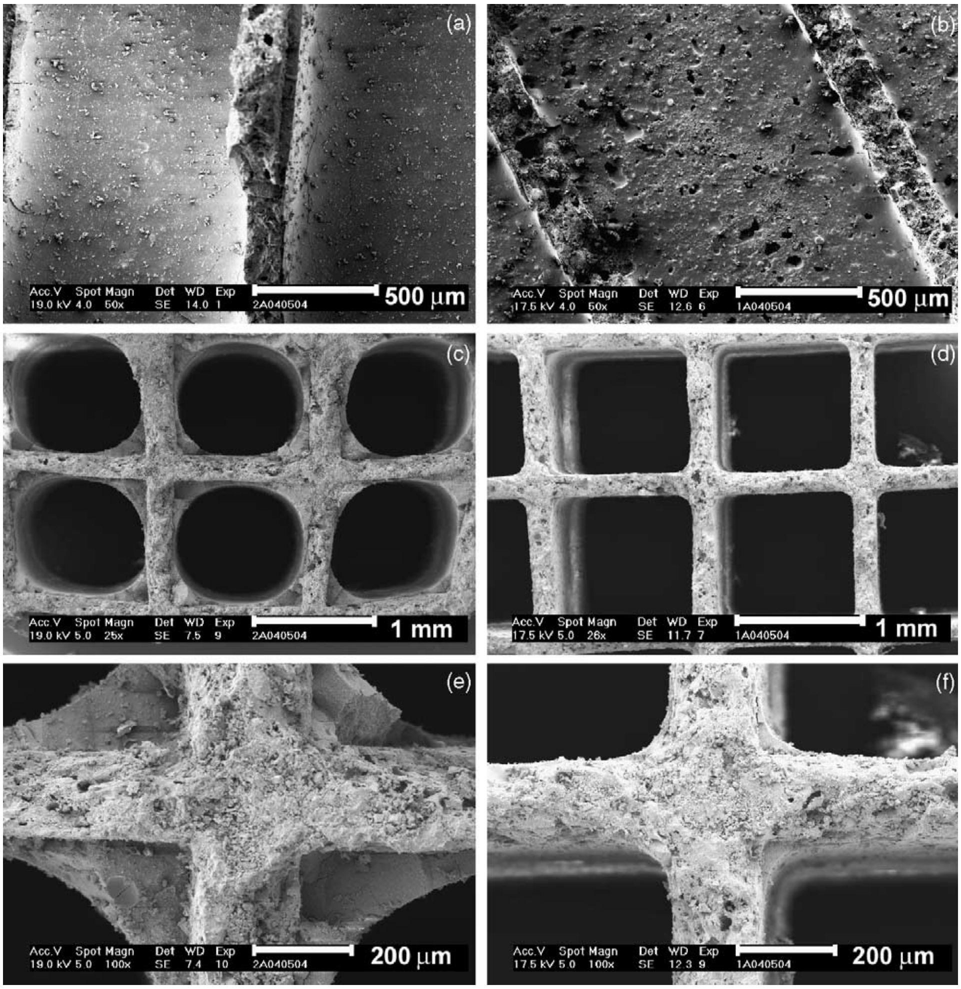

Fig. 1. SE images of the channels from α-Al_2O_3-coated monoliths after the first (b, d and f) and the last (a, c and e) coating; (a) and (b) are top views along the channels, (c)–(f) are cross-sections of the channels.

least one *trans* double bond were lumped into this *trans*-group.

3. Results

Fig. 1 shows SE images from an α-Al_2O_3-coated cordierite monolithic substrate after the first (right) and last (left) coating. The dipcoating method in α-Al_2O_3/water suspension mentioned above was applied with each monolithic substrate three times in order to block the macroporosity of the cordierite, completely (Fig. 1a and b). This figure also shows the general views of the monoliths after and before the treatment (Fig. 1c and d) as well as a detail perpendicular to the walls of cordierite rounded with this α-Al_2O_3 layer (Fig. 1e and f). The developed method is well reproducible. Fig. 2 shows the α-Al_2O_3 loading of the monoliths after each coating. The mean amounts of α-Al_2O_3, in percentage, after each coating were (values in parenthesis are the standard deviations): 26.8 (1.2), 43.7 (1.5) and 59.2 (0.9), respectively.

In Fig. 3, SE images corresponding to the carbon-coated monoliths are shown. A cross-sectional view, where the carbon layer is observed clearly on the α-Al_2O_3 rounded corner, is shown in Fig. 3a and, Fig. 3b contains a detail of this carbon surface. The carbon layer has a mean thickness of 14 μm. General views of carbon-coated monoliths with and without a α-Al_2O_3 layer between the carbon and the

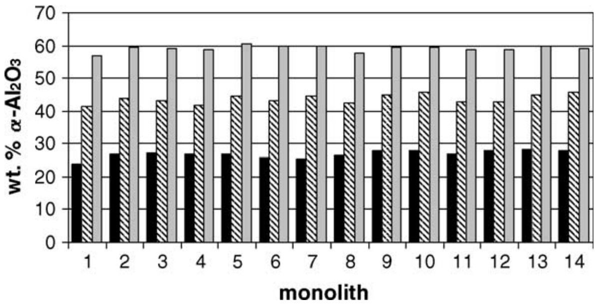

Fig. 2. α-Al_2O_3 loading of the monoliths after each coating. Black, striped and grey columns correspond with the first, second and third coatings, respectively.

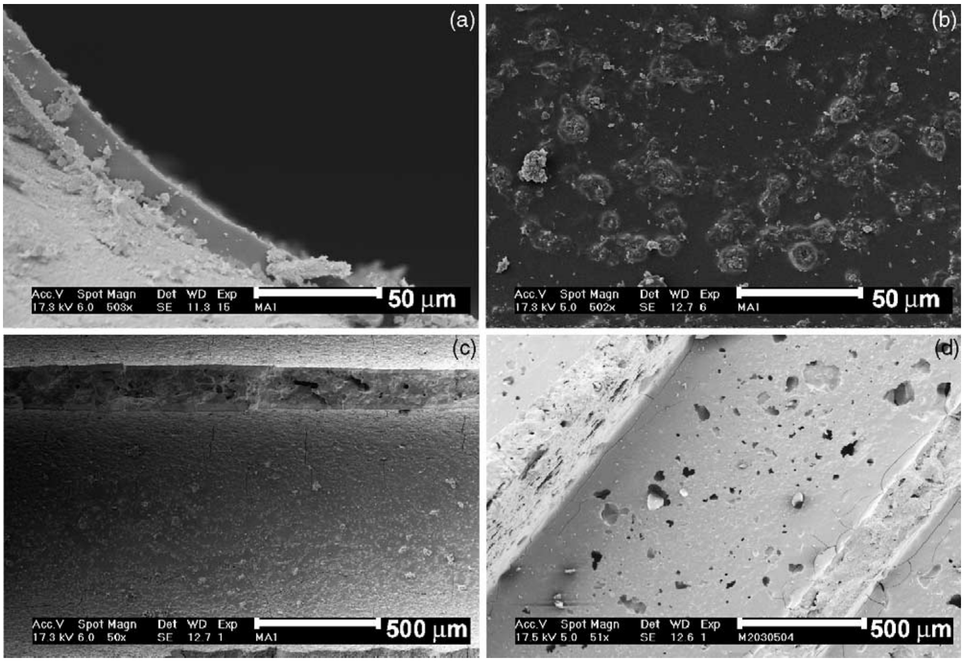

Fig. 3. SE images of the carbon layer on α-Al_2O_3-coated monolith: (a) cross-section view at 503× magnification, (b) top view at 502× magnification, (c) top view at 50× magnification and (d) the top view of the carbon layer formed directly on the cordierite surface at 50× magnification.

Table 1
Characterization data of the catalysts

Catalyst	α-Al_2O_3 ($wt_{catalyst}$%)	Carbon ($wt_{catalyst}$%)	Pd ($wt_{catalyst}$%)	Dispersion (%)	Particle size (nm)	Pd (wt_{carbon}%)
MC	0.0	16.1	0.65	11.5	9.7	4.1
HPMC	56.1	6.3	0.30	23.1	4.8	4.6

cordierite are shown in Fig. 3c and d, respectively. When the α-Al_2O_3 layer is not applied a part of the catalytic support (carbon) is deposited inside the walls [7].

Surface areas of the activated carbon layer were obtained by applying BET and DR equations to the N_2 and CO_2 adsorption isotherms, respectively, resulting in values of 2 $m^2\ g_{carbon}^{-1}$ for S_{N_2} and 246 $m^2\ g_{carbon}^{-1}$ for S_{CO_2}. TPD revealed a 20 wt% oxygen content in the activated carbon layer and a high proportion of this (41%) evolved as CO_2.

The α-Al_2O_3, carbon and Pd loading of the catalysts, together with dispersion and particle size of the Pd determined from CO-chemisorption, are presented in Table 1. Both, MC and HPMC, have similar Pd loading per gram of carbon (catalytic support), however the mean particle size of the metal in HPMC is considerably smaller than in MC.

The FAMEs conversion as a function of time, normalised for the amount of palladium is given in Fig. 4a. MC is somewhat more active although the difference becomes less

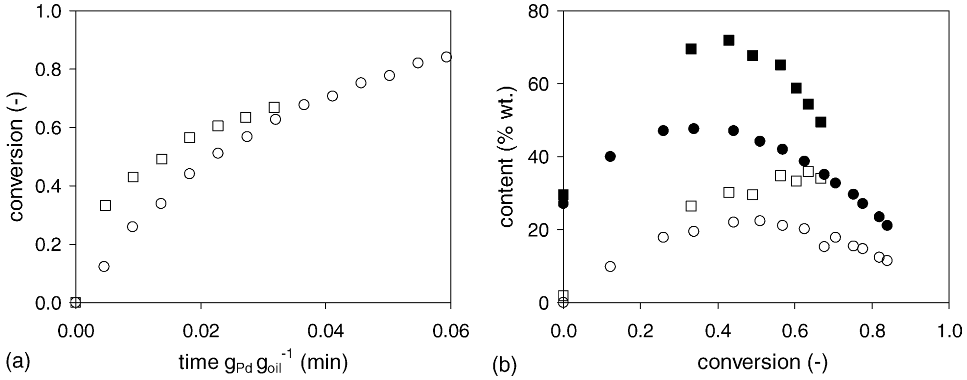

Fig. 4. Reaction performance data for the catalysts MC (square symbols) and HPMC (round symbols). (a) Conversion as function of time normalised per gram of Pd. (b) Product composition as function of conversion. Closed symbols represent *monoenes* and open symbols *trans* components.

Table 2
FAMEs composition (wt%) of the feed and around 50% conversion

FAME	Initial	MC at 49% conversion	HPMC at 51% conversion
Palmitate (c16:0)	5.7	5.7	5.7
Stearate (c18:0)	3.3	22.1	34.5
Oleate (*cis* c18:1)	25.6	41.0	25.8
Elaidate (*trans* c18:1)	<0.1	26.6	18.8
Linoleate (*cis*,*cis* c18:2)	64.3	1.2	11.1
trans Isomers of linoleate	<0.1	2.9	3.5
Linolenate (*cis*,*cis*,*cis* c18:3)	0.6	<0.1	<0.1
Other	0.3	0.4	0.5

at increasing conversions. Fig. 4b shows the product composition as a function of the conversion. There is a clear difference between the catalysts: at equal conversion the product formed by HPMC contains less *monoenes* and less *trans* FAMEs. The complete product distribution at 50% conversion is given in Table 2.

4. Discussion

α-Al_2O_3 is an attractive first coating because of its very low surface area and price. After this coating, all the macroporosity of the cordierite is blocked (Fig. 1). This process also produces round corners in order to reach a shorter and uniform diffusion distances in the washcoat. The typical cracks observed after the carbonization of PFA-coated monoliths show soft-edges, that are attributed to the shrinking of the coating during carbonization [7]. These soft-edged cracks are mainly observed around the corners of the square channels due to the fact that in these locations more PFA is deposited [7] (Fig. 3d). However, in the case of our carbon-coated monolith with round channels, soft-edged cracks only are observed at a very high amplification, as the thickness of the carbon layer is homogeneous along the whole perimeter of the rounded channel.

Surface area data of the activated carbon layer obtained by N_2 and CO_2 adsorption indicate the absence of mesopores and only microporosity is present. Therefore, considering that the size of a C:18 fatty acid molecule is around 2 nm, probably the hydrogenation reaction will mainly take place on the more external surface of the catalytic support. On the other hand, its high surface oxygen groups content has created potential anchoring sites for the cationic palladium complex.

The fact that MC and HPMC have similar Pd loadings per gram of carbon (Table 1), indicate that this metal is only deposited on the carbon and the presence of Pd within the α-Al_2O_3 layer is less likely. If so, it will not be accessible. The difference in the particle size of the samples (Table 1) might be related to the macropores of the cordierite, where the carbon penetrates when the α-Al_2O_3 layer is not present. In these places, the diffusional distances for reactants are longer compared to those situated around the channels.

Two simultaneous reactions take place in the hydrogenation of vegetable oils or FAMEs: hydrogenation and *cis–trans* isomerization of the carbon–carbon double bonds. The latter process has a lower order in hydrogen than the former so, *trans* formation can be minimized by operating at increased pressures [8]. Reduced formation of *trans* fats and *monoenes* at increased pressure was also observed with monolithic catalyst [5]. In this way, any change in operating conditions that increases the hydrogen concentration inside the monolithic catalyst (or reduces the gradient) will result in less *trans* formation. So, as the Pd in HPMC is more accessible to both reactants, smaller gradients of hydrogen and less consecutive reactions (*cis–trans* isomerization) are expected. Therefore, the rounded channels of HPMC at the same time would improve the mass transfer of hydrogen from the bulk to the catalytic surface and the removal of *cis* monoene before it isomerizes. Fig. 4b shows clearly that less *trans* is formed with this catalyst. In the MC, the diffusion distances are much longer due to the presence of catalyst throughout the monolith walls [9].

5. Conclusions

A new α-Al_2O_3-coated monolith of cordierite with rounded channels and the macroporosity blocked has been developed.

The activated carbon layer obtained on the monolithic structures, contain a high oxygen content and its specific surface area is somewhat microporous. Mesopores are not present.

Penetration of the carbon and Pd into the walls of the monolithic channels seems to be avoided when cordierite monoliths were previously coated with the α-Al_2O_3 layer. Although both types of prepared monolithic catalyst had similar Pd loading per gram of carbon, the mean particle size of the metal was considerably lower in the monolithic catalyst previously coated with the α-Al_2O_3 layer.

Palladium catalysts supported on the two different carbon-coated monolithic structures were active in the FAME hydrogenation reaction, however, the monolithic catalyst previously coated with the α-Al_2O_3 layer, called high performance monolithic catalyst, produced a lower amount of *trans* product. This improvement in the selectivity performance is due to a better accessibility of the active Pd, reducing diffusion limitations.

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