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Selective hydrogenation of fatty acid methyl esters over palladium on carbon-based monoliths Structural control of activity and selectivity

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Abstract

Three different carbon-based monoliths are studied in their performance as Pd-catalyst supports in the selective hydrogenation of fatty acid methyl esters of sunflower oil (FAME). The first monolithic support (HPM) was a classical square channel cordierite modified with α-Al_2O_3 blocking the macroporosity of the cordierite and rounding the channel cross section, on which, a uniform carbon layer was applied by carbonization of a polyfurfuryl alcohol coating obtained by dipcoating. The other two monolithic supports were composite carbon/ceramic monoliths (MeadWestvaco Corporation, USA), a micro- (WA) and a mesoporous (WB) sample.

The Pd/HPM catalyst shows a superior selectivity performance compared to the other two samples in the partial hydrogenation of FAME, in terms of the much lower formation of *trans* double bonds at similar levels of the double bond hydrogenation. This is ascribed to an optimal supply of the reactants and removal of products by only external mass transfer to the nearly nonporous carbon coating. The other two samples suffer from pore diffusion limitations to different extents.

Keywords: Carbon composites; Monolithic catalysts; Surface properties; FAME; Selective hydrogenation; Palladium

1. Introduction

Edible oils are 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 of poly-unsaturates, while avoiding the formation of saturates or of *trans* products. In recent years the negative health effects of *trans* fats have received increasing attention, and these fats are considered to be even more detrimental than saturated fats [1]. As a consequence there is growing interest in new hydrogenation processes that reduce the amount of *trans* fats formed, e.g. by supercritical hydrogenation [2] and through the use of structured catalytic packings or monoliths [3]. Further, carbon materials have important tuneable chemical and textural surface properties for their use as catalytic supports [4]. Recently [5], carbon coated monoliths have been used as catalyst support in this reaction showing that there exists a strong interplay between the carbon support properties and its performance in the Pd catalyzed selective hydrogenation of edible oils. With the aim to understand the role of the monolithic carbon materials in these reactions, the performance of palladium supported on different carbon-based monoliths has been studied in the selective hydrogenation of fatty acid methyl esters (FAMEs) as a model for unsaturated triglycerides.

2. Experimental

The high performance monolith (HPM) catalyst support was prepared from cordierite monolithic substrates by coating with an α-Al_2O_3 layer using a dipcoating method [6], in order to block the macroporosity and to prevent deposition of catalytic material in the wall of this monolith substrate, as well as to round the channel cross section [7]. The monolithic substrates had square cells, a cell density of 62 cells cm^{-2} (400 cpsi), a wall thickness of 0.18 mm, a length of 5 cm and a diameter of

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1 cm. In a second step a thin carbon layer of uniform thickness (14 μm, determined by SEM) has been formed on the α-Al_2O_3 layer [6], which served as a support for the active catalytic phase. The total carbon content of HPM was 6.3 wt.%.

Two composite carbon/ceramic monoliths, WA and WB samples (MeadWestvaco Corporation, USA), have also been selected as catalyst supports. Both monoliths have a cell density of 400 cpsi, length 5 cm, diameter 1 cm, and a total carbon content of 34.7 and 30.9 wt.% for WA and WB, respectively. The ceramic % weight composition of SiO_2/Al_2O_3/other amounted to 62.7/29.8/7.5.

The three monoliths (HPM, WA and WB) were subjected to an oxidation treatment of the carbon with an aqueous solution of 9.8 M H_2O_2 for 24 h at room temperature to create anchoring sites on the carbon for the metal. Pd was deposited by equilibration of the monolithic supports with an aqueous solution of tetraammine palladium (II) nitrate. Textural characterization of the samples was carried out by CO_2 and N_2 adsorption at 0 and −196 °C, respectively, and by mercury porosimetry. The BET [8] equation was used for analysis of N_2 adsorption isotherms, and the Dubinin-Raduskevich and Stoeckli [9] relations for analysis of CO_2 adsorption data. The liquid density of CO_2 at 0 °C was taken as 1.03 g cm^{-3} and the molecular area of N_2 at −196 °C as 0.162 nm^2. Mercury porosimetry was performed up to a pressure of 4200 kg cm^{-2} (Quantachrome Autoscan 60). This technique yielded the pore volume corresponding to pores with diameter between 3.7 and 50 nm, V_{MESO}, referred to as mesopore volume (note that the mesopore size range [10] is classically defined as 2–50 nm), the macropore volume (pores with diameter larger than 50 nm) V_{MACRO}, and the external porous surface area (surface area of macro and mainly mesopores), S_{EXT}.

The surface chemistry of the carbon/ceramic monoliths was characterised by temperature-programmed desorption (TPD). TPD experiments were carried out by heating the samples to 1000 °C in He flow (60 cm^3 min^{-1}) at a heating rate of 50 °C min^{-1}. The amount of evolved gases was recorded as a function of temperature using a quadrupole mass spectrometer (Balzers, model Thermocube) [11].

The Pd loading of the monolithic catalysts was determined by neutron activation analysis (NAA) using a germanium semiconductor as detector. The palladium dispersion, D, and its average particle size were obtained by CO-chemisorption at 40 °C assuming a CO:Pd = 1:1 stoichiometry, and that the average particle size = 1.12/D (nm). CO-chemisorption isotherms were measured in conventional volumetric equipment made of Pyrex glass and free of mercury and grease, which reached a dynamic vacuum better than 10^{-6} mbar at the sample location. Equilibrium pressure was measured with a Baratron transducer from MKS. All catalysts were pretreated at 300 °C in H_2 flow (purity of 99.999%) for 2 h, both prior to the characterization by CO-chemisorption and for the hydrogenation of FAME of sunflower oil.

XPS measurements were made with an Escalab 200R system (VG Scientific Co.) equipped with Mg Kα X-ray source ($h\nu$ = 1253.6 eV) and hemispherical electron analyzer. Prior to the analysis, the samples were crushed and evacuated at high vacuum and then introduced into the analysis chamber. A base pressure of 10^{-9} mbar was maintained during data acquisition.

TPR was carried out in a tubular quartz reactor (5 mm inner diameter) coupled to a TCD analyzer for monitoring H_2 consumption. Crushed monolith samples (150 mg) were heated at 2 °C min^{-1} from room temperature to 400 °C in an Ar flow (30 cm^3 min^{-1}) containing 8% of H_2.

Hydrogenation of the pure FAME of sunflower oil was carried out in a 300 ml autoclave (H_2 pressure of 2.0 MPa, 100 °C) equipped with a screw impeller stirrer working at 1600 rpm [12]. The composition of the FAME from sunflower oil is given in Table 4. The conversion is defined as the fraction of the carbon–carbon double bonds that have been hydrogenated with respect to the original amount of double bonds. '*monoene*' is referred to hereafter as the total amount of *trans* and *cis* mono-unsaturated esters in the product, '*trans*' is referred to hereafter as the total amount of *trans* carbon–carbon double bonds in the products. Poly-unsaturated esters containing at least one *trans* double bond were lumped into this *trans*-group.

3. Results and discussion

The specific surface areas are compiled in Table 1. The S_{BET} of the carbon in sample HPM is much lower than S_{CO_2}, which is indicative of small micropores or pore constrictions at the entrance of the micropores, making the microporosity almost inaccessible to the N_2 molecules at −196 °C. The N_2 adsorption isotherm of sample WA was of type I, indicative of a microporous material. The N_2 adsorption isotherm of sample WB, however, showed a progressive increase in adsorbed volume over a wide pressure range, suggesting a broad distribution of mesopores.

Both samples WA and WB, show similar S_{BET} values, being larger than S_{CO_2}, indicative of a heterogeneous micropore size distribution. While sample WA has only macropores, sample WB has meso and macropores, resulting in an S_{EXT} larger than that of sample WA.

Table 1
Surface areas and pore volumes of the monolithic supports

Monolithic support	[a]S_{CO_2} (m^2 g^{-1})	S_{BET} (m^2 g^{-1})	[b]S_{EXT} (m^2 g^{-1})	[b]V_{MACRO} (cm^3 g^{-1})	[b]V_{MESO} (cm^3 g^{-1})
WA	329 (947)	474 (1366)	4 (12)	0.325 (0.937)	0
WB	242 (782)	460 (1489)	62 (199)	0.233 (0.754)	0.138 (0.447)
HPM	17 (269)	(2)	(<1)	(n.d.)	(n.d.)

Data in parenthesis are given per gram of carbon. n.d.: not detected.
[a] By application of Dubinin-Raduskevich and Stoeckli equations to CO_2 adsorption data.
[b] By mercury porosimetry.

Table 2
Amounts of CO and CO_2 evolved up to 1000 °C and oxygen content of the monoliths

Monolith	CO_2 (μmol g^{-1}_{carbon})	CO (μmol g^{-1}_{carbon})	O ($wt._{carbon}$%)
WA	409	1166	3.18
WB	377	1127	3.01
HPM	2620	7295	20.1

Data are given per gram of carbon.

Table 3
Pd loading, dispersion and metal particle size of the catalysts

Monolithic catalyst	Pd (by XPS) ($wt._{total}$%)	Pd ($wt._{total}$%)	Dispersion (%)	Particle size (nm)
Pd/WA	n.d.	0.42	18.2	6.1
Pd/WB	n.d.	0.49	23.0	4.9
Pd/HPM	2.56	0.30	23.1	4.8

n.d.: not detected.

The amounts of CO and CO_2 evolved up to 1000 °C in the TPD experiments, as well as the oxygen content of the monoliths after the oxidation treatment are given in Table 2. The carbon in the HPM sample has the highest total oxygen content, while in the case of the WA and WB monolithic supports, the chemical surface properties are very similar.

All catalysts showed intense hydrogen consumption in TPR below 300 °C, indicating the decomposition of the tetraammine complex as well as the reduction of the Pd particles during the pre-treatment [13], as indicated in Fig. 1 for catalysts Pd/WB and Pd/HPM. The hydrogen consumption at higher temperatures is ascribed to hydrogenation of the carbon and possible methane formation.

Pd loading, dispersion and particle size of the catalysts are presented in Table 3. All catalysts have a comparable Pd loading based on the total sample mass, and although sample Pd/WA showed a slightly lower dispersion we consider that all catalysts have a similar Pd particle size. The Pd XPS-signal was negligible in samples Pd/WA and Pd/WB, whereas that in sample Pd/HPM indicated a high Pd concentration. As we have crushed the samples for XPS analysis this indicates that in the Pd/WA and Pd/WB samples the Pd is distributed homogeneously throughout the sample whereas for the HPM sample significant surface enrichment has taken place.

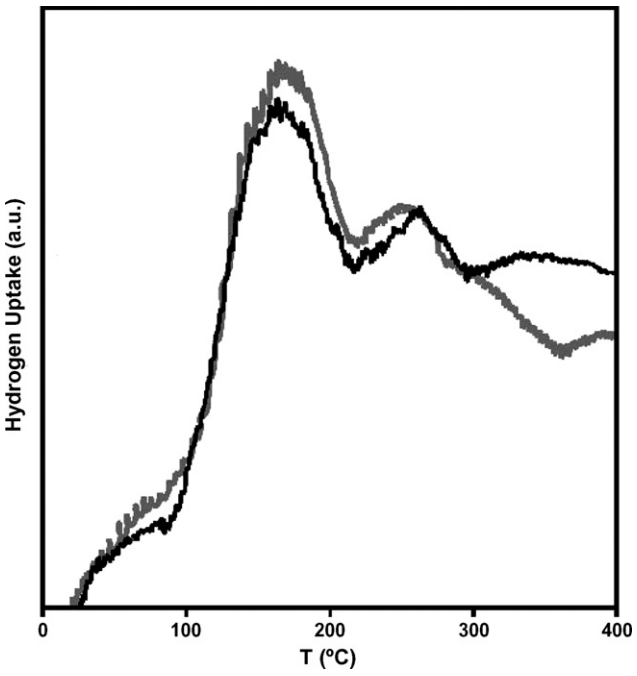

Fig. 1. TPR curves of Pd/HPM (black line) and Pd/WB (grey line).

Taking into account the mean Pd particle size of the samples (around 5–6 nm), the catalyst preparation method (equilibration from an aqueous solution), the XPS results and the type of porosity of the supports, it is concluded that the Pd crystallites are located at the external nonporous surface of the carbon layer in the Pd/HPM sample. In the case of the Pd/WA sample the Pd is located in the macropores, while in sample Pd/WB the Pd is distributed throughout the meso and macropore space. In view of their size the Pd particles will not be located in the micropores of the samples. Therefore, the microporosity will not affect the activity of the Pd catalysts.

Fig. 2 shows schematic cross sectional views of the monolithic channels for the three catalysts, indicating the effective surface area of the monolithic supports accessible to Pd particles in each sample (micropores are not drawn).

The activity of the catalysts for the FAME hydrogenation was compared by normalising the time with respect to the amount of FAME present per area of Pd (Fig. 3). The activity of sample Pd/WA is higher than that of Pd/HPM, while Pd/WB is the least active catalyst.

During hydrogenation the Pd/HPM catalyst produces the lowest amount of *monoene* at similar double bond conversion levels (Fig. 4), but also showed the lowest *trans* formation (Fig. 5). On the other hand, the least active catalyst Pd/WB produced much larger amounts of *trans* isomers.

The results can be interpreted by considering the reaction network. The FAME hydrogenation to saturation consists of consecutive steps, while the *cis–trans* isomerisation occurs as a parallel reaction of the unsaturated components. Further for the hydrogenation hydrogen is needed and generally first order in pressure [3], while in the isomerisation hydrogen is not consumed and the rate is only weakly dependent on the hydrogen pressure, although hydrogen must be present for the reaction to proceed [14]. Hence, the hydrogen concentration controls the reaction selectivity of hydrogenation versus isomerisation. A low hydrogen concentration favours the *cis–trans* isomerisation relative to the hydrogenation, but in the absence of hydrogen both reactions stop. Further, the diffusion-reaction model for porous catalysts always predicts a lower yield of intermediate products if diffusion limitations are present.

In view of the low hydrogen concentration in the pure FAME liquid (~55 mol H_2 m^{-3}) combined with a more difficult H_2 diffusional supply through the liquid filled pores makes it the limiting reactant. Since the transport in the mesoporous structure of Pd/WB is more difficult than in the macroporous Pd/WA sample, the latter suffers less from these limitations. So both the poorer selectivity (more *trans*) and the lower activity of

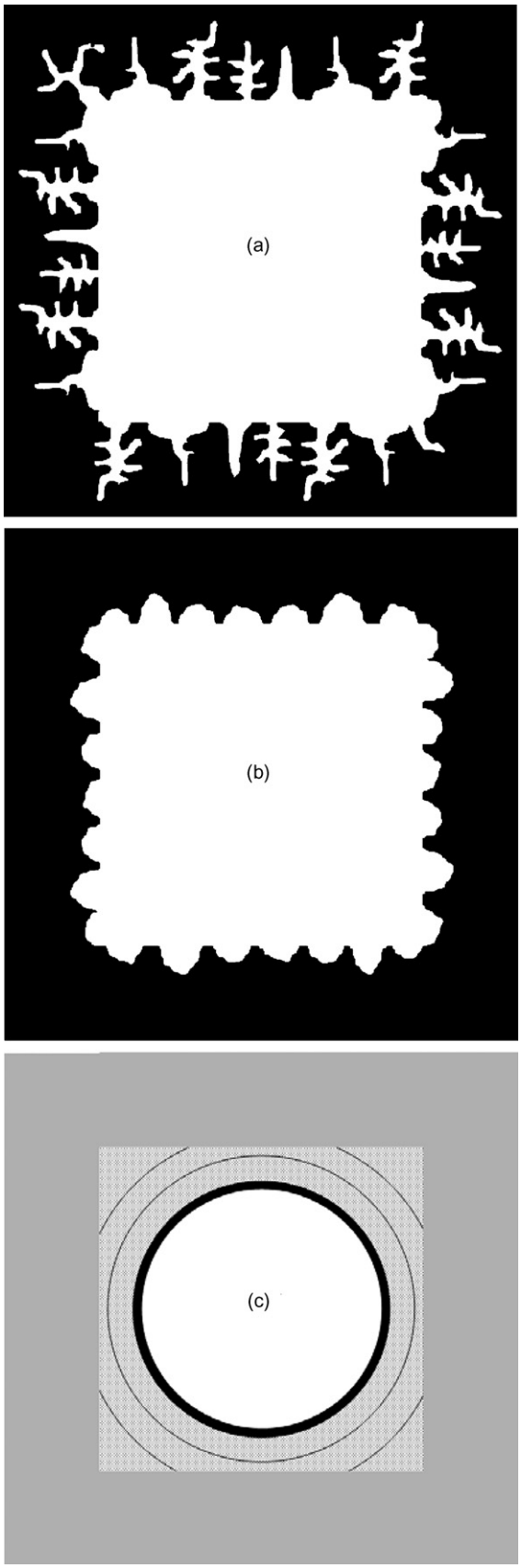

Fig. 2. Schematic representation of the channel cross section of the monolithic catalysts: (a) Pd/WB, (b) Pd/WA and (c) Pd/HPM.

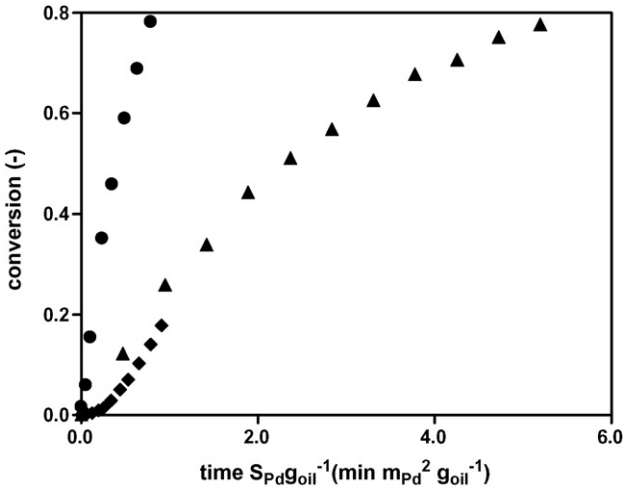

Fig. 3. Double bond conversion as function of time normalised to Pd surface area per amount of FAME treated. Key: (▲) Pd/HPM, (●) Pd/WA and (◆) Pd/WB.

the Pd/WB sample are therefore attributed to the stronger diffusion limitations in this sample. In this way, when sample Pd/HPM is used, the H_2 diffusional supply through the pores does not exist, because the carbon layer in this sample is nearly nonporous and so the Pd is concentrated at the external surface, as evidenced by XPS. So the only transport process is external transport, and the reaction-diffusion problem in the catalyst pores of the other samples does not apply for this catalyst. The lowest *trans* formation is ascribed to the better mass transfer resulting in the more favourable hydrogen/reactant ratio at the external surface, resulting simultaneously in a higher degree of further hydrogenation of the monoene (Fig. 4). This also explains the larger yield of monoene for sample Pd/WA. Here, the lower hydrogen concentration in the pores limits the consecutive hydrogenation of the monoene and yields relatively more *trans* than HPM. These transport limitation phenomena can be also related to the FAME composition obtained during reaction. Table 4 shows these values in the beginning of the

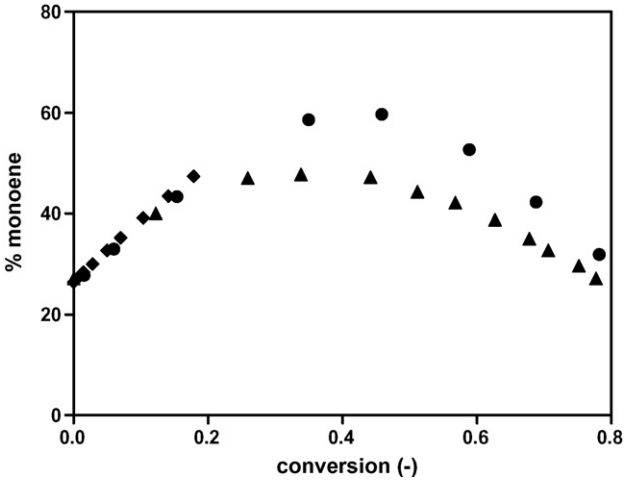

Fig. 4. *monoene* product content as function of double bond conversion. Key: (▲) Pd/HPM, (●) Pd/WA and (◆) Pd/WB.

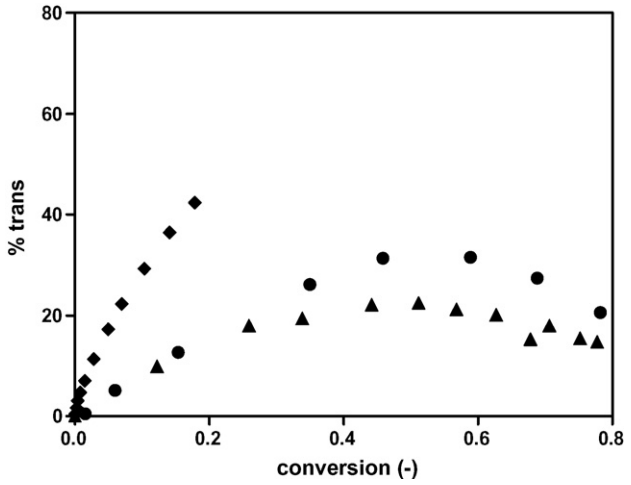

Fig. 5. *trans* product content as function of double bond conversion. Key: (▲) Pd/HPM, (●) Pd/WA and (◆) Pd/WB.

Table 4
FAME composition (wt.%) in the beginning of the reaction, and at 20% double bond conversion

FAME	Initial	Pd/WA	Pd/WB	Pd/HPM
Stearate (c18:0)	3.3	7.5	7.0	11.1
Oleate (*cis*-c18:1)	25.6	37.5	26.7	35.0
Elaidate (*trans*-c18:1)	<0.1	10.8	20.6	8.5
Linoleate (*cis*, *cis*-c18:2)	64.3	32.4	22.6	33.8
trans isomers of linoleate	<0.1	5.4	16.3	5.3
Palmitate (cl6:0) + others	6.6	6.4	6.8	6.3

reaction, and at 20% of conversion. The high level of *trans* isomers produced for Pd/WB is not only due to formation of *trans*-c18:1; a larger amount of *trans* isomers of linoleate are produced as well. This means that the main initial FAME reactant (linoleate) is extensively *trans*-isomerised without hydrogenation.

The results presented here are consistent with corresponding results on the use of other carbon-coated cordierite monoliths as catalyst support in the selective hydrogenation of FAME [5]. It is clear that diffusion limitations can be used as a tool to control selectivity.

4. Conclusions

The three carbon-based monoliths, HPM, WA and WB, can be used as supports of Pd in the selective hydrogenation of FAME.

The Pd/HPM sample, with rounded channels and uniform carbon layer, showed the best performance as Pd-catalyst compared to the other two samples in the partial hydrogenation of FAME, in terms of the much lower formation of *trans* double bonds at similar levels of double bond conversion. This behaviour is ascribed to the much shorter diffusion distances of the reactants and products, because of the Pd particles are placed at the external nonporous surface of the carbon layer.

Regarding to the two composite carbon/ceramic monoliths, WA and WB samples, the Pd-catalyst supported on the mesoporous sample (WB) was less active and produced larger amounts of *trans* isomers, attributed to H_2 diffusion limitations. For the most active, microporous Pd/WA catalyst, the H_2 supply is less limiting since the Pd particles are envisaged to be located only in the macropores of the carbon coating, and hence have a better accessibility.

Finally, this work demonstrates that the type of porosity of carbon materials can strongly affect the activity and selectivity in selective hydrogenations if used as catalyst support.

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