

Electronic Supplementary Information (ESI) available

2. Materials and Methods

2.1 Support Carbon and PdCl₂ Catalyst

In this work were used two commercial carbon nanofibers (PR24-PS and PR24-HHT) and two commercial high area surface graphite, HSAGs (H₁₀₀ and H₃₀₀) as supports. The carbon fibers were provided by Applied Sciences Inc. and the HSAGs were manufactured by Timcal Graphite & Carbon. PR24-PS nanofiber (designated PS) are pyrolytically stripped carbon fibers treated at 1100 °C, and therefore, less graphitized than PR-24HHT fibers. PR-24HHT fibers (designated HHT) were treated at high temperature (~3570 °C), have a stacked-cup morphology with a hollow core through the length of the fiber and also present a jagged outer surface with “round heads” or “loop” structures that connect multiple layers [1].

The catalytic materials were prepared by incipient wetness impregnation, with a 1 wt% Pd loading using acid aqueous solution of PdCl₂ as precursor. Subsequently to impregnation and evaporation of solvents overnight in an open recipient at room temperature, the samples were dried at 110 °C for 24h. The Pd based catalyst was labelled as Pd/PS, Pd/HHT, Pd/H₁₀₀ and Pd/H₃₀₀.

To characterize and prior to the reaction the catalysts were reduced under H₂ flow (25 cm³/min STP) at 250 °C for 1 h with a temperature ramp of 5 °C/min, in order to decompose the precursor and assure their initial metallic state. The catalysts were characterized by transmission electron microscopy to determine the Pd nanoparticle sizes using a microscope model JEOL 2100F field emission gun electron microscope operated at 200 kV and equipped with an Energy-Dispersive X-Ray detector. The small amount sample was suspended in ethanol solution using an ultrasonic bath. Some drops were added to the copper grid with carbon coated layers (Aname, Lacey carbon 200 mesh) and the ethanol was evaporated at room temperature before introduce in the microscope.

The X-ray diffraction (XRD) patterns of the catalyst were determined in a Polycrystal X'Pert Pro PANalytical diffractometer using Ni-filtered Cu K α radiation ($\lambda = 1.54 \text{ \AA}$, 45 kV and 40 mA) and the PANalytical X'Pert HighScore Plus software was used for the phases identification and by X-ray photoelectron spectroscopy to obtain the surface composition and the oxidation state characteristics of the Pd surface species. The textural properties of the catalyst were evaluated by N₂ physisorption at -196°C using an Autosorb, Micromeritics, model ASAP 2020. The surface area (S_{BET}) was estimated by applying the BET equation to the adsorption-desorption N₂ data to $P/P_0 < 0.25$.

2.2 Catalytic Test

The FA decomposition and the HBD were carried out in a continuous flow fixed-bed reactor. The reaction mixture consists of a flow rate of 54.23 cm³ (STP)/min of N₂ saturated with formic acid at 23 °C (≈ 7.8 vol%) or H₂ line flow (4.5 cm³ STP)/min and 1.5 cm³(STP)/min of 1,3-butadiene was fed to the reactor. The catalytic reactions were evaluated by operation the reactor with a mass/flow (W/F) ratio of 2.8×10⁻³ g min/cm³. Prior to testing reaction (in situ reduction), the catalyst (150 mg) was reduced in H₂ flow at 250 °C for 1 h using a temperature ramp of 5 °C/min; then it was purged and cooled in N₂ flow.

The experiments were realized following four stages, in order to determine the optimal reaction conditions for the two reactions. The first step consists in evaluating the conversion of formic acid, where the reaction temperature was varied between room temperature and 250 °C at atmospheric pressure, obtaining the light-off curves. In a second step the HBD with H₂ (ratio butadiene/H₂=1/3) was performed. The hydrogen amount was in large excess. Any significant mass transfer limitation was precluded by using this high space velocity and powders catalysts. In the third stage the HBD with H₂ provided by the in situ decomposition of FA was studied, and this experiment was repeated to confirm the behavior.

The products of FA decomposition were analyzed by an on-line gas chromatograph (Varian 3400) fitted with a 60/80 CarboxenTM 1000 column and a thermal conductivity detector (TCD) and flame ionization detector (FID). The reactants and products hydrogenation were analyzed using a 20% BMEA Chromosorb P80/100 column. The products determined in FA decomposition reaction were CO, CO₂ and H₂ and the amount of these compounds was calculated by the area of the chromatographic peak divided by the respective response factor. The conversion of formic acid was calculated as the sum of CO and CO₂ amount produced (μmmol/min) divided by the initial FA concentration (173 μmmol/min). The selectivity to CO₂ was estimated by dividing the CO₂ concentration by the sum of the products FA decomposition. The products detected in the HBD were 1-butene, 2-butenes (cis and trans 2-butenes) and butane. The conversion of BD was calculated as $\% \text{Conv}_{\text{BD}} = (C_{\text{BD},0} - C_{\text{BD},t})/C_{\text{BD},0} \times 100$, where $C_{\text{BD},0}$ is the concentration of BD at $t = 0$ and $C_{\text{BD},t}$ is the concentration of BD at time determined. The selectivity of HBD products $S_{\text{Prod},i}$ were defined as the percent fraction of each product and was calculated as $S_{\text{Prod},i,t} = C_{i,t}/C_{\text{Tot},t} \times 100$.

Electronic Supplementary Information (ESI) available. Figures

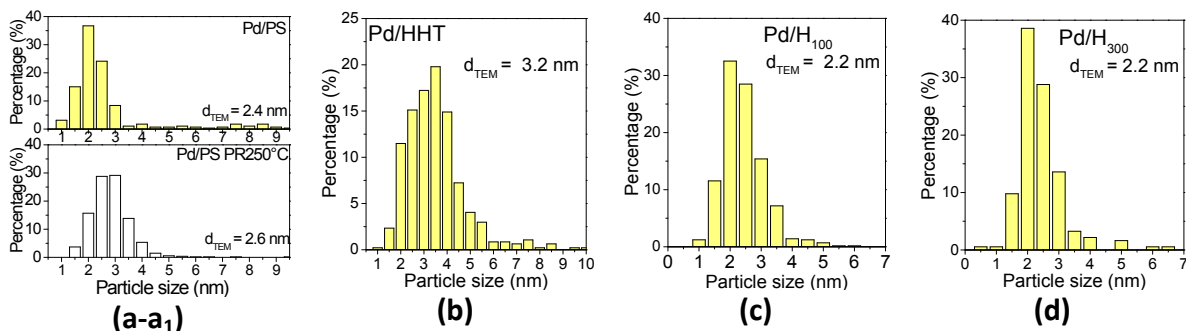


Fig. S1. (a-d) Particle size distribution histogram for (a-a₁) Pd/PS and Pd/PS PR250°C, (b) Pd/HHT, (c) Pd/H₁₀₀ and (d) Pd/H₃₀₀. The fresh Pd catalysts were reduced prior to obtaining the images TEM.

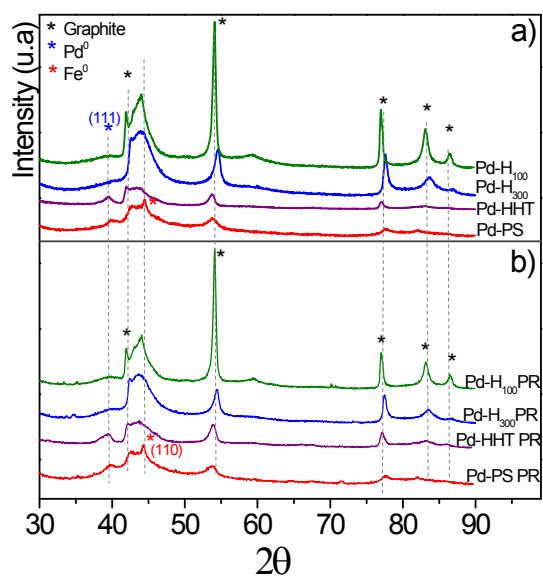


Fig. S2. XRD patterns of Pd based catalysts. (a) Reduced and (b) post- reaction HBD, PR.

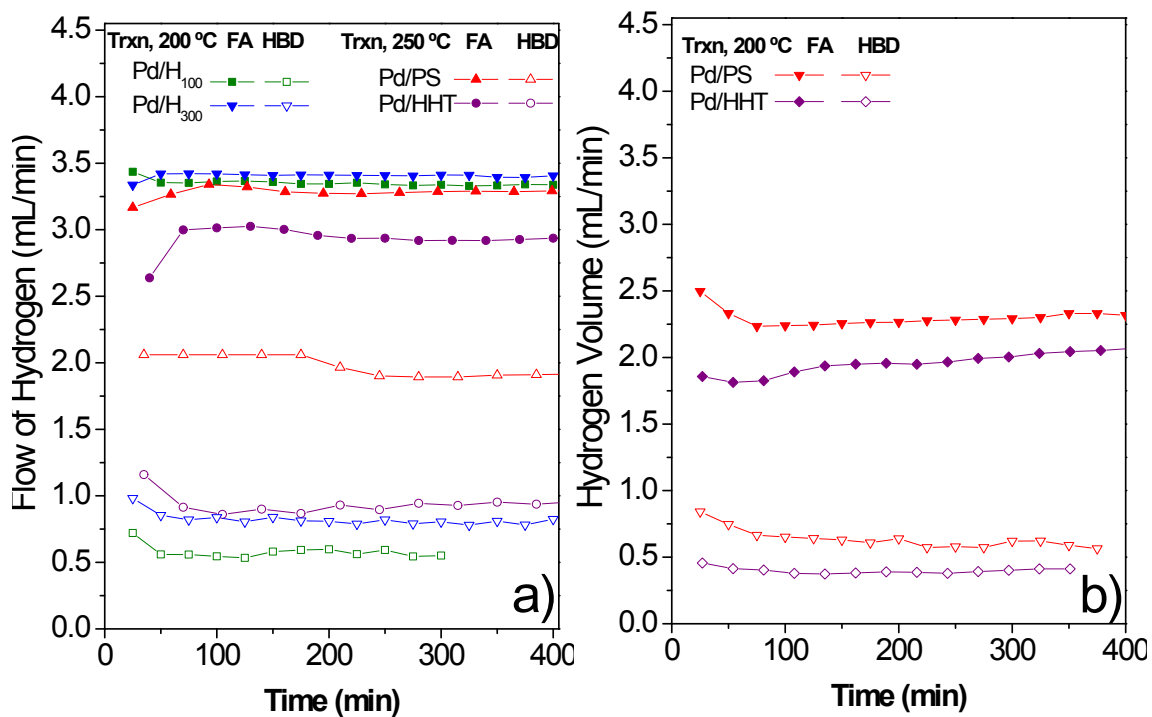


Fig. S3. Hydrogen volume produced in the FA decomposition (full symbols) and H₂ residual post HBD using H₂ from FA (open symbols) over Pd catalyst based carbon nanofibers.

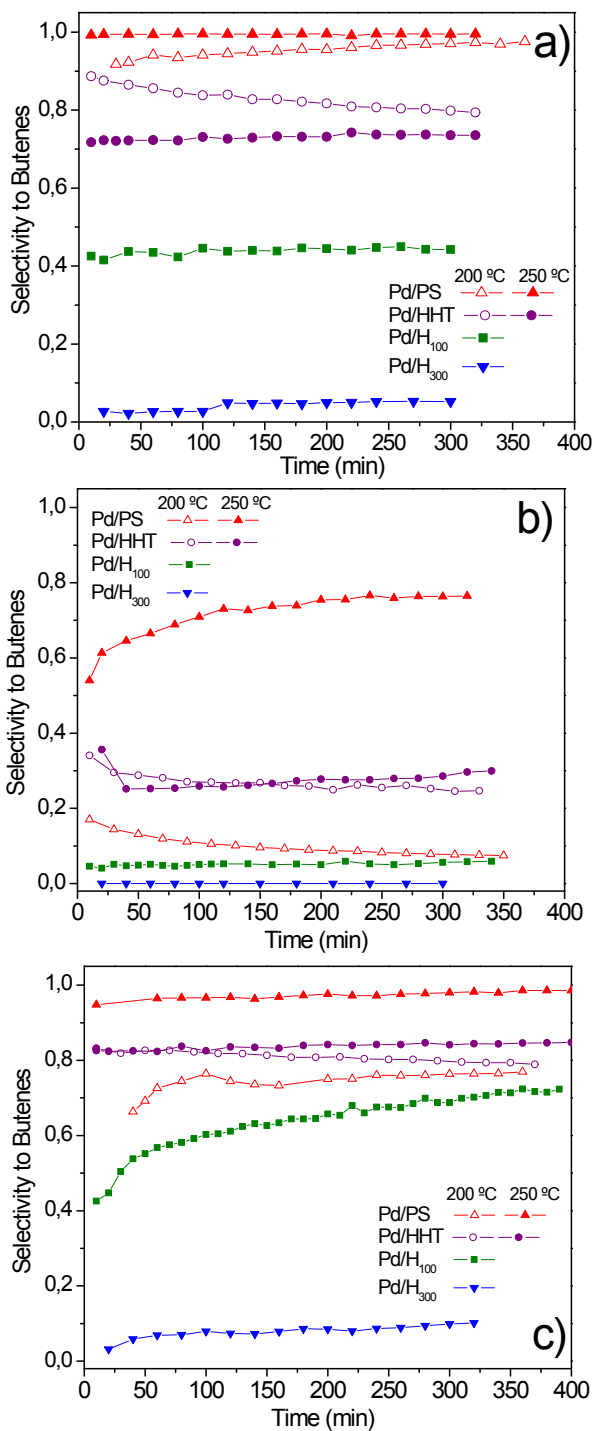


Fig. S4. Selectivity to butenes (1-butene and cis/trans-butenes). (a) Reaction using H₂ from FA and (b) Reaction using gas H₂ and (c) Reaction using H₂ from FA after decomposition Formic Acid reaction in a complete conversion of BD.

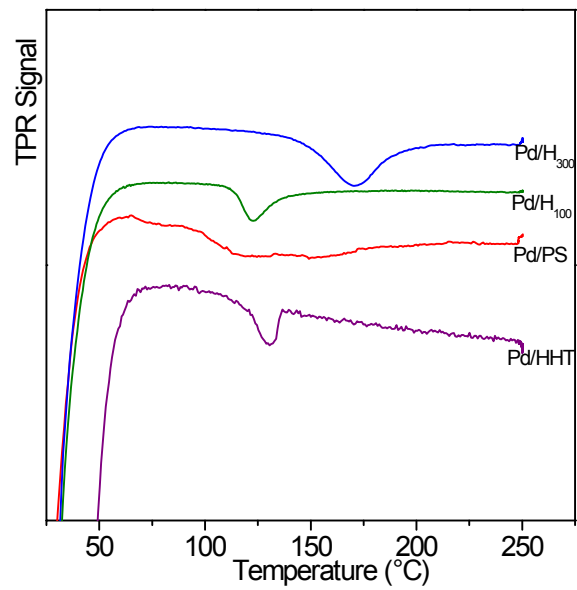


Fig. S5. The H₂-TPR analyses of Pd Catalysts.

References

- [1] E. Asedegbega-Nieto, B. Bachiller-Baeza, D.G. Kuvshinov, F.R. García-García, E. Chukanov, G.G. Kuvshinov, A. Guerrero-Ruiz, I. Rodríguez-Ramos. *Carbon*, 46, 1046-1052 (2008).