



# The effect of carbon nanofiber properties as support for PtRu nanoparticles on the electrooxidation of alcohols

David Sebastián<sup>a</sup>, Isabel Suelves<sup>a</sup>, Elena Pastor<sup>b</sup>, Rafael Moliner<sup>a</sup>, María J. Lázaro<sup>a,\*</sup>

<sup>a</sup> Instituto de Carboquímica, CSIC, Miguel Luesma Castán 4, 50018, Zaragoza, Spain

<sup>b</sup> Universidad de La Laguna, Dpto de Química-Física, Avda. Astrofísico Francisco Sánchez s/n, 38071 La Laguna, Tenerife, Spain

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## ABSTRACT

Carbon nanofibers (CNFs) characterized by different mean diameter, BET surface area, pore volume and crystallinity were prepared and studied as supports for PtRu nanoparticles to investigate the influence of the support characteristics on the performance for the electrooxidation of alcohols. A modified microemulsion procedure was used to deposit the metal nanoparticles minimizing the effect of the support on the catalyst particle size.

PtRu nanoparticles of ca. 2 nm size were obtained despite the relatively low surface area of CNFs (95–185 m<sup>2</sup> g<sup>-1</sup>) with a good distribution on the surface as confirmed by TEM micrographs and the high values of the electrochemically active surface areas (110–140 m<sup>2</sup> g<sup>-1</sup>) determined by electrochemical CO stripping. The most appropriate PtRu dispersion was achieved for those carbon nanofibers showing the best compromise in terms of BET surface area and graphiticity.

A cross-analysis of the supports physico-chemical properties, ECSA and mass activity for the methanol and ethanol oxidation reactions suggests that both PtRu dispersion and electronic properties as determined by the effect of CNF crystallinity play a significant role in determining the electrocatalytic activity. Different electrocatalytic activity behavior with CNF properties were found for methanol and ethanol. Methanol oxidation is favored using highly crystalline CNFs as PtRu support, despite their low surface area, whereas ethanol oxidation is hindered by diffusional problems when using highly graphitic CNFs due to their low pore volume, so the activity is maximized supporting PtRu on CNFs with a more accessible porosity.

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## 1. Introduction

Energy distribution in low molecular weight alcohols, such as methanol or ethanol, is an attractive option in terms of sustainability and low environmental impact. For their direct conversion into electrical energy, direct alcohol fuel cells (DAFC) are regarded as a very interesting choice in terms of efficiency for portable devices [1–7]. Methanol and ethanol are the most appropriate alcohols in DAFC. Methanol has been widely considered because it is the smallest alcohol molecule and its electrochemical oxidation is relatively fast if compared to alcohols with a higher number of carbon atoms [8]. The use of ethanol instead of methanol has gained interest as it has a higher energy density (about 30% higher), ethanol itself and its oxidation products are less toxic, the cross-over effect is less detrimental and can be easily produced from biomass (a renewable source) [9,10]. Unfortunately, the kinetics of ethanol oxidation

reaction (EOR) is even slower than that of methanol oxidation reaction (MOR), where the challenge is the cleavage of C–C bond at low temperature. The improvement of the oxidation kinetics in the DAFC is one of the targets for the implementation of this technology in portable devices, because it would allow increasing the noble metal utilization and reducing the overall cost [7,8]. The current highly performance solid electrolytes based in sulfonated polymers entails the electrooxidation of alcohols in acidic media, which needs the use of expensive noble metallic alloys based on platinum, being the pair platinum–ruthenium widely recognized [11–15].

One of the possible strategies is the optimization of the carbon support. Carbon supports (commonly carbon blacks) are used to maximize the noble metal utilization and reduce costs. The catalyst support is not a mere inert material to disperse the active phase and maximize the metal utilization, but it can also interact electronically with the metal and modify its intrinsic activity [16,17]. During the last decade, carbon nanofibers (CNFs) have been studied as catalytic supports giving place to improved performance in the oxidation of methanol compared to the classical carbon blacks [18,19]. This improved catalytic activity has been attributed to their

\* Corresponding author. Tel.: +34 976733977; fax: +34 976733318.  
E-mail address: [mlazaro@icb.csic.es](mailto:mlazaro@icb.csic.es) (M.J. Lázaro).

good compromise between the external porosity and structural features, derived from the nanosized diameter of the filaments, the orientation of the graphenes with respect to the fiber axis, as well as the high ratio of edge atoms to basal atoms on the surface [20]. Moreover, their peculiar filamentous structure leads to a negligible micropore content, which favors mass transport through the electrocatalytic layers [21]. Additionally, the well-developed graphite-like structure of CNFs can provide a high conductivity and a high resistance to corrosion. The edge-rich surface is expected to provide suitable sites for the stabilization of catalyst nanoparticles. Furthermore, regular arrangement of such sites can provide a more uniform distribution of catalyst particles on the surface [22]. Therefore, the high content of the edge surface is expected to interact with the nanosized metal and to contribute to the stabilization of the nanoparticles on the surface. Investigations up to date regarding PtRu/CNF catalysts include comparing CNFs with carbon blacks [23,24], studying the intrinsic structure in terms of graphene orientation [19,23,25], the study of catalyst properties modifying the metal composition [24], the metal concentration [26], or modifying CNF surface chemistry [27]. Nevertheless, nothing is yet known about the influence of the variation of important properties of CNFs, such as the surface area or the crystallinity, on the performance of PtRu/CNF based electrocatalysts towards the electrooxidation of alcohols.

Carbon nanofibers properties can be adjusted to favor certain processes. In a previous work we observed that a high graphitization degree of functionalized CNFs favors the electrooxidation of methanol on Pt electrocatalysts [20]. In a recent work [28] the effect of support properties has been studied for the reduction of oxygen (cathodic half-reaction) in platinum electrocatalysts, concluding that an optimum activity is found when using carbon nanofibers with a compromise between properties. CNFs also show an enhanced behavior in terms of activity and stabilization of metal particles when compared to the commercial carbon black. Nevertheless, the reaction mechanism is different for every electrocatalytic process and the results regarding the cathodic half-reaction are not extrapolable to the anodic process, as we will demonstrate along this paper. This work is aimed to analyze the effect of different characteristics (diameter, graphitization, etc.) of pristine herringbone type carbon nanofibers on the electrochemical oxidation of methanol and ethanol at low temperature.

## 2. Experimental details

### 2.1. Synthesis of PtRu nanoparticles and deposition on carbon nanofibers

In-house synthesized carbon nanofibers with diverse physical properties were used to evaluate their influence on the PtRu catalysts electrochemical behavior. Their synthesis procedure is detailed elsewhere [29,30]. Basically, the carbon nanofiber growth was carried out at five synthesis temperatures between 550 °C and 750 °C (supports will be labeled as 'CNF' followed by the synthesis temperature in Celsius degrees) at low weight hourly space velocity (WHSV) of 4 L g<sup>-1</sup> h<sup>-1</sup>, to achieve different graphitization degrees and different porosity features according to previous works [29,30]. Moreover, two additional CNFs were synthesized at higher WHSV (2.5 times higher, 10 L g<sup>-1</sup> h<sup>-1</sup>) at 550 °C and 750 °C, labeled as CNF550HV and CNF750HV (HV refers to high velocity). These samples are characterized by a higher pore volume with respect to those obtained at lower space velocity, which will be shown to have an important effect on the catalytic activity. The growth of nanofibers was carried out for enough reaction duration to obtain a high volumetric carbon content of 99%, monitoring the

conversion of methane into carbon by gas chromatography. It is known that the synthesis at lower temperatures than 550 °C leads to very low methane conversion, and consequently very low CNF growth rate for practical purposes, whereas synthesis at higher temperatures than 700 °C do not significantly improve crystallinity neither porosity of the nanofilaments, so the selected interval seems to be ideal in terms of the study of the support.

Platinum-ruthenium nanoparticles were synthesized by the water in oil microemulsion route [31,32]. The composition of the microemulsion and the preparation methodology have been adapted and optimized, taking into consideration the peculiar low surface area of carbon nanofibers, in order to obtain high electrochemical surface areas according to previous works with platinum [28]. Briefly, it consists of preparing a microemulsion composed by 16.5% surfactant (polyethylene glycol dodecyl ether, Brij<sup>®</sup>30, Sigma-Aldrich), 3.9% aqueous solution containing the metal precursors (0.05 M H<sub>2</sub>PtCl<sub>6</sub> and 0.05 M RuCl<sub>3</sub>) and 79.6% n-heptane as the hydrophobic phase. Subsequently, the appropriate amount of carbon support is dispersed in the microemulsion under sonication for at least one hour to achieve a metal concentration in the catalyst of 20 wt.%. The reduction step involves the slow addition of sodium borohydride in excess at room temperature and under vigorous stirring, left overnight under continuous stirring, and finally the catalyst is thoroughly washed with ethanol and water to remove the chemicals used during the synthesis, and dried overnight at 60 °C.

### 2.2. Solid-state characterization techniques

High-resolution transmission electron microscope (HRTEM) micrographs were obtained using a JEOL-2000 FXII microscope at 200 kV and with a spatial resolution of 0.28 nm. To obtain the micrographs, the catalyst samples were finely grinded and ultrasonically dispersed in ethanol. A drop of the resultant dispersion was deposited and dried onto a standard copper grid coated with Lacey carbon.

The crystallinity of platinum-ruthenium crystallites and carbon was studied by X-Ray Diffraction. XRD patterns were performed using a Bruker AXS D8 Advance diffractometer, using Cu-K $\alpha$  radiation. Crystallite sizes were calculated from the Scherrer's equation applied to the (002) peak for carbon and (220) peak for platinum related reflections.

Raman spectra were employed to evaluate the ordering degree of CNFs. The spectra were obtained using a Horiba Jobin Yvon HR800 UV, using the green line of an argon laser ( $\lambda = 514.53$  nm) as excitation source. The carbon ordering degree was evaluated by means of the relative intensities of D (ca. 1350 cm<sup>-1</sup>) and G (ca. 1590 cm<sup>-1</sup>) peaks.

Textural properties of carbon supports such as the specific surface area and the pore volume were calculated from nitrogen adsorption-desorption isotherms, measured at -196 °C using a Micromeritics ASAP 2020. Total surface area and pore volume were determined using the Brunauer-Emmet-Teller (BET) equation and the single point method, respectively. The micropore volume was calculated applying the t-plot method.

Electrical conductivity measurements were also performed pressing the carbonaceous powder at 10 MPa as described elsewhere [30]. The electrical resistance was measured by the four-point probe method applying electrical currents up to 0.02 A.

Energy dispersive X-ray (EDX) analyses and thermogravimetric analyses (TGA) in air were performed to quantify the metal loading in the PtRu/CNF electrocatalysts. EDX measurements were also used to determine the Pt:Ru atomic ratio. An EDX analyzer Röntec XFlash Si(Li) coupled to a Hitachi S-3400 N scanning electron microscope (SEM) was used for that purpose. For TGA experiments in air, a Setaram Setsys Evolution thermogravimetric analyzer was

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