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Electrocatalytic activity of Ni-doped nanoporous carbons in the electrooxidation of propargyl alcohol

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Abstract

Herein, we explore the immobilization of nickel on various carbon supports and their application as electrocatalysts for the oxidation of propargyl alcohol in alkaline medium. In comparison with massive and nanoparticulated nickel electrode systems, Ni-doped nanoporous carbons provided similar propargyl alcohol conversions for very low metallic contents. Nanoparticulated Ni on various carbon supports gave rise to the highest electrocatalytic activity in terms of product selectivity, with a clear dependence on Ni content. The results point to the importance of controlling the dispersion of the Ni phase within the carbon matrix for a full exploitation of the electroactive area of the metal. Additionally, a change in the mechanism of the propargyl alcohol electrooxidation was noted, which seems to be related to the physicochemical properties of the carbon support as well. Thus, the stereoselectivity of the electrooxidative reaction can be controlled by the active nickel content immobilized on the anode, with a preferential oxidation to (Z)-3-(2-propynoxy)-2-propenoic acid with high Ni-loading, and to propiolic acid with low loading of active Ni sites. Moreover, the formation of (E)-3-(2-propynoxy)-2-propenoic acid was discriminatory irrespective of the experimental conditions and Ni loadings on the carbon matrixes.

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1. Introduction

Nickel is a low cost and mass produced material, showing inherent catalytic properties in a wide number of processes such as organic electrosynthesis [1-4], degradation of organic hazardous molecules [5], energy conversion in alkaline fuel cells [6, 7], biosensing [8, 9] and electroanalysis [10-12], among the most representative.

The electrocatalytic properties of nickel hydroxide -Ni(OH)₂- and oxyhydroxide -NiOOH- electrodes, obtained in alkaline medium under anodic polarization conditions, have been explored extensively for the oxidation of aliphatic and aromatic alcohols and amino compounds via the participation of Ni(III) species [1, 3, 4, 13-22]. In contrast, few studies have focused on the performance of Ni(OH)₂/NiOOH couples in the electrooxidation of unsaturated alcohols (i.e., alken-1-ols or alkyn-1-ols) [1, 3, 23]. In this regard, our recent investigations have reported the electrooxidation of propargyl alcohol (PGA) at a NiOOH electrode, leading to the selective formation of 3-(2-propynyloxy)-2-propenoic acid (PPA) [23]. These results contrast with previous work by Schäfer and Kaulen [2] from 1979, who reported that the electrooxidation of PGA at a Ni electrode gives propiolic acid (PA), selectively. The differences between these results remain unclear, and open questions such as about the dependence on the Ni features (chemical state and accessibility) on the electrooxidation pathway still need to be studied in more detail. Moreover, despite the excellent results obtained with the Ni(OH)₂/NiOOH electrodes concerning stereoselectivity and conversion yields, there are two main limitations regarding their application in electrooxidative processes of alcohols. The first one is due to the significant deactivation of the Ni(OH)₂/NiOOH electrode surface, when large PGA concentrations are used [13, 24]. The second is the formation of γ -NiOOH species [14] during long cycling electrooxidative processes, which are ineffective to catalyze the alcohol oxidation.

Taking into account these limitations, it becomes necessary to move towards an optimal utilization of the electroactive catalyst on the electrode in terms of selectivity and reaction conversion. According to the literature, different strategies are being investigated to improve the catalytic activity of NiOOH species, including the use of alloys of metallic Ni with other metals such as Ti, Cu and Ru [25-28], or the dispersion of the metallic species on different carbonaceous supports [29, 30]. The objective of this study is the synthesis and performance of Ni species immobilized on distinct nanoporous carbon materials, as an alternative approach to improve the stability and catalytic activity of NiOOH redox species during the electrocatalytic oxidation of PGA.

Therefore, this paper will focus on the preparation and description of the structural properties of different Ni/carbon electrodes and on the study of their electrocatalytic activity towards PGA electrooxidation. As a support, a nanoporous carbon obtained from the pyrolysis of an organic salt (polystyrene sulfonic acid-co maleic acid) was used. This synthetic route allows for an excellent dispersion of metallic species (i.e., Ni in this work) within the carbon matrix [31, 32]. Various electrodes with different Ni loadings were prepared to evaluate the effect on the conversion yields and on the reaction mechanism. Although the benefits of the immobilization of Ni nanoparticles on non-porous carbon supports (i.e., glassy carbons and carbon blacks) have been extensively reported in the literature [13, 29], our findings demonstrate that the immobilization and high dispersion of the Ni-active species on highly nanoporous carbons offers important advantages in terms of electrode stability, conversion, efficiency and stereoselectivity for the electrooxidation of PGA towards the formation of PPA or PA, in comparison with a massive Ni sheet electrode (Ni-S). Moreover, we demonstrate that the mechanism of PGA electrooxidation can be controlled by the Ni content loaded on the carbon support, leading to full selectivity towards propiolic acid or (Z)-3-(2-propynoxy)-2-propenoic acid at low and high Ni contents, respectively. For comparative purposes, a commercial carbon black (Vulcan XC-72R) was also used, in which Ni nanoparticles (NiNP) were supported. The electrocatalytic activity of the unsupported NiNP was also compared with that obtained with the massive nickel electrode.

2. Experimental

2.1 Materials

Propargyl alcohol (PGA) and propiolic acid (PA) were of analytical grade (plus 99% purity, from Alfa Aesar). PGA was purified through distillation before use and its purity was determined by ^1H NMR. All the chemicals used were of the highest purity available. All solutions were prepared using doubly distilled water with a resistivity of 18.2 M Ω cm. Vulcan XC-72R carbon powder was purchased from Cabot Corporation (CAS No 1333-86-4).

2.2 Synthesis of electrocatalysts

Nickel nanoparticles (NiNP) were synthesized from the use of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, dissolved in ethanolic sodium hydroxide medium, using NaBH_4 as reducing agent, as described

elsewhere [33, 34]. Briefly, an ethanol solution containing NaOH/NaBH₄ was added to an ethanolic solution of NiCl₂. The final solution contained an equimolar ratio of NiCl₂ and NaBH₄ with stoichiometric ratios of NaOH to NiCl₂ of 1, 2, 5 and 10. The synthesis was performed under continuous magnetic stirring at room temperature. Thereafter, the NiNP were thoroughly washed with acetone (three times) and finally redispersed in an ethanol solution with a final concentration of circa 2.6 mg Ni/mL. The dispersions were stored at room temperature. For the preparation of the Ni/carbon black electrode materials (NiCB), nickel nanoparticles in an alcoholic suspension were mixed with carbon black powder in adequate amounts to obtain nickel loadings of ca. 20 and 6.7 wt.%, and dispersed by 90 minutes sonication (Selecta ultrasonic bath operating at 50/60 kHz, 360 W power output). Hereafter, the samples will be named as NiCB-*x*, where *x* stands for the nickel loading. The procedure for the synthesis of Ni-loaded nanoporous carbons has been described in detail elsewhere [31, 32]. Briefly, the carbon precursor (polystyrene sulfonic acid co-maleic acid sodium salt), was ion-exchanged with nickel nitrate for 24 h and then carbonized in nitrogen at 800°C. After carbonization, the sample was washed in distilled water, until reaching a constant pH of the leachate. The Ni-content of the carbon matrix was adjusted further by extensive washing with 1M HCl to eliminate all water and acid soluble inorganic salts. Hereafter, the samples will be named as PSNi-*x*, where *x* stands for the nickel loading (ca. 0.24 and 6.7 wt. %, for the samples washed with acid and water, respectively, as determined by X-ray photoelectron spectroscopy).

2.3 Characterization of the catalysts

N₂ adsorption isotherms were measured at -196°C (ASAP 2010, Micromeritics) for samples (ca. 0.15 g) previously outgassed overnight under vacuum (ca. 10⁻³ torr) at 120°C. The isotherms were used to calculate the specific surface area, S_{BET}, the total pore volume, V_T, and the pore volume and pore size distributions using the DR formalism and non-local density functional theory assuming slit-shaped pore geometry. Transmission electron microscopy (TEM) was performed on the samples with a JEOL JEM-2012 instrument with an accelerating voltage of 300 kV. Scanning electron microscopy (SEM) was performed on the samples with a Zeiss DMS 942 instrument operating at 30kV. X-ray photoelectron spectroscopy (XPS) experiments were recorded on a K-Alpha Thermo Scientific spectrometer using AlKα (1486.6 eV) radiation, monochromatized by a twin crystal monochromator and yielding a focused X-ray spot

with a diameter of 400 μm , at 3 mA $\times$ 12 kV. Deconvolution of the XPS spectra was carried out using a Shirley background.

2.4 Preparation of the catalytic inks and anodes

The catalytic inks consisted of alcoholic dispersions of the electrode materials (NiNP and NiCB-x were dispersed in ethanol, and PSNi-x in isopropanol) in 20-40 wt. % Nafion binder coming from a 10 % Nafion aqueous starting solution [30, 35]. The different anodes were prepared by spraying (air-brushing) the catalytic ink on a 5 x 5 cm^2 Toray paper (T, TGPH-120), supported on a hot metallic plate at 90 $^\circ\text{C}$ to facilitate solvent evaporation. The Ni loading of the electrodes was 1 mg cm^{-2} for NiNP anodes (with a Ni to Nafion ratio of 24), between 0.1 and 0.067 mg cm^{-2} for NiCB-x anodes (with a NiCB-x to Nafion ratio of 1.5) and between 0.0024 and 0.067 mg cm^{-2} for PSNi-x anodes (with a PSNi to Nafion ratio of 1.5). The addition of a proper amount of Nafion facilitated the cohesion between the anodic carbonaceous film and the Toray paper. The anodes were named as follows: Z/T, where Z stands for the electrode material and T indicates the Toray paper support (i.e., NiNP/T, NiCB-x/T and PSNi-x/T). The Ni loading is indicated separately (when necessary). Ni free anodes, based on Vulcan carbon black, and the sodium form of the polymer-derived carbon (PSNa) were also prepared with a Nafion ratio of 1.5. These are named as CB/T and PSNa/T. For purposes of comparison, the performance of a massive Ni sheet electrode (Ni-S) was also investigated. All anodes were topographically characterized using scanning electronic microscopy.

2.5 Electrochemical characterization

The electrochemical characterization of the anodes was carried out in a three electrode configuration glass cell, using the prepared anodes (NiNP/T, NiNCB-x/T, PSNi-x/T, CB/T, PSNa/T and Ni-S) as working electrodes (0.7 x 0.5 cm^2), a platinum wire as counter electrode and a Ag/AgCl (3.5 M KCl) reference electrode. The anodes were immersed in a 1 M aq. NaOH solution at a controlled potential of -0.5 V vs Ag/AgCl. Then, the anodes were activated by cycling between -0.5 and +0.6 V vs Ag/AgCl for 100 cycles at 100 mV s^{-1} , to form the NiOOH layer on the Ni surface. Cyclic voltammetry (CV) measurements were carried out at 293 $\pm$ 2 K under argon atmosphere, using an Autolab III potentiostat/galvanostat (Eco-Chemie). After surface

activation, voltammetries were recorded in the presence of PGA, with concentrations in the range of 1-50 mM.

2.6 Electrooxidation of propargyl alcohol

Preparative electrooxidation of PGA was performed with a potentiostat (AMEL instruments Model 2053), using an H-type electrochemical cell with divided compartments with a cationic ion exchange membrane (Nafion 117 DuPont, USA), where ca. 100 mL 1M NaOH solution were placed in each compartment. The different anodes were used as working electrodes, a ca. 15 cm² Pt wire as counter and Ag/AgCl (3.5 M KCl) as reference electrode -via Luggin probe-. Before starting the electrolysis, the anodes were activated as indicated above. PGA concentration in the anodic compartment was set at 250 mM, and the solutions were mechanically stirred with a magnetic bar at room temperature. The charge passed during the preparative electrolyses was measured using a Digatron coulometer. The conversion of the PGA electrooxidation reaction was followed by HPLC, coupled to an UV-Vis detector (wavelength was set between 210 and 240 nm), with a C18 Hypersil ODS reverse phase column (25 cm long, 4.0 mm internal diameter and 5 µm particle size). The mobile phase consisted of 20 mM NaH₂PO₄, adjusted at pH 2.5, using a flow rate of 0.5 mL min⁻¹, an injection volume of 100 µL, at a temperature of 30 °C. Before injection onto the column, the final reaction solution in the anodic compartment was neutralised by using 1.25 M phosphoric acid, until a pH of 3 was reached. For the final workup of the preparative electrolysis, liquid-liquid extraction of the acidified final anolyte solution was performed with ethyl ether, the solvent being dried in anhydrous sodium sulphate, and finally concentrated *in vacuo* at 40 °C. The reaction mixture was put in contact with a silica gel 60 glass plate (20 x 20 cm) for the separation of the reaction products, eluting the mixture with hexane:chloroform:ether (1:1:1, v/v/v). The analysis of the products, either PA or PPA, obtained from the chromatographic separation was confirmed by ¹H and ¹³C NMR spectroscopy at 400 MHz for ¹H and 75 MHz for ¹³C with a BRUKER AV300 Oxford instrument, where the Z to E ratios were calculated from the ¹H NMR spectrum of the final crude. High resolution mass spectrometry was carried out with a MICROMASS AUTOSPEC-ULTIMANT instrument. Details on the spectroscopic data of the obtained PGA electrooxidation products (Z-PPA, E-PPA and PA) are included in the Supplementary Information (SI).

3. Results and discussion

3.1 Synthesis and characterization of the electrocatalysts and anodes

Fig. 1 shows some representative TEM images of the unsupported (Fig.1A) and carbon black-supported (NiCB, Fig.1B) Ni nanoparticles prepared in this work. The nanoparticles show a quasi-spherical morphology and a particle size of about 2 nm, which is in agreement with previous work reporting the preparation of NiNP using NaBH_4 as reducing agent [33, 34] In addition, good particle dispersion on the carbon is observed, although a certain, but low degree of agglomeration is also detected.

Figure 1. Representative TEM images of the prepared nickel electrocatalysts: (A) unsupported nickel nanoparticles, NiNP; B) NiCB; C) PSNi-0.24; D) PSNi-6.7.

For a comparative study, representative TEM images of PSNi-0.24 and PSNi-6.7 samples are also shown in Fig. 1 (C and D). For the carbon materials with the lowest metal loading, the analysis of the particle size of the metallic particles is difficult due to the high metal dispersion. However, some nanoparticles are visible with a particle size of about 2 nm. In the case of the sample containing a higher Ni loading (6.7 %wt), the metallic particles are more visible with a particle size of about 2 nm and with a high degree of dispersion.

The electrochemical behaviour of the unsupported NiNP was investigated in a deoxygenated 1 M NaOH solution, using a glassy carbon (GC) electrode. The nanoparticles were casted on the GC substrate and covered by a Nafion thin film to avoid their detachment during the electrochemical measurements. The voltammograms showing the electrochemical response of the NiNP in a 1 M NaOH solution (Fig SI-1) exhibited the expected redox couples, which are associated to the nucleation of NiOOH and the formation of the pair $\text{Ni}(\text{OH})_2/\text{NiOOH}$ [36]. It is interesting to note that the anodic peak potential shifted downwards by about 50 mV upon cycling. This has been attributed to changes between different phases of nickel hydroxide/oxyhydroxide (i.e., $\alpha\text{-Ni}(\text{OH})_2$ to $\beta\text{-NiOOH}$ or $\alpha\text{-Ni}(\text{OH})_2$ to $\gamma\text{-NiOOH}$. [36]. On the other hand, the cathodic wave at 0.3 V is similar to that obtained during the activation of massive nickel electrodes [37, 38]. The activation of the NiCB composite followed a similar trend (see supplementary Fig. SI-2) suggesting that the dispersion of the nanoparticles on the carbon black does not modify their electrochemical features.

As described in the experimental section, different anodes were prepared with both NiNP and NiCB samples. Large differences were observed in the morphology of the anodes prepared from the base NiNP and by Ni-dispersion on carbon black (NiCB). Fig. 2 shows the SEM images where the NiNP were chaotically and heterogeneously deposited on the Toray substrate. In contrast, spraying the NiCB inks rendered a uniform coverage of the substrate, with all the Toray fibers homogeneously covered by the ink, as shown in Fig. 2C and 2D. It can be inferred that the dispersion of the nanoparticles on the carbon black surface minimizes their agglomeration during spraying, in the preparation of the anodes.

Figure 2. SEM micrographs of the anodes NiNP/T (A and B), NiCB/T (C and D), PSNi-0.24/T (E and F) and PSNi-6.7/T (G and H).

It is well known that the nanoparticulated systems provide an improved catalytic performance as compared to massive systems due to their high surface to volume ratio, although their performance is greatly affected by size, shape, nature and bulk/surface composition of the nanoparticles [39, 40]. Thus, based on the better coverage of the anode support obtained with the NiCB inks, an improved electrocatalytic response of NiCB/T anode would be expected, compared to that of NiNP/T. Fig. 2 also shows the morphology of the anodes prepared by spraying PSNi-x inks onto the Toray substrate. The PSNi-x film is less homogeneously deposited than that of NiCB, which can be attributed to the particle size and/or the less hydrophobic nature of these nanoporous carbons.

The main physicochemical features of the Ni-doped nanoporous carbons, obtained from the pyrolysis of the organic polymer precursor are summarized in Table 1. Data corresponding to the nickel free material -sodium salt form of the carbon polymer precursor -PSNa- is also included for the sake of comparison.

Table 1. Main physicochemical parameters of the synthesized nanoporous carbons, including specific surface area (S_{BET}), pore volumes and pH of the point of zero charge (pH PZC).

	S_{BET} [m ² g ⁻¹]	V_{TOTAL} [cm ³ g ⁻¹]*	$V_{\text{MICROPORES}}$ [cm ³ g ⁻¹]**	$V_{\text{MESOPORES}}$ [cm ³ g ⁻¹]**	pH PZC
PSNa	1740	1.63	0.49	0.31	3.9
PSNi-6.7	559	0.49	0.20	0.11	7.2
PSNi- 0.24	710	0.62	0.30	0.14	5.2
CB	250	0.55	0.04	--	--
* evaluated at $p/p_0 \sim 0.99$ from the N_2 adsorption isotherms					
** evaluated by DFT method applied to the N_2 adsorption isotherms					

As seen, the polymer-derived carbons present a high textural development with a predominantly microporous structure (see Table 1). The carbonization of transition metal-based salts of polystyrene sulfonic acid co-maleic acid results in formation of

porous materials, due to the expansion of the matrix during carbonization in the presence of the metals undergoing reduction and oxidation reactions [32]. The final pore structure is strongly dependant on the nature of the metal cation incorporated to the polymer precursor. A more elaborated discussion on the role of the metal in porosity development is included in our previous works [31, 32, 42]. As expected, the acidic washing increased the textural properties of the Ni-doped carbon due to the cleaning of the surface, leading to a better accessibility of a higher fraction of pores [31, 32], especially of the micropores. Comparatively, the nickel-free carbon (sample PSNa) exhibited higher textural development, due to the lower chelating effect of the monovalent cation [32, 41]. Due to the fine dispersion of the metal precursor in the organic polymer precursor (easily controlled by cation-exchange in solution), nickel species end up homogenously distributed within the carbon matrix after carbonization.

SEM images of PSNi-x samples are shown in Fig. 3. None of these carbons exhibited metallic aggregation on the surface, as expected due to the low particle size of the nickel nanoparticles incorporated to the carbon matrix. The EDX mapping of the nanoporous polymer-derived carbons confirmed the uniform distribution of nickel species within the carbon matrix in the bulk particles (Fig. 3 B, D). Similar results have been reported for the incorporation of other transition metals (i.e. Ag, Co, Ni), as opposed to Cu-doping, where some aggregates of a few nanometres in size have been reported [31]. Moreover, the resulting carbons also present large surface areas and high pore volumes (see Table 1), due to the expansion of the matrix during carbonization in the presence of the metals undergoing reduction and oxidation reactions [32]. As expected, the acidic washing increased the textural properties of the Ni-doped carbon due to the cleaning of the surface, leading to a better accessibility of a higher fraction of pores [31, 32], especially of the micropores. Comparatively, the undoped carbon (sample PSNa) exhibited higher textural development, due to the lower chelating effect of the monovalent cation [32, 41].

As for the surface chemistry of the Ni-doped carbons, the samples have an acidic character (even after washing the samples with water) as a result of the presence of carboxylic and sulphonic acid groups, originating from the organic polymer precursor. During the carbonization process, nickel forms sulfides, sulfates and oxides (see thermogravimetric analysis in suppl. Fig. SI-3), a small water-soluble fraction being released during washing out with water (sample PSNi-6.7). After acidic washing to

decrease the Ni content (sample PSNi-0.24), most sulfides and sulfates are removed, but nickel hydroxides still remain on the surface, as evidenced by thermal analysis (see also Fig. SI-3) [32, 42].

Figure 3. SEM micrographs of the synthesized Ni-doped nanoporous carbons: A) sample PSNi-6.7, magnification x500; C) sample PSNi-0.24, magnification x500. Plots B and D highlights in red the distribution of nickel on the samples, as detected by EDX.

The identification of nickel oxides and hydroxides as the most abundant chemical phases on the surface of the Ni-doped nanoporous carbons was confirmed by XPS analysis (Table 2 and supplementary Fig. SI-4 and SI-5), regardless the Ni content. The XPS patterns of the Ni2p spectra (Fig SI-5) showed the two edges of $2p^{1/2}$ (ca. 869-885 eV) and $2p^{3/2}$ (ca. 850-867 eV). The spin energy separation of the $2p^{3/2}$ and $2p^{1/2}$ of 17.6 eV are characteristic of the $Ni(OH)_2$ phase, according to the literature. The $Ni2p^{3/2}$ envelope was deconvoluted into three components, which were assigned to Ni(II)/(III) ions in various Ni-O environments [43, 44]. The $Ni2p^{3/2}$ spectral lines consist of a main peak and an associated satellite located at 6 to 8 eV higher binding energy (peak positioned at 862 eV), that appears as a result of multielectron excitation. The main

peak was fitted in two components, appearing at 856.1 and 856.7 eV. According to the literature, these can be assigned to Ni_2O_3 and $\text{Ni}(\text{OH})_2$, respectively. The peak positioned at 862.4 eV corresponds to the satellite peak. Based on the positions of the $\text{Ni}2\text{p}$ peaks, it seems that there is no reduction of the nickel ion during the carbonization of the organic polymer, since no contribution of a peak at $\sim 852.8\text{--}853.3$ eV, assigned to elemental nickel, was found. Moreover, nickel sulfides can also be disregarded, since no peak at the binding energy range corresponding to NiS (ca. 853.1 eV) was observed. Additionally, the assignment of the $\text{O}1\text{s}$ XPS lines is consistent with the $\text{Ni } 2\text{p}^{3/2}$ spectra, with the peak at 531.3 eV confirming the Ni-OH and Ni-O bonds arising from $\text{Ni}(\text{OH})_2$ and higher valence nickel oxides such as Ni_2O_3 , $\beta\text{-NiO}(\text{OH})$, or $4\text{Ni}(\text{OH})_2\cdot\text{NiOOH}\cdot x\text{H}_2\text{O}$.

Table 2. Atomic weight percentage data obtained from the XPS experiments performed on the nanoporous carbons PSNa and PSNi-x

	C (%)	O (%)	S (%)	Ni (%)
PSNa	88.6	8.1	3.3	--
PSNi-6.7	63.3	26.7	3.3	6.7
PSNi-0.24	86.93	6.22	7.6	0.24

The electrochemical characterization of the PSNi-x/T catalysts has been performed in a 1 M NaOH solution, cycling the electrode between -0.5 V and +0.6 V for 100 scans at 100 mV/s. Even at the lowest Ni loading, the redox peaks associated with the oxidation of Ni(II) to Ni(III) species and further the reduction of the nickel oxyhydroxide to nickel hydroxide on the reverse scan are still observable, as shown in Fig. 4. For a comparative study, the electrochemical behaviour of the nickel free microporous carbon (prepared using the sodium salt of the organic polymer) was also studied (sample PSNa), as shown by the cyclic voltammetry in Fig. SI-6. This anode was prepared with a PSNa coverage of 1.0 mg cm^{-2} on the Toray paper.

Figure 4. CV behaviour during the activation of PSNi-0.24/T in 1 M NaOH at a scan rate 100 mV s^{-1} over a potential range of -0.5 V to +0.6 V. Scans shown: 1st, 2nd, 3rd, 10th, 20th and 100th. Arrows indicate the direction of increasing scans. Geometric area of the electrode: $0.5 \times 0.7 \text{ cm}^2$.

3.2. Voltammetric behaviour of NiNP/T, NiCB-x/T and PSNi-x/T anodes.

Fig. 5, 6 show the voltammetric response of the different anodes in the presence of propargyl alcohol (PGA) at substrate concentration between 1 and 50 mM. First of all, the performance of the NiNP/T anode with geometric area of 0.125 cm^2 and a Ni content of 1 mg cm^{-2} was analyzed in the presence of different PGA concentrations, as shown in Fig. 5, and an almost constant anodic peak current (due to the oxidation of PGA) was obtained over 50 scans up to a concentration of 50 mM. Analogously, the voltammetric response of a NiCB/T anode with geometric area of 0.125 cm^2 and a Ni content of 0.1 mg cm^{-2} showed a similar current profile to that of NiNP/T at PGA substrate concentrations between 1-50 mM (see Fig. 6). It is most significant that the

currents obtained with the NiCB/T are of the same order of magnitude as those of the NiNP/T anode, given that the Ni content is estimated to be 10 times lower than in the former. This suggests a better optimization of the electrocatalytic activity of nickel in NiCB/T, likely due to an increase in the electroactive area of the anode. This shows the beneficial effect of the nanoparticle dispersion on a carbon black support on the

electrooxidation of PGA.

Figure 5. Cyclic voltammetry response of the anode NiNP/T in 1M NaOH (dashed line) and with propargyl concentration of 1, 2, 5, 10, 20 and 50 mM (solid lines). Scan rate 10 mV s^{-1} . Third scan shown. Inset shows the dependence of the anodic current of PGA electrooxidation with PGA concentration.

The voltammetric response of the Ni-doped nanoporous carbons (PSNi-x/T), Fig. 6A and B, presents current profiles for the anodic oxidation of PGA similar to those discussed before. It is worth noting that for PSNi-0.24/T with a geometric area of 0.250 cm^2 and a Ni content of $0.0024 \text{ mg cm}^{-2}$, -ca. 40 times lower loading than anode NiCB/T- the oxidation currents recorded are only half of those obtained with the NiCB/T.

Figure 6. Cyclic voltammetry response of the anodes built on Ni-doped nanoporous carbons in 1M NaOH (dashed line) and with propargyl concentrations of 1, 2, 5, 10, 20 and 50 mM (solid lines). Scan rate 10 mV s^{-1} . Third scan shown. Insets show the dependence of the anodic current of PGA electrooxidation with PGA concentration. (A, B) NiCB samples with 0.067 and 0.1 mg cm^{-2} nickel loadings, respectively; (C,D) PSNi-x samples with 0.0024 and 0.067 mg cm^{-2} nickel loadings, respectively.

As a general rule, it was observed that the plots of anodic current of the electrooxidation of PGA deviated from linearity for all the studied anodes, with the exception of PSNi-0.24/T, where a linear fit with a $R^2 = 0.998$ was obtained (inset Fig. of Fig. 5, 6). Hence, adsorption of PGA is taking place during the electrooxidation process by the redox couple oxyhydroxide/hydroxide on the NiNP surface, when using NiNP/T and NiCB/T electrodes, where a higher Ni content is a common variable for both films. We applied the Freundlich equation $I_o = kC_i^{1/n}$, where I_o is the anodic current (in amperes) from the oxidation of PGA obtained from Fig. 5 and 6, C_i is the PGA concentration (in M), k is the adsorption coefficient, and n is a correlation coefficient indicating the adsorption

behaviour. Accordingly, no significant differences were found in the fitting parameters of all the anodes used, with k values of 0.064, 0.041 and 0.042 for the NiNP/T, NiCB-20/T and PSNi-0.24/T anodes, respectively. Such low k values indicate a poor affinity of PGA to the nickel surface. However, considering the large textural features of the polymer derived carbons (Table 1), the electrochemical response of PSNi- x /T anodes was investigated further upon pre-adsorption with a 20 mM PGA in 1M NaOH at an applied potential of -0.5 V (for 45 -70 min). Data showed that both the electrochemical profile and the anodic current were similar to those obtained under non-preloading conditions. Furthermore, the adsorption of PGA on these microporous materials was found to be negligible after immersing the electrodes (both Ni-doped and Ni-free) for 2 h at room temperature in 1M NaOH solutions containing 50 or 250 mM PGA. Thus, the electrooxidation of PGA at PSNi- x /T anodes is due to an improved electrocatalytic activity of the nickel aggregates dispersed on the carbon matrix, with little influence or any likely contribution of adsorption of the substrate on the inner porosity of the anodes. On the other hand, cyclic voltammetric experiments carried out on the PSNa anode (i.e., the Ni-free nanoporous carbon) showed that there was no electrooxidation of PGA.

3.3 Preparative electrolyses

The efficiency of the electrooxidation of propargyl alcohol on the different anodes prepared was evaluated in comparison to the performance of a nickel massive electrode (Ni-S). Aside from the conversion of PGA, the influence of the electrode material on the stoichiometry of the products and on possible mechanism pathways were studied with the electrodes in hand. Identification of the final products and estimation of their relative abundance were carried out by ^1H NMR spectrometry. Since none of the Ni-free carbons showed any electrocatalytic activity for PGA oxidation (see discussion above), the preparative electrolyses were carried out with the Ni-doped anodes. Thus, all data has been referred to the influence of Ni catalyst loading and content and is summarized in Table 3.

A general reaction scheme for the electrooxidation of PGA under a controlled potential of 0.540 V is proposed in Scheme 1, indicating the formation of the different products depending on the characteristics of the anode. In this regard, it should be noted that the mechanism for the oxidation of PGA has been discussed previously in the literature, but has not yet been clarified satisfactorily. Thus, Schaefer and Kaulen described the formation of PA as a product in the electrooxidation of PGA at NiOOH electrodes in a 1

M NaOH solution at temperatures below 5 °C [2, 3]. In our previous study we have reported the formation of PPA for the electrooxidation carried out at room temperature [23]. In this work, both the *Z* and *E* PPA isomers and PA were detected as final products, although their relative abundance was highly dependent on the anode characteristics, as will be discussed below.

Scheme 1A

Scheme 1B

Scheme 1. (A) Products of the electrochemical oxidation of PGA at NiNP/T, NiCB/T and PSNi-x/T anodes and (B) tentative mechanism for the formation of Z-PPA. I represents the haptic-propiolate complex formation to the NiOOH surface, II represents the Ni(II) complexation and the addition of the alkoxy group to the haptic complex.

First of all, PGA conversions ranged from 65 % to 80 % for all the electrolysis runs, regardless of the nature of the anode. Comparing the massive Ni electrode with the nanoparticulated anode (NiNP/T), no clear influence of electrode material can be found on the product distribution of the PGA electrooxidation. For the electrolyses carried out using NiCB/T anodes, the PGA conversion slightly decreased from 80 % to 73 %, when the Ni content on the catalytic ink was reduced from 20 to 6.7wt.%. Despite the large reduction of the nickel content, the loss of conversion suggests that thicker coverage of the carbon black would prevent the full exploitation of the electroactive metal likely due to an agglomeration of the nickel nanoparticles.

Table 3. Summary of the electrolysis products ratios *Z-PPA:E-PPA:PA* obtained from the electrooxidation of *PGA* at Ni-S, NiNP/T, NiCB-x/T and PSNi-x/T electrodes. 250 mM *PGA* starting concentration. Electrosynthesis were performed at 0.540 V vs Ag/AgCl. Geometric area of the electrode: 3.8 x 3.8 cm². * Electrolysis carried out using 50 mM *PGA*.

Electrode	PSNi-x/T		NiCB-x/T		NiNP/T*	Ni-S
Ni [wt. %]	0.24	6.7	6.7	20		
Ni loading [mg cm ⁻²]	0.0024	0.067	0.067	0.1	1	
PGA Conversión [%]	67	66	73	81	95	76
Charge passed [C]	4446	4440	4756	5266	1615*	3787
Z-PPA:E-PPA:PA ratio						
<i>Z-PPA</i>	0.07	1.00	0.04	1.00	1.00	1.00
<i>E-PPA</i>	0.02	0.08	0.01	0.01	0.01	0.04
<i>PA</i>	1.00	---	1.00	---	—	---

Along with the changes in conversion, a drop in the Ni-loading had an important effect on the distribution of the products obtained from the electrolyses (Table 3). Thus, whereas *PA* was the most abundant product when using the catalytic ink loaded with 6.7 wt. % Ni, only the *Z* and *E-PPA* isomers were obtained for the catalytic ink loaded with 20 wt.% Ni, with a 1.00 (*Z*) to 0.01 (*E*) ratio. Consequently, a larger Ni loading on the carbon black brought about an almost selective electrocatalytic oxidation of *PGA* to *Z-PPA*. By contrast, electrolyses carried out on NiNP/T anodes using 50 mM *PGA* with a Ni coverage of 1 mg cm⁻² led exclusively to the formation of the *Z* isomer of *PPA*, indicating an electrochemical behaviour analogous to that of a massive Ni anode (see Table 3). According to the literature, the selective formation of the (*Z*) isomer proceeds through a hapto-propiolate complex with the NiOOH surface via the triple bond of the alkyne moiety [23] It seems that when the nickel content dispersed on the carbon black is too low, the hapto-propiolate complex on the NiOOH surface exists only in low concentrations, and hence the formation of *PA* takes place.

For the Ni massive electrode, the electrooxidation reaction at room temperature is still stereoselective, leading to the formation of the Z-isomer, with a Z- to E-isomeric ratio of 1.00 to 0.04, but with a slightly lower PGA conversion. This would suggest that not only the conversion but also the stereoselectivity of PGA is dependent on the Ni-content on the anode, the (Z) isomer being favored at high nickel loadings, compared to the preferential formation of PA at low Ni coverages. This is not a general rule, however, as will be addressed below. Furthermore, the use of Ni massive anodes has some drawbacks in terms of a scale-up of the process. For instance, the Ni-S anodes suffer from loss of product selectivity at PGA concentrations close to or higher than 250 mM, with a rise in concentration of the E-isomer of PPA, along with a marked deactivation or blockage of the Ni surface. Such fouling or inactivation of the Ni surface (NiOOH) can largely be suppressed upon dispersion of the NiNP on carbon black, thus preserving the stereoselectivity of the process.

For the Ni-doped nanoporous carbons (PSNi-x anodes), conversions of propargyl alcohol were slightly lower than those obtained for the NiCB/T anodes. However, it is interesting to note that the conversion was about the same, when the nickel content was decreased by a factor of 30 (from 6.7 to 0.24 wt.%). This suggests that there is a full exploitation of the Ni electroactive surface in PSNi-0.24/T, likely due to the excellent Ni dispersion on the carbon matrix. At the same time, this would suggest that for high metal loadings most of the nickel incorporated on either the nanoporous carbon or the carbon black supports would not be fully accessible during PGA electrooxidation. Concerning the selectivity, these anodes do not follow the trend observed for Ni-S and NiCB/T. In fact, the anode PSNi-6.7/T, containing a similar nickel loading than NiCB/T presented a completely different distribution of products (Table 3), with PPA being formed with a (Z) to (E) ratio of 1.00 to 0.08 and no formation of PA. When the nickel content of the anode was reduced to 0.24 wt. %, the selectivity of the electrooxidative reaction changed towards PA.

The key to understand these trends has to be related to the dispersion of the active metallic species on the electrode surface, rather than to the overall metal content. Indeed, the better dispersion of nickel supported on carbon black as compared to that on the polymer-derived carbon was confirmed by the EDX (Fig. 7), with fewer aggregation events of Ni particles observed on the anode surface of NiCB-6.7 when compared to PSNi-6.7. That fact may explain why for the same Ni loading of 6.7 wt %, we have different product selectivity.

Although the water washed samples showed a rather good Ni dispersion on the microporous carbon with a 0.24 wt % content, the differences in selectivity could indicate that not all of the nickel surface is exposed to PGA molecules during the electrooxidation. If the incorporation of the nickel species occurs inside the porosity, they would not be expected to contribute to the anodic oxidation, at least not to a large extent, since PGA is not adsorbed inside the microporosity of the carbon electrode. Also, it may occur that there are specific sites on Ni-particles that would electronically be more susceptible to triple bond complexation than others. This is going to be difficult to assess on a molecular level. Moreover, fouling might lead to E-/Z- isomerisations which could also happen as the products might stay longer on the electrode surface before dissociation.

Figure 7. SEM micrographs of (A) NiCB catalytic ink sprayed onto the carbon cloth (anode NiCB-6.7/T) and (C) PSNi catalytic ink sprayed onto the carbon cloth (anode PSNi-6.7/T). Figures B and D highlights in red the presence of Ni for the NiCB-6.7/T and PSNi-6.7/T anodes, respectively.

4. Conclusions

The use of nickel nanoparticulated systems dispersed and immobilized on various carbon supports was investigated for the electrooxidation of propargyl alcohol. Data has revealed that both conversion and selectivity of the anodic reaction strongly depends on

the dispersion of the nickel species and on the coverage of the nickel on the support. At high Ni loadings (Z)-3-(2-propynoxy)-2-propenoic acid was the predominant electrolysis product, whereas at low loadings propiolic acid becomes that most abundant product. Both compounds, propiolic acid and the Z and E isomers of 3-(2-propynoxy)-2-propenoic acid, are of great interest from an industrial viewpoint as polishing agents in electroplating baths, as corrosion inhibitors and as intermediates in the organic synthesis, for which their selective preparation is most advantageous. The benefits of using the Ni-dispersed carbon anodes are evident in the inhibition of an inactivation or fouling of the Ni surface (NiOOH) as characteristically happens in massive Ni anodes.

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