



# Supported Catalysts

# Influence of Carbon Supports on Palladium Nanoparticle Activity toward Hydrodeoxygenation and Aerobic Oxidation in Biomass Transformations

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**Abstract:** Three palladium catalysts at similar loadings supported on few-layers graphene (FLG), carbon nanotubes (CNT) and carbon nanofibers (CNF) have been prepared by wet impregnation of palladium nitrate with the purpose of determine the influence of the support on Pd catalytic activity. The supports and catalysts have been characterized by chemical analysis, Raman spectroscopy, XRD, electron microscopy and XPS. The average Pd particle size depends on the carbon support, ranging from 1.6 nm for CNF to 2.6 nm for FLG. The catalytic activity of these catalysts was evaluated for two different reactions of interest for biomass transformations, namely hydrode-

## Introduction

For the sake of sustainability, there is much current interest in developing processes to obtain bulk chemicals from biomass.<sup>[1,2]</sup> Most of the biomass transformation reactions require catalysts to achieve high conversion and selectivity towards the target product. Since there are numerous reactions in biomass transformations consisting in hydrogenations and aerobic oxidations, many of these processes can be promoted by supported palladium catalysts.<sup>[3,4]</sup> Among the preferred supports, carbon derived materials have been widely used due to their availability, large surface area, tunability of surface properties and the ability of these carbon supports to stabilize small Pd nanoparti-

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oxygenation of vanillin to 2-methoxy-4-methyl-phenol (creosol) that requires a bifunctional catalyst with hydrogenating and Lewis acid sites, and aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid. Both compounds have application either as food flavouring additive and polyester co-monomer. For the two reactions the activity order of the fresh catalyst was Pd/FLG > Pd/CNF > Pd/CNT, indicating that FLG contributes favorably to the activity in spite of the larger Pd size of the nanoparticles on this support, a fact that has been attributed to the interaction with the prismatic planes on where Pd nanoparticles are located.

cles (NPs).<sup>[5]</sup> Since different allotropic forms of carbon have become commercially available, and considering the influence that the support plays on the catalytic activity and stability of supported metal nanoparticles (MNPs), there have been an interest in comparing the performance of these MNPs supported on different carbon nanoforms.<sup>[6]</sup> In this regard it has been found that carbon nanotubes (CNTs) and few-layers graphenes (FLG) can be used as supports of MNPs due to the interaction between the extended  $\pi$  orbital of the CNT and FLG and the partially empty d orbitals of transition metals.<sup>[7]</sup> In addition, carbon nanofibers (CNFs) consisting in 1D thick carbon materials with long aspect ratio can be advantageous also from the point of view of their availability.<sup>[6]</sup>

In the present study a series of three Pd catalysts supported on CNT, FLG or CNF has been prepared with the purpose of evaluating the influence of the nature of the carbon support on the palladium catalyst for two different reaction types of interest in biomass transformation. Although there are some reports on the activity of other bimetallic catalysts for these reactions,<sup>[4]</sup> since palladium is among the most efficient catalysts, the focus of the present study is the influence of the nature of the carbon supports on the catalytic activity of Pd nanoparticles for two important reactions in the transformation of biomass. Specifically, the reactions under study are shown in Scheme 1. As it can be seen there, one of them is the hydrodeoxygenation of vanillin (V), an abundant starting material,<sup>[8]</sup> to 2-methoxy-4-methylphenol (MMP, creosol) that is an important product in the food flavoring industry. This reaction requires a bifunctional catalyst having hydrogenating activity as well as some acidity.<sup>[9]</sup> In the literature there are precedents reporting





a) Hydrodeoxygenation of vanillin



Scheme 1. Two selected biomass transformations that can be catalysed by Pd NPs supported on carbon materials.

the catalytic hydrodeoxygenation of vanillin, a reaction requiring bifunctional acid/base and hydrogenating sites, using supported noble metal nanoparticles such as Pt, Au and Pd. Of them, Pd was among the most active catalyst.<sup>[10]</sup> The reported studies deal with the catalytic activity of Pd nanoparticles on metal oxides and large area active carbons. However, the possible role of the nature of the carbon support has not been yet addressed. This is important in order to understand better the role of the carbon support on the catalytic function. The second reaction consists in the aerobic oxidation of 5-hydroxymethylfurfural (HMF) to furan dicarboxylic acid (FDCA) that can be a biomass-derived monomer for the preparation of sustainable polyesters.<sup>[11,12]</sup> HMF is the main platform chemical obtained from cellulose that accounts for 40 % of all the biomass feedstock.<sup>[1,13]</sup> Pd containing catalysts have also been used to promote the aerobic oxidation of HMF.<sup>[14]</sup> In this reaction, the main issue was to achieve high selectivity towards the wanted dicarboxylic acid. Also for this reaction, comparison with other noble metals such as Pt or Au shows the higher activity of Pd.<sup>[11]</sup> Although active carbon has also been used as support for Pd nanoparticles in HMF oxidation, a detailed study on the influence of different type of carbons has still not been made, this being the main objective of the present study.<sup>[15]</sup> The data obtained have allowed to rationalize the activity of Pd nanoparticles and their stability as depending on the basal/prismatic plane ratio of the carbon support.

#### **Results and Discussion**

#### **Catalyst Support and Catalyst Characterization**

Three kinds of carbon materials presenting different arrangement of the graphene layers, CNTs, CNFs, and FLG were used as support for palladium deposition. CNT, CNF and FLG supports were previously oxidized with nitric acid to increase the concentration of surface carboxylic groups, which should act as anchoring sites for MNPs.<sup>[16]</sup> The elemental analysis, XPS and XRD patterns, and nitrogen adsorption data of these three supports are listed in Table 1. TEM micrographs of the supports are provided in Figure S1.

These materials show different arrangements of the graphene layers. Among the filamentous carbon materials, we can distinguish between CNTs, for which the graphene layers are parallel to the filament axis, and CNFs, for which an angle exists between the filament axis and the graphene layers. The average angle with respect to the filament long axis is  $\approx 26^{\circ}$  for CNF. For this latter support, disordered amorphous carbon can be occasionally observed at its surface, resulting in a mixture of edges and disordered carbon (Figure S2). The mean external diameter of CNFs is 50 nm, and their mean inner diameter is 6 nm. The CNTs are multi-walled, with an average external diameter of 15 nm, and an internal diameter of 7 nm. They are composed of 5-10 graphene layers. The FLG consists in graphitic flakes of turbostratic carbon of around 1 µm<sup>2</sup>, the number of graphene layers ranges between 5 and 50. The elemental analysis shows a high level of purity for these materials (90-97 %). The treatment with nitric acid, for a given type of material, results in an increase of the amount of surface oxygen, as revealed by XPS. The percentage of oxygen determined by XPS for the purified supports was: 0.8 for CNTs, 0.9 for FLG and 1.5 for CNFs. The textural properties of the supports have been evaluated from nitrogen adsorption/desorption isotherms. These carbon materials present pore volumes of 0.2 to 1.2 cm<sup>3</sup> g<sup>-1</sup> and are predominantly mesoporous. For the filamentous carbons, the pores arise from interstices between entangled fibers or tubes. The specific surface area of the supports

Table 1. Chemical, textural, and crystallite parameters of the carbon supports used in the present study.

Supports	Elemental analysis	XPS analysis		Textural proper	rties	Crystallite p		
	C [%]	C [%]	O [%]	BET surface area [m <sup>2</sup> g <sup>-1</sup> ]	Pore volume [cm <sup>3</sup> g <sup>-1</sup> ]	d <sub>002</sub> [nm]	L <sub>C</sub> (002) [nm]	L <sub>a</sub> (110) [nm]
CNT <sub>COOH</sub>	90.4	94.3	5.7	220	1.2	0.3407	4.48	7.95
FLG <sub>COOH</sub>	97.1	96.2	3.8	51	0.2	0.3393	10.34	16.05
CNF <sub>COOH</sub>	95.7	93.4	6.6	71	0.3	0.3434	4.64	10.95





ranged between 50 and 220 m<sup>2</sup> g<sup>-1</sup>. Type IV isotherms with type H<sub>2</sub> hysteresis loops were obtained (Figure S3), suggesting that the supports are mainly mesoporous and contain, as expected, a small number of micropores. Since the ratio between the basal plane and "non-basal plane" surface areas should be an important factor in determining the surface reactivity of these materials, DFT calculations, derived from nitrogen adsorption data, were used for the determination of surface heterogeneities in these supports by adsorptive potential distribution.<sup>[17]</sup> Thus, the absolute and relative proportion of basal plane and "non-basal plane" surface areas can be determined from the nitrogen adsorption measurement, followed by an evaluation of the adsorption data using DFT.<sup>[18]</sup> The "non-basal plane surfaces" can be further subdivided into prismatic surfaces and "defect surfaces" (the latter contain surface groups and other surface defects). Figure 1 depicts the percentages of prismatic: basal: defect surfaces of the three supports. The highest proportion of basal surface area is observed for CNTs, followed by FLG. The fact that the produced FLG flakes present a significant number of layers (5-50) and defect density (see Raman spectra) could explain this result. As expected, CNF presents a significant amount of defects. This should be related to the surface of the CNF being composed of a mixture of



Figure 1. Percentage of prismatic (black): basal (light grey): defect surfaces (dark grey) surface area of the supports. a) CNT; b) FLG, and c) CNF.

edges and disordered carbon, as already discussed (Figure S2). From this characterization, we can anticipated that the CNF support with high proportion of edges and defects should not favor metal sintering due to a limited metal diffusion on such a surface.

The  $d_{002}$  graphene interlayer distances, the average crystallite size considering the particles as parallelepiped in the basal plane (parallel to the hexagonal layers, L<sub>a</sub>) and parallelepiped height (perpendicular to the hexagonal layers, L<sub>c</sub>). These parameters were determined from the position of the corresponding peaks in XRD.<sup>[19]</sup> The corresponding diffractograms are given in Figure S4. The highest intensity for the graphite (002) peak ( $2\theta = 26^\circ$ ) and therefore  $d_{002}$  values close to the value for graphite (0.335 nm), was observed for the FLG support. This support shows also the largest crystallite size.

The Raman and detailed XPS characterizations of the carbon supports are reported in Table 2. The best fit for the main C1s spectrum (Figure S5) was obtained by deconvoluting the experimental high resolution XPS peak into seven line shapes: i) peak i, at around 283.7 eV, is attributed to the presence of point defects (C vacancies, pentagon and heptagon rings, Stone-Wales defects); ii) peak ii, at 284.6 eV, represents sp<sup>2</sup> C-C bonds; iii) peak iii, at 285.1–285.2 eV, is assigned to sp<sup>3</sup> carbon species; iv-vi) the peaks at 286.0-286.2 (iv), 287.3-287.5 (v), and 288.4-289.2 eV (vi), correspond to carbon atoms attached to different oxygen-containing groups; and vii) the  $\pi$ - $\pi$ \* transition loss peak is detected at 290.6-291.2 eV.[20] For all the investigated supports, significant amounts of oxygenated species were detected (peaks iv, v and vi in XPS C1s peak), resulting from HNO<sub>3</sub> oxidation. The amount of  $sp^3$  carbon follows the order CNF > CNT > FLG. The amount of  $sp^2$  carbon follows the opposite order. FWHM of the C 1s peak has been used to assess the graphitic nature of the supports, with a larger FWHM corresponding to a more disordered structure.<sup>[21]</sup>

Raman spectroscopy was also used to evaluate the degree of structural order of the supports. It provides analogous information to XRD, although it has the advantage of surface specificity, thus allowing the study of very heterogeneous materials. The most important parameter calculated Raman spectroscopy is the ratio between the integrated intensities of the D band  $(I_D)$  at  $\approx 1380 \text{ cm}^{-1}$ , attributed to the defects of the graphitic structure, and G band  $(I_G)$  at  $\approx 1580 \text{ cm}^{-1}$ , which is ascribed to a graphitic (ordered) structure, both bands belonging to the first-order Raman spectrum for carbon materials. Another parameter, measurable by Raman spectroscopy, which is relevant to catalyst preparation, is the  $L_D$ ;  $L_D$  is a typical inter-defect distance, with the defect being considered a point-like (zero-dimensional) structure.

Table 2. Raman analyses [intensity ratio of the Raman G and D bands  $(I_D/I_C)$  and inter-defect distance  $(L_D)$  and microcrystallite size  $(L_a)$ ] and XPS C1s peak components of the carbon supports employed in the present study.

Supports	Raman analysis			XPS analysi	XPS analysis, C1s peak							
	$I_{\rm D}/I_{\rm G}$	L <sub>D</sub> [nm]	L <sub>a</sub> [nm]	FWHM [eV]	i	ii	iii	iv	V	vi	vii	
CNT <sub>COOH</sub>	1.01	11.9	19	0.72	1.3	56.6	9.8	10.0	7.0	5.6	9.6	
FLG <sub>COOH</sub>	0.64	15.0	30	0.69	0.9	62.1	7.0	9.6	6.0	5.1	9.3	
$CNF_{COOH}$	1.24	10.7	15	0.76	4.6	52.1	10.5	10.4	7.2	6.3	9.0	





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From all these analyses, some conclusions can be drawn regarding palladium catalyst preparation and use. Firstly, if we consider the prismatic: basal: defect surfaces of the supports. the palladium-carbon support interface/interaction should be different for these catalysts. It is expected to have a higher proportion of Pd-prismatic surface interaction for FLG, and a higher proportion of Pd-defect surface interaction for CNF. CNTs constituting an intermediate situation. Secondly, considering the surface area of the supports, and the long range order according to Raman, XRD and XPS analyses, it can be anticipated that palladium surface migration, and thus possible sintering should be favoured on FLG. On CNFs, the presence of disordered carbon on their surface should limit this unwanted agglomeration. Finally, considering the high proportion of oxygenated surface species, the palladium dispersion should be relatively high for the three supports.

The 2 w/w% Pd catalysts were prepared by wet impregnation using hydrated Pd nitrate. This precursor was chosen because its reduction yields impurity-free Pd particles. Table 3 shows the characterization data for the Pd catalysts. The specific surface area of the catalysts did not change significantly compared to the bare supports. XRD analyses show a very small and broad Pd(111) peak at  $2\theta = 40.1^{\circ}$  characteristic of metallic palladium (Figure S6), pointing to a small Pd particle size. The palladium particle size was measured from TEM micrographs, and the metal dispersion was calculated from an equation for metal dispersion from TEM, assuming a spherical particle geometry, as described elsewhere.<sup>[24]</sup>

Table 3. Metal loading, surface area, Pd mean size and dispersion for the investigated catalysts.

	Pd [%]	BET surface area [m <sup>2</sup> g <sup>-1</sup> ]	Particle size [nm] <sup>[a]</sup>	Pd dispersion [%]
Pd/CNT <sub>COOH</sub>	2.04	232	2.2 ± 1.1	49
Pd/FLG <sub>COOH</sub>	1.87	50	2.6 ± 1.6	43
Pd/CNF <sub>COOH</sub>	1.70	82	1.6 ± 0.9	67

Representative micrographs, and particle size distributions are shown in Figure 2. It is worth mentioning that for CNTs that present an inner cavity, some particles should be located in this cavity. The higher palladium dispersion was obtained on CNFs, presumably because of a higher concentration in surface oxygenated species (Table 1), and a higher concentration of defects (XRD, Raman, and XPS analyses). Similar dispersion were obtained on CNTs and FLG. This results might appear surprising, considering the fact that CNTs have a larger surface area (220 m<sup>2</sup> g<sup>-1</sup>) compared to FLG (50 m<sup>2</sup> g<sup>-1</sup>), and larger amount of surface oxygen groups (Table 1). We propose that this result arises from the surface on which these MNPs are deposited: mainly prismatic surface for FLG, and basal surface for CNTs. Figure 2b clearly shows that Pd NPs are preferentially deposited on the edges and prismatic planes of the FLG support.



Figure 2. Representative micrographs and particle size distribution for: a) Pd/ CNT-HRTEM (scale bar = 50 nm); b) Pd/FLG-STEM-HAADF (scale bar = 20 nm); and c) Pd/CNF-HRTEM (scale bar = 10 nm).

The catalysts have also been analyzed by XPS (Figure S7 and Table 4). The XPS Pd 3d peak for all catalysts was wide, indicating either multiple oxidation states of the Pd species, or several different interactions of the oxidized carbon support. Peaks at 335.5 and 340.5 eV, were assigned to Pd<sup>0</sup> 3d<sub>5/2</sub> and 3d<sub>3/2</sub>, respectively, while the  $3d_{5/2}$  and  $3d_{3/2}$  peaks for Pd<sup>2+</sup> are at 337.8 eV and 343.4 eV. The XP spectra of palladium catalyst showed peaks for Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$  with Pd<sup>0</sup> and Pd<sup>2+</sup> combined lines, but Pd<sup>2+</sup> line as dominant. The presence of higher Pd oxidation states are indicated by the Pd  $3d_{5/2}$  peak at a binding energy of 339 eV, which can be assigned to PdO<sub>2</sub> or Pd(OH)<sub>4</sub>. From the deconvolution pf the XPS Pd 3d peak it

Table 4. XPS Pd 3d peak components and the ratios between reduced and oxidized Pd atoms for each catalyst.

Catalyst		XPS analys	XPS analysis, Pd 3d peak							
	i	ii	iii	iv	V	vi	Pd <sup>0</sup> /Pd <sup>2+</sup>	$Pd^{0}/Pd_{ox}$		
Pd/CNT <sub>COOH</sub>	12.30	8.18	39.92	26.54	7.85	5.22	0.31	0.26		
Pd/FLG <sub>COOH</sub>	12.30	8.18	39.44	26.22	8.33	5.53	0.31	0.26		
Pd/CNF <sub>COOH</sub>	18.01	11.97	38.37	25.50	3.70	2.46	0.47	0.43		

[a] From TEM.



appears that, while Pd/CNT and Pd/FLG have a similar distribution of Pd<sup>0</sup> vs. oxidized Pd atoms, Pd/CNF has a larger population of reduced Pd<sup>0</sup>.

#### **Catalytic Reactions**

The three supported Pd catalysts were used for the two processes of relevance in biomass transformation indicated in Scheme 1. As commented in the introduction, one of the reactions under study was the hydrodeoxygenation of vanillin to 2methoxy-4-methylphenol. This transformation encompasses two consecutive steps, the first one being hydrogenation of conjugated aldehyde group to a benzylic alcohol requiring hydrogenation sites followed by hydrodeoxygenation of the hydroxyl group by different sites. Both steps, hydrogenation of carbonyl groups and removal of oxygen are very common in biomass transformation by bifunctional catalysts and, therefore, the results achieved for the transformation of vanillin to MMP with the different Pd catalysts should also be readily expanded to many other hydrogenations and hydrodeoxygenations. The reaction was carried out under moderate hydrogen pressure (5 bar) in water as solvent at the boiling temperature in the presence of the three Pd-catalysts under study.

The only product observed in the process as reaction intermediate is vanillyl alcohol (VA). Figure 3 shows the temporal evolution of vanillin conversion as well as the yields of VA intermediate and the wanted MMP. As it can be seen in this Figure 3, even though the palladium content is similar for the three materials, the solids exhibit contrasting catalytic activity. The order of activity based on conversion of V being Pd-FLG > Pd-CNF > Pd-CNTs. Besides conversion of V, subsequent disappearance of vanillyl alcohol and MMP also follows the same order as the disappearance of vanillin. While the relative activity of Pd/CNF vs. Pd/CNT can be explained based on the smaller particle size of Pd NPs in Pd/CNF compared with Pd/CNT, the high activity of Pd/FLG cannot be predicted based on Pd particle size that is



Figure 3. Vanillin conversion (a), vanillyl alcohol evolution (b) and 2-methoxy-4-methylphenol (c) formation using Pd/CNT ( $\blacksquare$ ), Pd/CNF ( $\bigcirc$ ) and Pd/FLG ( $\blacktriangle$ ) as catalysts. Reaction conditions: Catalyst (10 mg), vanillin (20 g L<sup>-1</sup>; 0.13 m), 2 mL of H<sub>2</sub>O, 5 bar H<sub>2</sub>, 100 °C.



higher in Pd/FLG compared to the other two catalysts (Pd dispersion on FLG is lower than for the other two carbon supports). Thus, other properties of FLG as support and, particularly, the presence of prismatic planes on which the Pd NPs are interacting with the support should be playing a role determining Pd catalytic activity. Thus, considering that Pd NPs are the active sites and carbon supports play a major role interacting with those Pd NPs, it is proposed that the main factor responsible for the higher activity of Pd/FLG compared to the other two catalysts would be the specific location of the Pd NPs on the prismatic planes present on FLG.

Stability of carbon-supported Pd catalysts was studied by performing a series of catalytic tests. The results are presented in Figure 4 (Pd/CNF) and S8 (Pd/FLG)-S9 (Pd/CNT) in the supporting information. As it can be seen in these Figures one of the most surprising results was that, although the temporal profiles of three consecutive runs for vanillin disappearance using Pd/FLG as catalyst were coincident, indicating that the catalytic activity for hydrogenation of V into VA is maintained, the rate of the second step of hydrodeoxygenation decreases considerably upon reuse, particularly from the fresh to the first used catalyst. Although, as it can be seen in Table 5, a slight growth of the average Pd NP size was observed for the three supported Pd, the size increase was about 1 nm. Thus, it seems that this decay in activity cannot be attributed to the minor changes in the Pd NP size distribution. Therefore, other causes have to be invoked to explain catalytic activity decay.



Figure 4. Vanillin conversion (a), vanillyl alcohol evolution (b) and 2-methoxy-4-methylphenol (c) formation using Pd/CNF as catalyst during four consecutive uses. Legend: First use ( $\blacksquare$ ), second use ( $\bigcirc$ ), third use (▲) and fourth use ( $\triangledown$ ). Reaction conditions: Catalyst (10 mg), vanillin (20 g L<sup>-1</sup>; 0.13 м), 2 mL of H<sub>2</sub>O, 5 bar H<sub>2</sub>, 100 °C.

Since it seems that the second hydrodeoxygenation step is the one limiting the overall conversion of V into MMP, it could be that Pd/FLG becomes deactivated due to the strong adsorption of the aromatic intermediate VA or MMP. To support this possibility, the TPD profile of the used Pd/FLG catalyst after exhaustive washings was performed and compared to that of the fresh Pd/FLG sample. The results are presented in Figure S10 confirming that the spent Pd/FLG catalyst desorbs in the range of temperature from 250 to 700 °C a considerable





Table 5	. Characterization	data of four-time	es used palladium	catalysts for v	anillin hydro	deoxygenation	or 5-hydroxy	/methylfurfural	oxidation,	including pai	rticle
size, me	etal leaching and	estimated TON ar	nd TOF for these r	eactions.							

Entry	Catalyst	Reaction	Particle size [nm]	Pd Leaching [%]	TON <sup>[a]</sup>	TOF <sup>[b]</sup> [h <sup>-1</sup> ]
1	Pd/CNT	Hydrodeoxygenation of V	$3.4 \pm 3.4$	0.1	140	21
2	Pd/CNT	Oxidation of HMF	$3.9 \pm 3.6$	3.0	80	813
3	Pd/FLG	Hydrodeoxygenation of V	$2.3 \pm 0.8$	2.3	149	78
4	Pd/FLG	Oxidation of HMF	15.9 ± 11.3	6.6	85	829
5	Pd/CNF	Hydrodeoxygenation of V	2.8 ± 1.1	0.5	164	72
6	Pd/CNF	Oxidation of HMF	6.7 ± 11.3	2.1	94	901

[a] TON: mol of converted substrate (V or HMF) divided mol of supported palladium after one use. [b] TOF: mol of converted V or HMF divided mol of supported palladium at 1 and 0.083 h, respectively.

amount of adsorbed reaction intermediates that are absent in the fresh catalysts. However, control experiments, performing the reaction under the general conditions but adding on purpose at initial reaction time 30 % of VA or MMP, did not show any sign of catalyst deactivation either in the temporal profile of vanillin conversion or in the evolution of reaction intermediates. These poisoning experiments rule out VA or MMP as catalyst poison. It is proposed that other by-products could be responsible for this deactivation. This proposal is somehow supported by comparison of the composition by elemental analysis of the three palladium catalysts, fresh or after the reaction (see Table S1 in the supporting information). In the cases of Pd/ CNT and Pd/CNF the differences in the carbon and hydrogen between the fresh and used materials were not relevant. In contrast, for Pd/FLG a decrease in the carbon content of about 5 % upon catalyst use was measured, suggesting that this material has adsorbed reaction intermediates, products or substrates, causing its deactivation. Therefore, it seems that deactivation in the case of Pd/FLG could occur by strong adsorption of byproducts.

In contrast to Pd/FLG, for Pd/CNT and, particularly, Pd/CNF (compare Figure 4 with S8 and S9), although the fresh materials are initially less active, both, Pd/CNT (Figure S9) and Pd/CNF (Figure 4), maintain a significant degree of catalytic activity in the two steps, indicating their higher stability under the reaction conditions. In this regard, Pd/CNF combines both a reasonable catalytic activity and a notably high reusability. Chemical analysis of the liquid phase after removal of the solid Pd/CNF catalyst showed that the Pd content in the liquid was only about 0.1 wt.-% of the initial supported palladium content, indicating the heterogeneous nature of the catalytic process. Higher palladium leaching was observed when using the Pd/ CNT (0.3 wt.-%) sample and, particularly, when using Pd/FLG (2.3 wt.-%). Heterogeneity of hydrodeoxygenation of vanillin to MMP was also supported by performing a hot filtration test in which the reaction was carried out in the presence of Pd/CNF solid under the general reaction conditions and, then, filtering the catalyst after depressurization of the reaction, while the mixture was still hot ( $\approx$  80 °C) at 30 % conversion. It was observed that the reaction completely stops after filtration of catalyst (Figures S11a-c).

The second reaction under study was the aerobic oxidation of HMF to 2,5- FDCA using molecular oxygen under pressure. This oxidation generally requires the presence of a base in order to take place, although there are scattered examples for which bases are not needed. A control experiment in the present case using Pd/FLG in the absence of base for the oxidation of HMF was unsuccessful, meaning that bases are needed under the present reaction conditions. After a series of preliminary trials,  $K_2CO_3$  was found a convenient base for the process in our case. The role of the base is to promote the formation of alcoholate that should bind to the surface of Pd NPs stronger than the corresponding alcohol. The reaction is carried out in water as solvent at 160 °C. During the course of the reaction hydroxymethylfuroic acid (HMFCA) was observed as the major reaction intermediate, accompanied by lesser proportions of the corresponding aldehydes DFF and FFCA (Scheme 1b). A summary of the results is presented in Figure 5, where the relative activity order can also be inferred.



Figure 5. 5-hydroxymethylfurfural (HMF) oxidation (a) and 2,5-furandicarboxylic acid (FDCA) formation (b) using Pd/FLG ( $\blacksquare$ ), Pd/CNT ( $\bigcirc$ ) and Pd/CNF (▲) as catalyst. Reaction conditions: Catalyst (10 mg), HMF (9.5 g L<sup>-1</sup>; 75 mM), K<sub>2</sub>CO<sub>3</sub> (21 g L<sup>-1</sup>; 152 mM), 2 mL of H<sub>2</sub>O, 5 bar O<sub>2</sub>, 160 °C. Note that plots a) and b) display different reaction times due to the occurrence of two consecutive steps.

From the temporal evolution of HMF conversion and FDCA formation it can be deduced that Pd/FLG is again more active than Pd/CNF, Pd/CNT being the less active material in the series. Heterogeneity of the process in the case of Pd/FLG was confirmed by performing a hot filtration test at 30 % conversion and by analysis of the Pd in liquid phase at final reaction time. The results presented in supplementary information (Figure S11d and e) shows that, although formation of FDCA does not progress upon removal of the solid catalyst, oxidation of HMF does not stop completely. This further progress of HMF oxidation could be attributed to the small percentage of Pd leached to the liquid phase (about 2 % of the total initial Pd content in the Pd/FLG sample). Thus, both measurements hot filtration test and Pd analysis suggest the occurrence of a minor contribution to the catalysis of a homogeneous component due to the presence of leached Pd.





Stability of the catalyst was also studied by performing a series of consecutive reuses under the same reaction conditions (Figures S12–S15). As in the case of the hydrodeoxygenation of vanillin (V), Pd/FLG undergoes a significant decay in the catalytic activity in the reuse, Pd/CNF being again the most stable material. Pd/CNT exhibits an intermediate performance between those of Pd/FLG and Pd/CNF. Reusability tests for Pd/CNF are presented in Figure 6, while supporting information contains information for the other two catalysts (Figures S12–S15).



Figure 6. 5-hydroxymethylfurfural (HMF) conversion (a) and 2,5-furandicarboxylic acid (FDCA) formation (b) upon three consecutive uses of Pd/CNF as catalyst. Legend: First use ( $\blacksquare$ ), second use ( $\bigcirc$ ), third use (▲) and forth use ( $\triangledown$ ). Reaction conditions: Catalyst (10 mg), HMF (9.5 g L<sup>-1</sup>; 75 mM), K<sub>2</sub>CO<sub>3</sub> (21 g L<sup>-1</sup>; 152 mM), 2 mL of H<sub>2</sub>O, 5 bar O<sub>2</sub>, 160 °C.

In order to understand the origin of deactivation, TEM images of fresh and used supported Pd catalyst were compared. The particle size distributions for Pd NPs on the three carbon supports after use in 5-hydroxymethylfurfural oxidation are shown in Figures S16–S18, while Table 5 shows the distributions for all supported Pd catalysts. It was observed that in the case of Pd/FLG a remarkable increase in the Pd NP particle size from  $2.6 \pm 1.6$  to  $15.9 \pm 11.3$  occurs after the 5-hydroxymethylfurfural oxidation reaction. In the case of Pd/CNT, some scattered big Pd NPs are also observed in the used sample . Considering that carboxylic acids are formed in the oxidation process and that by Coulombic interactions these compounds can increase the size of metal NPs, the data obtained by TEM images for Pd/FLG and Pd/CNT indicating a certain growth of Pd NPs are not without precedent. In the case of Pd/CNF the increase in Pd particle size is also clear, although it seems that the average is still sufficiently low (6.7 nm) to exhibit a good catalytic performance. Not surprisingly, considering the mobilizing effect of carboxylic acids for metal ions, palladium leaching from the solid catalyst to the solution was significantly higher for the oxidation of HMF than for the hydrodeoxygenation of vanillin (see Table 5), reaching in the worst case a Pd leaching of 6.6 % of the initial Pd content of the Pd/FLG.

#### Conclusions

The present results have shown that although regardless the support Pd NPs exhibit a general activity for catalyzing hydrodeoxygenations and aerobic oxidations of interest in biomass transformation, the nature of the carbon support plays a significant role determining the activity of the fresh samples and the stability of Pd NPs under the reaction conditions. It has been found that Pd supported on FLG is initially the most active catalyst for both processes, but it undergoes deactivation in significant extent upon reuse. Among the causes of deactivation, poisoning in the case of hydrodeoxygenation and Pd particle size growth in the case of the aerobic oxidation appear the most probable ones. In this regard, CNFs as support presents a compromise between activity of the fresh material and stability upon reuse. This role of CNFs has been interpreted as derived from the stabilization of particle size and the lack of poisoning by adsorption as indicated by elemental analysis. Characterization of the supported Pd catalyst has shown that for similar particle size and loading, it is not only the Pd dispersion the only parameter controlling the catalysis, but the nature and proportion of the basal, non-basal and defects planes of the support can have also a decisive importance in determining the activity and stability of the Pd NPs. In this regard, based on the characterization of CNF by electron microscopy, it is proposed that the superior catalytic activity of Pd NPs on CNF derives from a good balance with amorphous regions on the surface and basal and non-basal planes to stabilize Pd NPs.

#### **Experimental Section**

**Materials:** Vanillin, vanillyl alcohol, 2-methoxy-4-methyl-phenol, 5-(hydroxymethyl)furfural, 5-hydroxymethyl-2-furancarboxylic acid, 5formyl-2-furoic acid, 2,5-furandicarboxaldehyde, 2,5-furandicarboxylic acid and palladium(II) nitrate dihydrate were supplied by Sigma-Aldrich. Other reagents or solvents employed in the present work were analytical or HPLC grade.

**Material Preparation:**  $CNT_{COOH}$  synthesis. An AlCoFeO<sub>4</sub> catalyst was reduced in a fluidized bed reactor under a nitrogen (225 mL min<sup>-1</sup>) and hydrogen (150 mL min<sup>-1</sup>) flow at 650 °C. After the reduction step, the ethylene flow was adjusted to 225 mL min<sup>-1</sup> for 30 min to produce CNT. The CNT were recovered and then purified using an aqueous solution (50 vol.-% H<sub>2</sub>SO<sub>4</sub>) under reflux at 140 °C for 3 h. The acidic solution was then filtered and the solid washed with distilled water. The resulting solid was dried in an oven at 80 °C overnight. The purified CNT was then functionalized with HNO<sub>3</sub> under reflux at 140 °C for 3 h. The acidic solution was then solid over at 80 °C overnight to produce functionalized CNT (CNT<sub>COOH</sub>).

**FLG**<sub>COOH</sub> synthesis. A CoFe<sub>2</sub>O<sub>4</sub> catalyst was reduced in a fluidized bed reactor under a nitrogen (225 mL min<sup>-1</sup>) and hydrogen (150 mL min<sup>-1</sup>) flow at 650 °C. After reduction step, the ethylene flow was adjusted to 225 mL min<sup>-1</sup> for 30 min to produce FLG. The FLG was recovered and purified at room temperature overnight using HCI. The acidic solution was then filtered and washed. The resulting solid was dried in an oven at 80 °C overnight. The purified FLG was then functionalized with HNO<sub>3</sub> under reflux at 140 °C for 3 h. The acidic solution was filtered and washed. The resulting solid was dried in an oven at 80 °C overnight to produce functionalized FLG (FLG<sub>COOH</sub>).

**CNF**<sub>COOH</sub> synthesis: A CoFe<sub>2</sub>O<sub>4</sub> catalyst was reduced in a fluidized bed reactor under a nitrogen (225 mL min<sup>-1</sup>) and hydrogen (150 mL min<sup>-1</sup>) flow at 450 °C. After the reduction step, the ethylene flow was adjusted to 225 mL min<sup>-1</sup> for 30 min to produce CNF. The CNF were recovered and then purified at room temperature overnight using HCI. The acidic solution was then filtered and washed. The resulting solid was dried in an oven at 80 °C overnight. The purified CNF was functionalized using HNO<sub>3</sub> under reflux at 80 °C for 3 h. The acidic solution was then filtered and washed. The





resulting solid was dried in an oven at 80 °C overnight to produce functionalized CNF ( $CNF_{COOH}$ ).

**Pd/carbon nanomaterials.** A wet impregnation method was used to prepare the palladium catalysts supported on carbon nanomaterials. The desired amount of  $Pd(NO_3)_2 \cdot 2H_2O$  was added to an acetone solution (100 mL) containing 1 g of carbon nanomaterial, so as to introduce 2 w/w% of metal phase. The solution was then sonicated at room temperature for 1 h and magnetically stirred overnight. The solution was then filtered and washed with acetone that ensures that only strongly bound Pd species remains adsorbed on the support. The main factors responsible for Pd loading are specific surface area and surface acidity of the carbon materials.<sup>[25]</sup> The resulting solid was dried in an oven at 120 °C overnight. Finally, the catalyst was reduced in a horizontal tube oven under a nitrogen and hydrogen flow (20 vol.-% H<sub>2</sub>) at 300 °C for 2 h.

Materials Characterization: N2 sorption: The surface area was measured using the Brunauer, Emmet, and Teller (BET) method. The pore radius distribution was determined by the Barrett, Joyner, and Halenda (BJH) method. TEM micrographs were taken with a JEOL JEM 1011 microscope operating at 100 kV. Palladium particle size distribution was calculated using the ImageJ software measuring at least 250 particles. XRD patterns were recorded at room temperature with a Panalytical X'PERT PRO diffractometer, employing a Cu- $K_{\alpha}$  radiation ( $\lambda = 1.54$  Å) and a parabolic MPD-mirror for Cu radiation. The diffractograms were acquired in  $2\theta$  range of 5–90°, using a continuous scan mode with an acquisition step size of 0.0170° and a counting time of 299.72 s. Raman spectra were measured in a micro Raman Spectrometer HR 800 Jobin Yvon Horiba using a laser of 532 nm wavelength as excitation source. Nitrogen adsorption measurements were performed at -196 °C using a 3Flex Surface Characterization Analyzer (Micromeritics GmbH). The surface area was measured using Brunauer, Emmet and Teller (BET) method. The pore radius distribution was determined by the Barrett, Joyner and Halenda (BJH) method. Before analysis, the samples were degassed at 150 °C using a Micromeritics VacPrep 061 Sample Degas System until a static pressure of less than 0.01 Torr (0.0133 mbar) was reached. The elemental results were obtained using a CHN Perkin-Elmer elemental analyzer. Palladium loadings were determined using an iCAP 6300 ICP Spectrometer, by digestion of the samples in hot aqua regia. The adsorptive potential distributions were calculated from the adsorption isotherms using the standard software implemented in the apparatus (3Flex Version 4.04). The calculation of the DFT, basal plane and "non-basal plane" surfaces as well as of the respective ratios has been performed as described previously.<sup>[18]</sup> The surface chemical composition of the carbon materials was analyzed by XPS (Kratos AXIS Ultra HSA spectrometer), using a Mg- $K_{\alpha}$  radiation (1486.7 eV). The existing elements, and their corresponding concentrations, were determined by recording a survey spectra up to a binding energy (BE) of 1300 eV. High-resolution XPS spectra of the C1s, and Pd3d core levels and full-width-at-half-maximum (FWHM) values were used to assess the chemical state of these elements at the catalyst surface, according to the NIST database. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was employed to determine the amount of possible Pd leaching from the catalyst to the solution upon reaction.

**Catalytic Tests:** Hydrodeoxygenation of vanillin was carried out in a pressurized glass reactor with head stirrer. Briefly, vanillin (40 mg) dissolved in  $H_2O$  (2 mL) was placed together with the required amount of catalyst (i.e. 10 mg). The mixture was sonicated in an ultrasound bath (450 W) for 30 min to ensure a good dispersion of the catalyst. Then, the reactor was purged five times with  $H_2$  and, then, pressurized at 5 bar. The system, whilst stirring, was heated at 100 °C employing a preheated oil bath. This event was considered the 0 reaction times. At the required times, aliquots were taken from the reactor (100  $\mu$ L), diluted with H<sub>2</sub>O (100 mL) and filtered (0.2  $\mu$ m Nylon filter) before analysis by HPLC.

The oxidation of HMF was carried out in a pressurized glass reactor with head stirrer. HMF (19 mg) was dissolved in H<sub>2</sub>O (2 mL) containing K<sub>2</sub>CO<sub>3</sub> as base (42 mg) and, then, the required amount of catalyst was added (i.e. 10 mg). The mixture was sonicated for 30 min with a power of 450 W. This relatively low sonication power ensures good dispersion of the catalyst in the reaction mixture without producing structural damage. The reactor was purged with oxygen five times and pressurized with oxygen (5 bar) before heating the system at 160 °C, whilst stirring, in a preheated oil batch. The initial reaction rate was considered when the reactor was introduced into the bath.

Reusability experiments for each reaction were carried out under the corresponding conditions indicated above. At the end of the reaction the catalyst was recovered by filtration employing a nylon membrane (0.2  $\mu$ m). The used catalyst was thoroughly washed with water and ethanol and, then, dried in an oven at 100 °C. The resulting solid was employed in a subsequent catalytic cycle. This procedure was repeated three times.

The heterogeneity of the reaction was tested by performing the hot filtration test. This test consists in removing the catalyst from the reaction mixture after depressurization, filtering the suspension without cooling ( $\approx$  80 °C) at a certain conversion. The hot filtrate was allowed to react further, in the absence of solid, under the reaction conditions.

**Analysis of the Reaction:** The reagents and products of both reactions under study (Scheme 1) were analyzed by HPLC using a photodiode array as detector. Previously filtered reaction aliquots were injected in the HPLC system equipped with a reverse-phase chromatography column [Kromasil-CN for vanillin (V) reaction or Kromasil-C18 for HMF reaction] as stationary phase. Mobile phase working under isocratic conditions for compounds V and HMF were H<sub>2</sub>O:CH<sub>3</sub>CN (40:60 vol.-%) or H<sub>2</sub>O, respectively.

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**Keywords:** Heterogeneous catalysis · Palladium nanoparticles · Carbon support · Biomass transformation

[1] A. Corma, S. Iborra, A. Velty, Chem. Rev. 2007, 107, 2411–2502.

 <sup>[2]</sup> G. W. Huber, S. Iborra, A. Corma, Chem. Rev. 2006, 106, 4044–4098; R. M. Navarro, M. A. Peña, J. L. G. Fierro, Chem. Rev. 2007, 107, 3952–3991;





J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen, *Chem. Rev.* **2010**, *110*, 3552–3599.

- [3] J. N. Chheda, G. W. Huber, J. A. Dumesic, Angew. Chem. Int. Ed. 2007, 46, 7164–7183; Angew. Chem. 2007, 119, 7298.
- [4] C.-H. Zhou, X. Xia, C.-X. Lin, D.-S. Tong, J. Beltramini, Chem. Soc. Rev. 2011, 40, 5588–5617.
- [5] S. Crossley, J. Faria, M. Shen, D. E. Resasco, *Science* **2010**, *327*, 68–72; X. Xu, Y. Li, Y. Gong, P. Zhang, H. Li, Y. Wang, J. Am. Chem. Soc. **2012**, *134*, 16987–16990.
- [6] E. Lam, J. H. Luong, ACS Catal. 2014, 4, 3393–3410.
- [7] S. Navalon, A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *Coord. Chem. Rev.* 2016, *312*, 99–148; G. G. Wildgoose, C. E. Banks, R. G. Compton, *Small* 2006, *2*, 182–193; J. Zhu, A. Holmen, D. Chen, *ChemCatChem* 2013, *5*, 378–401.
- [8] F. G. Calvo-Flores, J. A. Dobado, ChemSusChem 2010, 3, 1227–1235; B. M. Upton, A. M. Kasko, Chem. Rev. 2016, 116, 2275–2306.
- [9] F. Zhang, Y. Jin, Y. Fu, Y. Zhong, W. Zhu, A. A. Ibrahim, M. S. El-Shall, J. Mater. Chem. A 2015, 3, 17008–17015.
- [10] J. L. Santos, M. Alda-Onggar, V. Fedorov, M. Peurla, K. Eranen, P. Maki-Arvela, M. A. Centeno, D. Y. Murzin, *Appl. Catal. A* **2018**, *561*, 137–149; P. Hao, D. K. Schwartz, J. W. Medlin, *Appl. Catal. A* **2018**, *561*, 1–6; F. Zhang, S. Zheng, Q. Xiao, Y. Zhong, W. Zhu, A. Lin, M. Samy El-Shall, *Green Chem.* **2016**, *18*, 2900–2908.
- [11] S. E. Davis, M. S. Ide, R. J. Davis, Green Chem. 2013, 15, 17-45.
- S. Dutta, S. De, B. Saha, ChemPlusChem 2012, 77, 259–272; Z. Zhang,
  K. Deng, ACS Catal. 2015, 5, 6529–6544.
- [13] S. P. Teong, G. Yi, Y. Zhang, Green Chem. 2014, 16, 2015–2026.
- [14] B. Siyo, M. Schneider, J. Radnik, M.-M. Pohl, P. Langer, N. Steinfeldt, Appl. Catal. A 2014, 478, 107–116.
- [15] P. V. Rathod, V. H. Jadhav, ACS Sustainable Chem. Eng. 2018, 6, 5766– 5771.

- [16] B. F. Machado, M. Oubenali, M. R. Axet, T. T. NGuyen, M. Tunckol, M. Girleanu, O. Ersen, I. C. Gerber, P. Serp, J. Catal. 2014, 309, 185–198.
- [17] T. Placke, V. Siozios, R. Schmitz, S. F. Lux, P. Bieker, C. Colle, H.-W. Meyer, S. Passerini, M. Winter, J. Power Sources 2012, 200, 83–91.
- [18] Placke, T., Siozios, V., Rothermel, S., et al. (2015). Assessment of Surface Heterogeneity: a Route to Correlate and Quantify the 1st Cycle Irreversible Capacity Caused by SEI Formation to the Various Surfaces of Graphite Anodes for Lithium Ion Cells. *Themed Issue: Lithium Ions in Solids – Between Basics and Better Batteries / Paul Heitjans. Zeitschrift für Physikalische Chemie*, 229(9), pp. 1451–1469. Retrieved 22 Mar. 2019, from doi:10.1515/zpch-2015-0584.
- [19] T. V. Reshetenko, L. B. Avdeeva, Z. R. Ismagilov, V. V. Pushkarev, S. V. Cherepanov, A. L. Chuvilin, V. A. Likholobov, *Carbon* **2003**, *41*, 1605– 1615.
- [20] H. Estrade-Szwarckopf, Carbon 2004, 42, 1713–1721; K. Ganesan, S. Ghosh, N. G. Krishna, S. Ilango, M. Kamruddin, A. K. Tyagi, Phys. Chem. Chem. Phys. 2016, 18, 22160–22167; T. I. T. Okpalugo, P. Papakonstantinou, H. Murphy, J. McLaughlin, N. M. D. Brown, Carbon 2005, 43, 153–161.
- [21] J.-O. Müller, D. S. Su, U. Wild, R. Schlögl, Phys. Chem. Chem. Phys. 2007, 9, 4018–4025.
- [22] L. G. Cançado, A. Jorio, E. H. Martins Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. O. Moutinho, A. Lombardo, T. S. Kulmala, A. C. Ferrari, *Nano Lett.* **2011**, *11*, 3190–3196.
- [23] L. G. Cançado, K. Takai, T. Enoki, Appl. Phys. Lett. 2006, 88, 163106.
- [24] S. Domínguez-Domínguez, A. Berenguer-Murcia, B. K. Pradhan, A. Linares-Solano, D. Cazorla-Amorós, J. Phys. Chem. C 2008, 112, 3827–3834.
- M. L. Toebes, J. A. van Dillen, K. P. de Jong, J. Mol. Catal. A 2001, 173, 75–98; D. J. Suh, T.-J. Park, S.-K. Ihm, Carbon 1993, 31, 427–435; M. Kang, M. W. Song, K. L. Kim, React. Kinet. Catal. Lett. 2002, 76, 207–212.

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## Supported Catalysts

 Influence of Carbon Supports on
 Palladium Nanoparticle Activity toward Hydrodeoxygenation and Aerobic Oxidation in Biomass Transformations



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Carbon nanofibers appears to be the best choice among few-layers graphene and carbon nanotubes as support of Pd nanoparticles for the two different reactions shown in the scheme

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