

Pt and Pd on activated carbon for oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid

Pt y Pd soportado en carbón activado para la oxidación de 5-hidroximetilfurfural a ácido 2,5-furanodicarboxílico

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Abstract

The liquid phase transformation of 5-hydroxymethylfurfuraldehyde (5-HMF) towards 2,5-furandicarboxylic acid (2,5-FDCA) using Pt and Pd catalysts supported on activated carbon and with the presence of CaCO₃ and NaOH, is reported. The catalysts were characterized using different techniques, such as: H₂ chemisorption at room temperature, X ray photoelectronic spectroscopy (XPS) and thermogravimetric analysis (TGA). The results indicate that the particle size followed the order: PtCl/C < PdCl/C < PdN/C, which is closely related to the catalytic behavior. It was found that the metal particles are present in the Pd⁰ and Pt⁰ form. PtCl/C was most active catalyst using CaCO₃ as weak base.

Keywords: Aerobic oxidation, activated carbon, 2,5-furandicarboxylic acid.

Resumen

En este trabajo se estudió la transformación en fase líquida de 5 hidroximetilfurfural (5-HMF) a ácido 2,5-furandicarboxílico con el uso de catalizadores de Pt y Pd soportados en carbón activado con la presencia de NaOH ó CaCO₃. Los catalizadores fueron caracterizados por quimisorción de H₂ a temperatura ambiente, espectroscopia de rayos X (XPS) y análisis termogravimétrico (TGA). Los resultados indican que el tamaño de partícula de los catalizadores sigue el orden PtCl/C < PdCl/C < PdN/C el cual esta estrechamente relacionado con la actividad catalítica. Se encontró que las partículas metálicas están presentes como especies de Pd⁰ and Pt⁰. Siendo el catalizador de Pt-Cl/C con el uso de CaCO₃ como aditivo.

Palabras clave: Ácido 2,5-furandicarboxílico, carbón activado, oxidación aeróbica.

1. Introduction

The lignocellulosic biomass has been considered as a renewable source for obtain chemicals and biofuels (1), therefore their catalytic transformations and derivatives, have received great attention (2). In this sense, biomass can provide a rich source of sustainable products and compatibles with environmental issues. Among them, 2,5-furandicarboxylic acid (2,5-FDCA) is an important building block with wide potential to be used as the next generation of polymers and fine chemical (3) and it can to be considered like substitute of the tereftalic acid in order to obtain polyethylene tereftalate (4).

The most common method to access to 2,5-FDCA starting the oxidation of 5-hydroxymethylfurfuraldehyde (5-HMF) (5), includes reaction conditions, such as: high temperature and pressure, use of metallic salts and organic solvents that make the process quite costly and polluting (6). Therefore, a new synthetic route for the clean synthesis of 2,5-FDCA should be designed in the presence of heterogeneous catalysts (7). 5-HMF catalytic oxidation with molecular oxygen using water as solvent is an environmentally friendly alternative with respect to the use of organic solvents; however, a high pH is often necessary for the reaction to occur (8, 9).

It has been studied, the catalytic oxidation of 5-HMF to 2,5-FDCA, using stoichiometric amounts both of the oxidizing agent and catalytic systems containing noble metals, such as: Au, Ru, Pd and Pt (10). Gold catalysts present higher catalytic performance in aerobic oxidation of 5-HMF to 2,5-FDCA (11). However, Au catalysts are less efficient in the oxidation of the hydroxyl group that oxidation of the carbonyl group, and the presence of additives or basic supports is necessary, to reach the oxidation of 5-HMF to 2,5-FDCA. Casanova et al. (12), claim that the oxidation of 5-HMF is very selective to 2,5-FDCA, with yield 99% under mild conditions (65-130 °C, 10 bar air pressure and water as solvent) with nanoparticles gold supported on cerium oxide (Au-CeO₂) and titanium oxide (Au-TiO₂) as catalysts; being the first the most active

and selective (13). Gorbanev et al. (8) explored this reaction using Au/TiO₂ and water as solvent at room temperature. They found that the selectivity towards 2,5-FDCA and oxidation intermediate product (5,2-HFCA) depend on added amount of a base and the oxygen pressure, affording a maximal yield of 71% 2,5-FDCA at full conversion.

Mei et al. (9) studied palladium nanoparticles supported on graphene oxide, magnetically separable (C-Fe₃O₄-Pd) in aerobic oxidation of 5-HMF, obtaining a 98.2% conversion of 5-HMF and 91.8% yield of 2,5-FDCA, after 4 hours at 80°C using a molar ratio K₂CO₃/HMF equal to 0.5, and they established that the base concentration and the reaction temperature affect both the conversion of 5-HMF and selectivity to 2,5-FDCA. On the other hand, Siyo et al. reported the preparation and catalytic behaviour of Pd colloids (1.8 nm) deposited in ZrO₂/La₂O₃ (14). It was obtained a high selectivity of 90% to 2,5-FDCA, possibly due to the basicity of the reaction medium.

Platinum catalysts supported on carbon, exhibit greater catalytic performance in the oxidation of 5-HMF to 2,5-FDCA (15). With catalysts of Pt, the oxidation of 5-HMF proceeds favorably towards the diacid; and, a gradual increase in the reaction temperature (from 75 to 140°C) and oxygen pressures (from 1 to 10 bar) are required to promote the production of 2,5-FDCA, taking in account that the concentration NaOH determines the product distribution. However, one of the major drawbacks with the NaOH in such catalytic systems is the formation of the salt associated to 2,5-FDCA, which is impossible to use directly in the polymer industry and the separation of 2,5-FDCA from aqueous liquid mixture requires the addition of strong mineral acids, such as: HCl and H₂SO₄. On the other hand, Yi et al. (16) reported with catalysts Ru/C in aqueous medium without the addition of NaOH, reaching yields of 88% of the intermediary FFCA and complete conversion of 5-HMF. Subsequently the oxidation of FFCA was conducted with peracetic acid at room temperature to obtain 95% 2,5-FDCA.

In this work palladium and platinum catalysts supported on activated carbon were studied in the aerobic oxidation of HMF. It was evaluated, the metal precursor effect and the addition of NaOH or CaCO₃ on the catalytic performance. The addition of CaCO₃ offers the possibility of its easy separation due to lower solubility, avoiding the tedious neutralization process. Moreover, the addition of CaCO₃ could act as a neutralizer to 2,5-FDCA.

2. Experimental

2.1 Catalysts synthesis

In the current work, a commercially available coal was used as catalyst support (RX3 NORIT®: surface area = 1320 m²×g⁻¹ and pore volume = 0.69 cm³×g⁻¹). Palladium and platinum catalysts were prepared by the incipient wetness technique with 1% wt metal loading. Acidic solutions (pH = 1) of PdCl₂, Pd(NO₃)₂ and H₂PtCl₆ were used to prepare PdCl/C, PdN/C and PtCl/C, respectively. The catalysts were dried at 100 °C and subsequently were reduced in a H₂ flow at 500 °C for 2 h prior to catalytic tests.

2.2 Catalysts characterization

Hydrogen consumption and metallic dispersion were determined by hydrogen chemisorption at 30 °C in a Micromeritics AutoChem II equipment, using H:M = 1 atomic ratio. The samples were reduced *in situ* at 500 °C during 30 min and degassed in an argon stream at 400 °C for 30 min. Finally, the hydrogen chemisorption was determined at room temperature injecting pulses of a 5 % (v/v) H₂/Ar mixture.

The electronic state of the surface species was determined by X-ray Photoelectronic Spectroscopy (XPS). For monometallic catalysts the measurements were acquired in a VG-Microtech Multilab equipment with a MgK_α (hn: 1253.6 eV) radiation source and a pass energy of 50 eV. Samples were treated *in situ* in the presence of a H₂ stream following the same pretreatment conditions for each catalyst. A careful deconvolution of the spectra was made and the areas of the peaks were estimated by calculating the integral of each peak after subtracting

a Shirley background and fitting the experimental peak to a combination of Lorentzian/Gaussian lines of 30-70% proportions. The reference binding energy (BE) was C 1s peak at 284.5 eV.

Thermogravimetric and differential thermal analysis (TGA/DTA) were performed in an equipment SETARAM SA using a heating speed of 5 °C×min⁻¹ from room temperature until 800°C.

2.3. Catalytic tests

The catalytic activity experiments were performed in a stainless-steel batch type reactor. 1 mmol of 5-HMF, 0.1 g of catalyst in 5 mL H₂O and 2 mmol of base (NaOH or CaCO₃) were charged into the reactor. The reaction temperature and pressure were fixed at values of 120 °C and 20 bar (oxygen pressure), respectively. Three control experiments were performed to evaluate if the origin of catalytic activity comes from the catalysts. They were: i) in absence of catalyst and base, ii) in absence of base only and iii) in absence of catalyst only. After 10 h of reaction, a sample was removed and filtered using filter of pore size 0.2 μm. Reaction products were identified and quantified by using a liquid chromatograph coupled with a high-resolution UV-Vis detector (λ = 245 nm) and column Biorad aminex HPX-87H and 5 mM of H₂SO₄ flowing at 0.5 mL/min.

3. Results and discussion

3.1. Catalyst characterization

Hydrogen consumption and metal dispersion is determined by chemisorption at 30 °C using an atomic ratio H/M = 1 (M = Pt or Pd). In table 1, atomic ratio H/M and particle size is showed. These results indicate that lower ratio H/M for Pt catalyst than Pd catalyst. Although, this ratio is higher when the precursor of nitrate salt was used in the preparation of Pd catalysts. Lower values of metal dispersion obtained could be explained by the presence of different carbon surface functional groups. For all catalysts, the atomic ratio H/M, suggests an order of particle size: PtCl/C < PdCl/C < PdN/C.

Table 1. Crystal size and metal dispersion obtained by H_2 chemisorption measurements.

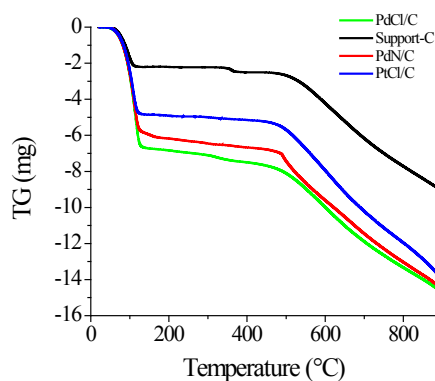
Catalysts	$d_{(H/M)}$	d_p (nm)
PdCl/C	0.040	25
PdN/C	0.072	14
PtCl/C	0.019	9

Previously, the XPS analysis were made in other paper of the authors (17). Briefly in the table 2 can be seen that the binding energy signal of Pd $3d_{5/2}$ appears at 334.9 and 335.3 eV for PdN/C and PdCl/C, respectively. These signals could be assigned to Pd⁰ species for PdN catalyst. While, on the PdCl catalyst surface, Pd⁴⁺ (with $d \gg 0$) electrodeficient species were observed after the reduction pretreatment at 400 °C for both catalysts. On the other hand, for Pt catalyst, the signal of Pt $4f_{7/2}$ appears at 70.8 eV, which is associated to Pt⁰ species on the reduced catalyst.

Table 2. Binding energy of Pt $4f_{7/2}$ and Pd $3d_{5/2}$ by XPS technique of the catalysts studied.

Catalyst	Pd $3d_{5/2}$ (eV)	Pt $4f_{7/2}$ (eV)
PdCl/C	335.3	--
PdN/C	334.9	--
PtCl/C	--	70.8

The TGA profiles for all catalysts are showed in figure 1. It can be seen that three regions are well distinguished. In the first, a slight weight loss at temperatures below 120 °C is caused by evaporation of physically adsorbed water. The second region indicates weight loss to temperatures in the range from 120 to 500 °C, which is related to the presence of Cl⁻ or NO₃⁻ ions that avoids the deposition of Pd and Pt by protecting the surface through adsorption. The last one shows a significant decrease of the weight at the temperature range from 500 to 900 °C, which is mainly associated with the decomposition of the support. It is noted that in comparison with the support, the catalysts have higher thermal stability.

**Figure 1.** TGA profiles for PtCl/C, PdCl/C, PdN/C and RX3.

3.2. Catalytic activity

Table 3 summarizes the results of catalytic activity in term of yields for the obtained reaction products at different reaction conditions. Identification process was possible by comparison with original samples. The control reaction both in absence of catalyst and base (entry 1), only led 5 % of yield to 5-hydroxymethyl-2-furancarboxylic acid (HFCA). This intermediate product increased with the presence of the base (entry 2 and 3). HFCA is favored by the aldehyde group oxidation according to the Cannizzaro reaction. 2,5-dihydroxymethylfurfural (DHMF), the other Cannizzaro product also was observed. It is well known that weak bases are not favorable for the oxidation of Cannizzaro, indicating that the reaction mechanism could be different. HFCA should be subsequently converted to FFCA and posteriorly to 2,5-Furan dicarboxylic acid (FDCA). Entry 4 and 5 show the results obtained with only Pd-Cl/C and Pt-N/C, respectively. It was observed a very low yield towards HFCA, which suggests that a basic compound is necessary to obtain high yields to FDCA.

The effect of the base employed on the reaction yield can be observed in entries 6-9. When comparing the performance of the Pd-Cl/C and Pd-N/C catalysts similar behavior is observed in presence of NaOH, but is distinct when is used CaCO₃ and especially the differences in activity observed between PdCl/C and PdN/C could be attributed to, at least in part, to the residual chlorine on the catalyst surface and to the electronic

effects due to electrodeficient species present on the chloride catalyst. The chlorine could not be completely eliminated from the pores of the support after the temperature pretreatments of the catalysts, which is in according to the TGA and XPS results and the previous reports (17). Possibly the chloride residual inhibits the oxidation posterior of HFCA y consequently decreases the formation of FDCA.

To clarify the effect of base and compare the catalytic performance between Pt and Pd catalysts in the same conditions was used the catalysts prepared with precursor chlorinated (entry 10-11), it is observed that Pt showed differences with Pd, however, the PtCl/C catalyst favors the formation of FDCA, although with lower conversions. This behavior could be associated to the particle size as it was obtained by chemisorption measurement. It appears that particle size and the mechanism of reaction including the base employed, influences on the catalytic activity. A higher particle size favors the oxidation at intermediates, and distinct mechanisms of reaction with NaOH or CaCO₃ are followed.

When is used NaOH and an oxygen pressure, the conversion from 5-HMF to HFCA is achieved. Subsequently, HFCA oxidizes to FFCA. These steps do not require a catalyst (18). With the catalysts of Pd or Pt, FDCA formation occurs by oxidation of FFCA. In the case of NaOH, it can be explained according to the proposed mechanism by Amaniampong and Colleagues (19). Although these authors propose a possible mechanism with Au/TiO₂, it is possible that the behavior may be similar. Hydrogen moieties originated from H₂O may react with adsorbed O₂ on the catalyst surface, which produces reactive species OOH. These species decompose to form O* and OH species. The species O* react rapidly with HMF and facilitate the reaction to 2,5-FDCA. In fact, water favors the adsorption and activation of O₂ in the catalyst surface. NaOH favors the formation of OH⁻ species adsorbed on the metal. On the other hand, the addition of CaCO₃ acts more as a neutralizer of 2,5-FDCA, which shifts the reaction equilibrium. But a reaction mechanism cannot be raised with the results obtained.

Table 3. Yield (%) to the different products in the oxidation of 5-HMF at 12 h of reaction. 5-hydroxymethyl-2-furancarboxylic acid (HFCA), 5-formyl-2-furan carboxylic acid (FFCA), 2,5-Furan dicarboxylic acid (FDCA) and 2,5-dihydroxymethylfurfural (DHMF).

Entry	Catalyst and/or base	Yields			
		HFCA (%)	FFCA (%)	FDCA (%)	DHMF (%)
1	Blank	5	-	-	-
2	NaOH	58	-	-	35
3	CaCO ₃	2	-	-	-
4	Pd-Cl/C	8	-	-	-
5	Pt-N/C	8	-	-	-
6	PdCl/C-NaOH	54	6	30	-
7	PdCl/C-CaCO ₃	25	5	6	-
8	PdN/C-NaOH	44	4	28	-
9	PdN/C- CaCO ₃	76	0	16	-
10	PtCl/C -NaOH	8	0	50	-
11	PtCl/C - CaCO ₃	11	0	14	3

4. Conclusions

PdCl/C, PdN/C and PtCl/C were evaluated in the oxidation of 5-HMF to 2,5-FDCA. The effect of deposited metal and precursor salt were studied. The atomic ratios H/M obtained by H₂ chemisorption for all catalysts, suggests an order particle size: PtCl/C < PdCl/C < PdN/C, which is closely related to the catalytic activity results. The presence of NaOH favors intermediates products which can be oxidized to FDCA and it seems be that exist an inhibition of adsorption of OH⁻ ions on chlorinated residues. In the case of Pt and Pd the main effect is associated to particle size.

5. References

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