

Original Research

Pd-Ni-B/C Nanocatalysts for Electrochemical Oxidation of Ethanol in Alkaline Media

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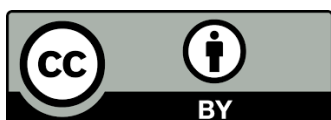
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Abstract

This paper describes the synthesis of Pd_{0.70}-Ni_x-B_y nanoparticles (x:y = 0.30:0, 0:0.30, 0.25:0.05, 0.20:0.10, 0.15:0.15, and 0.10:0.20) supported on carbon Vulcan XC-72 R by the chemical reduction method using ethylene glycol as a reducing agent for the study of the electrochemical oxidation of ethanol in alkaline media. Neither surfactants nor templates were used during the syntheses. The catalysts were physically characterized by transmission electron microscopy that showed the formation of nanoparticles with diameters of approximately 3 nm. Analyses of X-ray dispersive energy spectroscopy coupled with scanning electron microscopy identified the presence of the synthesized metals in concentrations close



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to the nominal ones. The electrochemical study was performed by CO-stripping, cyclic voltammetry, chronoamperometry, and steady-state polarization curves. The catalytic efficiency was also evaluated against the oxidation of CO, which is the principal intermediate adsorbed on the surface of catalysts during ethanol oxidation. The Pd_{0.70}Ni_{0.15}B_{0.15}/C catalyst showed the lowest oxidation onset potentials for both CO (0.37 V) and ethanol oxidation (0.51 V) compared with the Pd/C catalyst (0.63 V and 0.64 V). Chronoamperometric tests also revealed that the Pd_{0.70}Ni_{0.15}B_{0.15}/C catalyst displayed current densities four times higher than those of the Pd/C catalyst, probably because of the electronic and geometric effect that favors the removal of intermediate species from the catalyst surface. The synthesized ternary catalysts were more efficient toward the electrochemical oxidation of ethanol in alkaline media than Pd_{0.7}Ni_{0.3}/C and Pd/C catalysts. Thus, the synergistic effect of boron on the structure of binary nanoparticle catalysts supported on carbon for use in direct alcohol fuel cells was demonstrated for the first time.

Keywords

Ternary catalysts; ethanol electrochemical oxidation; alkaline media; direct ethanol fuel cell; chemical reduction method

1. Introduction

Energy sources are essential in the modern world for the development of society and its main activities [1]. In this context, alternative energy sources are required to meet energy demands and ensure global sustainability [2]. Direct ethanol fuel cells (DEFCs) appear as an alternative source of energy since ethanol offers the following advantages: It can be obtained from biological processes, such as the fermentation of some bacteria, making the price of ethanol more viable than gasoline; its complete oxidation to CO₂ releases 12 e⁻ per each oxidized molecule, presenting a high energy density (8.01 kWh kg⁻¹), comparable to gasoline (12,7 kWh kg⁻¹); in addition, it is a non-toxic liquid, has easy logistics for transport, storage and assembly in a short time [3, 4].

However, in the complete oxidation of ethanol to CO₂, aldehydes are formed before the C–C bond cleavage. If the cleavage does not occur, acetic acid may be formed in excess, decreasing the system's efficiency by adsorption onto the electrode surface. Then, the ethanol oxidation reaction (EOR) occurs by a mechanism releasing 4 electrons (e⁻) per molecule of ethanol oxidized, reducing the kinetics of the EOR. This inability to break the C–C bond is related to using anodic catalysts with low activation energies [5].

Therefore, it is essential to develop strategies that can increase the efficiency of oxidation rates and the durability of the electrocatalysts. Studies have focused on Pd-based electrocatalysts to guarantee improved catalytic activities. Pd-based catalysts exhibit a higher power density in an alkaline medium than Pt-based catalysts. They are a promising option for Pt replacement due to their high electrochemical stability and relatively larger reserves [6-8].

Several authors have indicated that the addition of a cocatalyst to Pd in an alloy improves stability and tolerance to poisoning and can also modify the electronic and crystalline structure of these metals, which favors easier C–C cleavage and increases the catalytic activity towards the EOR [6, 9,

10]. The formation of Pd alloys with Pt, Ni, Ag, Au, Cu, Zn, Co, and others, forming binary or ternary electrocatalysts, enhances the catalytic activities of Pd. This enhancement is due to changes in the *d* band center caused by the electronic effect, which modifies the electronic properties of Pd, weakening the CO adsorption on the metal surface and easing its oxidation. The electronic effect occurs through the transfer of electrons from the atoms of the added metal to neighboring Pd atoms [10, 11]. Furthermore, these metals can favor the adsorption of oxygen species and the adsorption and desorption of CO_{ads} on the metal, promoting the better oxidation of alcohol on the surface of the catalysts [12].

The combination of Pd with Ni showed promise for EOR [9, 10, 13, 14]. The improvement in the catalytic activity of this material was attributed to the strong electronic synergistic effects, which can facilitate the oxidation of adsorbed CO to CO₂ at lower potentials than pure Pd, increasing the oxidation kinetics and reducing poisoning rates. The formation of alloys with two or more metals alters the adsorption energy of the adsorbates on the surface of the primary metal in the alloy. This shift change favors greater feasibility and flexibility in improving the electronic and geometric properties of the Pd surface, thus protecting the catalyst from CO poisoning [15].

The addition of B into the Pd-Ni binary alloy favors the catalytic performance and stabilizes the structure of the nanoparticles. It is due to the electronic effect related to the change in the energy shift of the 5*d* band of Pd, which can weaken the CO adsorption on the surface and increase the tolerance toward CO in Pd, significantly affecting the catalytic properties. Furthermore, introducing B and Ni can reduce the catalyst costs implemented at the anode in fuel cells [16]. Wang et al. [17] prepared Pd+B alloy nanowires (NWs) for ethanol oxidation in an alkaline medium. In the cyclic ethanol oxidation voltammograms, the NWs of the binary PdB alloy showed a higher electrocatalytically active surface area (ECSA) of 41.1 m² g_{Pd}⁻¹ compared with Pd NWs, PdB nanoparticles (NPs), and Pd/C 27, 6, 34.4 and 24.1 m² g_{Pd}⁻¹, respectively. In addition, the PdB NWs exhibited more negative peak potentials and larger peak surface areas than the other catalysts, indicating greater ease of removal of CO-related poisons. For comparison, the authors also evaluated the behavior of PdB NWs for methanol and glycerol oxidation and showed a ~3.0-fold increase in bulk activities compared with commercial Pd/C. In addition, PdB NWs indicated a 2.63-fold increase in activity for electrochemical glucose detection than commercial Pd/C. This increased activity occurs because B promotes a change in the electronic structure of the Pd surface, contributing to the removal of intermediates during EOR.

To our knowledge, no studies have been performed on synthesizing and analyzing trimetallic catalysts using boron as a cocatalyst for ethanol oxidation. The atomic lattice of B is smaller than that of Ni and Pd. Therefore, the reduction in the distance between Ni and Pd through adding B becomes interesting, bringing the active sites closer to the metals [7, 9, 16, 17]. This combination of elements has yet to be explored. Therefore, we developed ternary carbon-supported Pd-Ni-B alloys for EOR in alkaline media as an alternative anode catalyst for DEFCs. We used a chemical reduction method using ethylene glycol as the reducing agent and NaOH as the reducing accelerator. This methodology uses the synthesis procedure without the complication of ligands (covering agents or surfactants). According to the literature [18-20], using the ligand renders incomplete exposure of catalytically active sites. It inhibits efficient contact between nanoparticles and support and influences the catalytic reactions, impairing their catalytic activity. Hence, the catalytic behavior and the effect of the catalyst's composition of the synthesized alloys (Pd_{0.7}Ni_{0.3}/C, Pd_{0.7}Ni_{0.25}B_{0.05}/C, Pd_{0.7}Ni_{0.2}B_{0.1}/C, and Pd_{0.7}Ni_{0.15}B_{0.15}/C) on the EOR activity in alkaline media were studied. Physical

characterizations were conducted to identify nanoparticles' formation and determine the particles' average size. The electrochemical activity of the catalysts developed toward the EOR was studied using cyclic voltammetry, polarization curves, and chronoamperometry. The evaluation of catalytic efficiency was also carried out toward the oxidation of CO.

2. Materials and Methods

2.1 Materials

All chemicals were analytical-grade reagents. Palladium chloride (PdCl_2 – Sigma-Aldrich, 99%), nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ – Sigma-Aldrich, 99%), sodium borohydride (NaBH_4 – Sigma-Aldrich, 98%), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$ – Sigma-Aldrich, 99,8%), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$ – Sigma-Aldrich, 99,8%), 2-Propanol ($(\text{CH}_3)_2\text{CHOH}$ – Sigma-Aldrich, 99,5%), sodium hydroxide (NaOH – Sigma-Aldrich, 98%), potassium hydroxide (KOH – Sigma-Aldrich, 99%), Nafion[®] solution (Sigma-Aldrich, 5% aliphatic alcohols and water) were used without any pretreatment. Carbon Vulcan XC-72R was purchased from Cabot. All solutions were prepared with ultrapure water (18.2 M Ω cm at room temperature).

2.2 Synthesis of Catalysts

Pd-Ni nanoparticles were synthesized by chemical reduction using ethylene glycol as a reductant agent with a theoretical value of 10% by weight of metals concerning carbon support [21]. Briefly, the $\text{Pd}_{0.7}\text{Ni}_{0.3}/\text{C}$ catalyst was synthesized using 70% Pd and 30% Ni, with carbon powder as support (Vulcan XC-72R, Carbon Black, 240 m² g⁻¹). The synthesis was initially carried out with the addition of 70 ml of ethylene glycol and 25 ml of 0.10 mol L⁻¹ sodium hydroxide solution, then 0.08 g of carbon powder was incorporated into the solution, and the suspension was heated to 110°C on a hot plate, for the activation of ethylene glycol [21]. Subsequently, the appropriate amounts of PdCl_2 and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were added. This set was stirred for 3 h to complete the reduction of metal ions at a temperature of around 110°C. Finally, the suspension was vacuum filtered with ultrapure water and dried in an oven for approximately 12 h at 70°C for further physical and electrochemical characterization.

Pd-Ni-B nanoparticles with a fixed Pd proportion (70%) varying the Ni: B ratio (Ni: B mass ratio of 25:5, 20:10, and 15:15), resulting in the following catalysts: $\text{Pd}_{0.7}\text{Ni}_{0.25}\text{B}_{0.05}/\text{C}$, $\text{Pd}_{0.7}\text{Ni}_{0.2}\text{B}_{0.1}/\text{C}$, and $\text{Pd}_{0.7}\text{Ni}_{0.15}\text{B}_{0.15}/\text{C}$, respectively, were synthesized by chemical reduction with ethylene glycol [21]. All experiments were carried out in aqueous solutions at room temperature, following the same procedure described above, but with NaBH_4 (precursor of B ions), which was added together with PdCl_2 and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the solution containing ethylene glycol and NaOH . In addition, the Pd/C catalyst (10wt.% pf Pd) was prepared similarly to the synthesis procedure described above for synthesizing Pd-Ni nanoparticles, but using only PdCl_2 .

2.3 Physical Characterization

The crystalline structure of the catalysts was determined by X-ray diffraction (XRD) analyses performed using a BRUKER diffractometer model D8 ADVANCE, operating with Cu K α radiation ($\lambda = 0.15406$ nm). The diffraction patterns were registered with 2θ ranging from 20° to 80°, with a scan rate of 2° min⁻¹. The crystalline phases were indexed according to reference standards from the Joint

Committee of Powder Diffraction Data Standards (JCPDS) database using X'Pert HighScore Plus software. In duplicate, the elemental compositions of the samples were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) using a Spectro spectrometer model Arcos. The detection limit (LD: $0.01 \text{ mg}\cdot\text{L}^{-1}$), and quantification limit (LQ: $0.10 \text{ mg}\cdot\text{L}^{-1}$).

Transmission electron microscopy (TEM) images were obtained using a JEM-1400 electron microscope operated at 120 kV to provide information on morphology, average diameter, and particle size distribution. For TEM measurements, the catalytic powders were dispersed in H_2O and $\text{C}_2\text{H}_5\text{OH}$ under ultrasound for 2 min. The suspension was then placed in a 3 mm carbon-coated grid, and the sample was dried under vacuum at room temperature. The average particle size and size distribution were determined from the TEM micrograph, considering at least 50 particles, and using the FIJI (ImageJ)-free software [22, 23].

Scanning electron microscopy (SEM) analyses were performed using a JEOL JSM-IT 200 microscope operated at 20 kV and equipped with an X-ray energy dispersive system (EDX). These techniques were used to estimate the chemical compositions of the catalysts. The Co standard was used for calibration, and a 20 kV electron beam of 25-mm focal length was applied. The sample area analyzed was $320 \times 320 \mu\text{m}$.

The mass of the Pd/C, $\text{Pd}_{0.7}\text{B}_{0.3}/\text{C}$, and $\text{Pd}_{0.7}\text{Ni}_{0.15}\text{B}_{0.15}/\text{C}$ catalysts was determined by thermogravimetric analysis (TGA) performed using a thermal analysis system (STA7200RV, Hitachi). All experiments were carried out in synthetic air (75% N_2 and 25% O_2) from 25 to 900°C using a heating rate of $10^\circ\text{C}/\text{min}$ with $50 \text{ mL}\cdot\text{min}^{-1}$ flow.

2.4 Electrochemical Characterization

A conventional three-electrode glass cell (Pyrex® glass) was used for all electrochemical experiments. A glassy carbon (GC) disk with a geometric area of 0.071 cm^2 (3 mm in diameter) was used as a support to fix the nanoparticles. Before each measurement, the GC electrode was polished with alumina ($\text{Al}_2\text{O}_3 - 1 \mu\text{m}$) to clean and renew the electrode surface and then washed with ultrapure water. Subsequently, this electrode was covered with a thin layer composed of the synthesized suspended supported nanoparticles. The counter electrode was a platinum sheet (1 cm^2), and the reference system used was a hydrogen electrode prepared in the same solution immersed in a Luggin capillary. All potential data in this study are expressed on the scale of the reversible hydrogen electrode (RHE).

Electrochemical measurements were performed at room temperature using an Autolab Model PGSTAT 302N potentiostat/galvanostat (Metrohm, Brazil). A 1.0 mol L^{-1} aqueous KOH solution was used to produce hydrogen (H_2) at the reference electrode, applying a constant negative potential of approximately -6.0 V . This solution was also the alkaline concentration used as the electrolyte in all electrochemical experiments.

A 3-mg catalyst suspension was mixed with $30 \mu\text{L}$ of Nafion® and $1000 \mu\text{L}$ of 2-propanol to prepare the catalytic layer. The mixture was sonicated for 20 min until a homogeneous black ink was formed. Then a $5 \mu\text{L}$ aliquot of this suspension was deposited on the surface of the GC electrode. The electrode was dried at room temperature. The solution was deaerated with nitrogen flow (N_2) for 15 min prior to the electrochemical test to eliminate all dissolved O_2 . The electrodes were first subjected to 500 scanning cycles at 500 mV s^{-1} between 0.05 and 1.2 V to obtain stationary responses and activate the catalytic sites of the electrocatalysts. Subsequently, cyclic voltammetry

(CV) experiments were performed at a scan rate of 20 mV s⁻¹ in a potential window between 0.05 and 1.2 V. The second cycle was used to study the reactions occurring on the catalyst's surface. Furthermore, 1.0 mol L⁻¹ of ethanol was added to the solution to analyze the EOR, and measurements were made under the same conditions described above. Further, all measurements were made in triplicate to verify reproducibility.

Chronoamperometric (CA) tests were performed at 0.50 V for 30 min. The catalytic activity of these materials toward the EOR was also tested using quasi-steady-state anode polarization curves obtained from the potentiostatic current values measured after 200-s polarization every 20 mV between 0.05 and 0.80 V in an aqueous solution containing KOH + CH₃CH₂OH. The stability study of the synthesized catalysts was carried out in 1.0 mol L⁻¹ CH₃CH₂OH and 1.0 mol L⁻¹ KOH solution. Stability was determined by comparing the voltammetric response of the second cycle with the 500th cycle, obtained at a scan rate of 50 mV s⁻¹ in a potential range between 0.05 and 1.2 V. These tests had an approximate duration of 7 h.

The electrodes were subjected to only 30 scanning activation cycles for the CO Stripping tests. CO stripping experiments were carried out in a 1.0 mol L⁻¹ KOH solution after bubbling CO gas in the electrochemical cell for 15 min, maintaining the potential at 0.05 V *versus* RHE. The electrolyte was then purged with high-purity N₂ for 45 min to remove residual CO in the solution. The CO-stripping CV test (2 cycles) was performed in the potential region between 0.05 and 1.20 V at 20 mV s⁻¹. This analysis was performed to calculate the active electrochemical area (ECA) and study the tolerance to CO poisoning [24] in all catalysts. The area below the peak of CO oxidation was used to calculate the ECA since the oxidation of a monolayer of CO adsorbed linearly on Pd involves a charge of 420 μC cm⁻² [25].

3. Results and Discussion

3.1 Physical Characterization

Figure 1 shows the XRD patterns of the prepared catalysts. At approximately 25°, a characteristic broad diffraction peak of carbon black is identified, the other peaks located at about 2θ = 40.63°, 47.19°, and 68.60° corresponding, respectively, to the reflection planes (111), (200), (220) of the face-centered cubic structure of Pd (JCPDS: 00-005-0681). All catalysts exhibited a typical XRD pattern of Pd with no other peaks, indicating that the introduction of B did not affect their crystal structure. The crystallite size (*t*) was calculated using Scherrer's equation (Equation 1), where λ is the wavelength of the X-ray, β is the full width at half maximum (FWHM) of the respective peaks, and θ is the peak position. The (111) diffraction is a single peak and had the maximum intensity for all catalysts and therefore was selected for the crystallite size evaluation [26].

$$t = \frac{0.90\lambda}{\beta \cos \theta} \quad (1)$$

Crystallite sizes ranged from 2.2 nm to 3.6 nm in the synthesized catalysts (Table S1). This increase is related to the isotropic expansion of the Pd crystal lattice for this catalyst through the incorporation of Ni atoms into the interstice of Pd-Pd lattice spaces, which has already been demonstrated in other studies [24]. Even in the sample with a 30% B content, the B peaks were undetected; this may be related to amorphous B deposition [27]. Thus, XRD data suggest the

formation of the Pd alloys and that the interaction between Pd, Ni, and B affects the Pd lattice parameter.

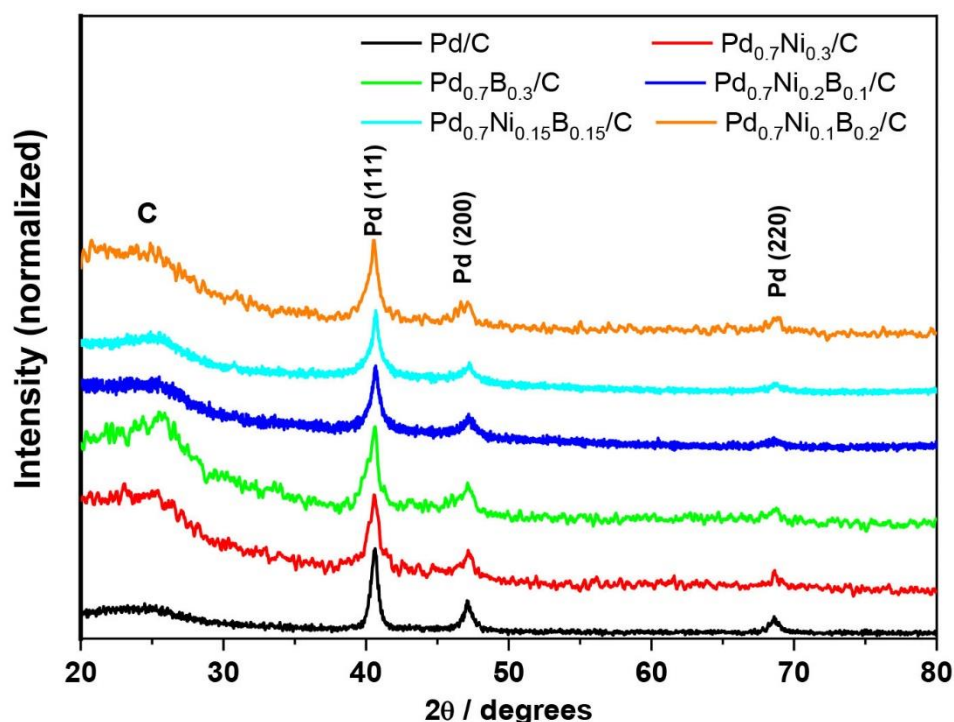


Figure 1 XRD patterns obtained from the Pd/C, Pd_{0.7}Ni_{0.3}/C, Pd_{0.7}B_{0.3}/C, Pd_{0.7}Ni_{0.2}B_{0.1}/C, Pd_{0.7}Ni_{0.15}B_{0.15}/C, and Pd_{0.7}Ni_{0.1}B_{0.2}/C catalysts.

For synthesized catalysts, the elemental composition can vary greatly, which can tremendously impact catalytic performance. Therefore, to evaluate the catalytic activity of the catalysts, the elemental compositions were analyzed by ICP-AES, which is a suitable method for quantitatively determining elemental concentrations of Pd-supported carbon [28]. Thus, Table 1 shows the ICP-AES data taken for the Pd_{0.7}Ni_{0.3}/C and Pd_xNi_yB_z/C catalysts.

Table 1 Elemental composition of the synthesized catalysts determined by ICP-AES.

Catalysts	The atomic ratio of elements (at.%)		
	Pd	Ni	B
Pd _{0.7} Ni _{0.3} /C	75.5	24.5	---
Pd _{0.7} Ni _{0.25} B _{0.05} /C	74.7	24.9	0.4
Pd _{0.7} Ni _{0.15} B _{0.15} /C	79.0	20.0	1.0
Pd _{0.7} Ni _{0.10} B _{0.20} /C	84.5	14.3	1.2

The ICP-AES analysis detected the presence of all components of the synthesized catalysts. However, the amount of boron in the catalysts is lower than the nominal expected composition. This fact indicates the difficulty of introducing boron atoms in the structure of the catalysts. Notably, the higher the B content, the lower the Ni content in the catalysts. Hence, the boron atoms have entered into the structure of the catalysts substituting Ni, and their presence seems to hinder the inclusion of Ni into the Pd structure. It has been shown in the literature [29-31] that added B can

react not only with carbon material but also with the active metal, thus affecting the activity and stability properties of the catalysts. As discussed hereafter, the changes in the composition of the catalysts result in the different catalytic activity of the catalysts. Moreover, the reduced amounts of boron in the catalysts are still responsible for the changes in the catalytic performance of the catalysts.

For example, Xu et al. [31] reported that adding B to metallic surfaces helps to increase the catalytic activity and promotes low catalyst deactivation during the reaction, as boron B exhibits similar chemisorption on the surface of Ni. This behavior is related to the chemisorption of B in Ni catalysts, which increases the stability of Ni catalysts.

Figure 2 illustrates the EDX spectra of the synthesized samples. Elementary mapping images obtained from SEM-EDX were taken to identify and observe the distribution of the elements in the synthesized catalysts. The EDX spectra in Figure S1 show the elements C, O, Ni, and Pd in the samples. The presence of oxygen can be explained by its bond with carbon, the formation of surface oxides, or the synthesis in a non-inert atmosphere, which makes the presence of oxygen sensitive. The SEM-EDX data confirm the presence of the metals Pd and Ni in the synthesized catalysts and the carbon substrate present in the catalysts, confirming the deposition of the metals in the support. Note that Ni and Pd elements are well dispersed on the carbon substrate for all catalysts (Figure 2). In addition to qualitative confirmation of the depositions of metals, the analysis allowed us to estimate the atomic proportion values in the chemical composition of the catalysts, making it possible to compare them with the nominal proportion of the synthesized catalysts (Table 2). However, it is unlikely to determine the presence of B, as it has an EDX energy similar to that of carbon [32, 33].

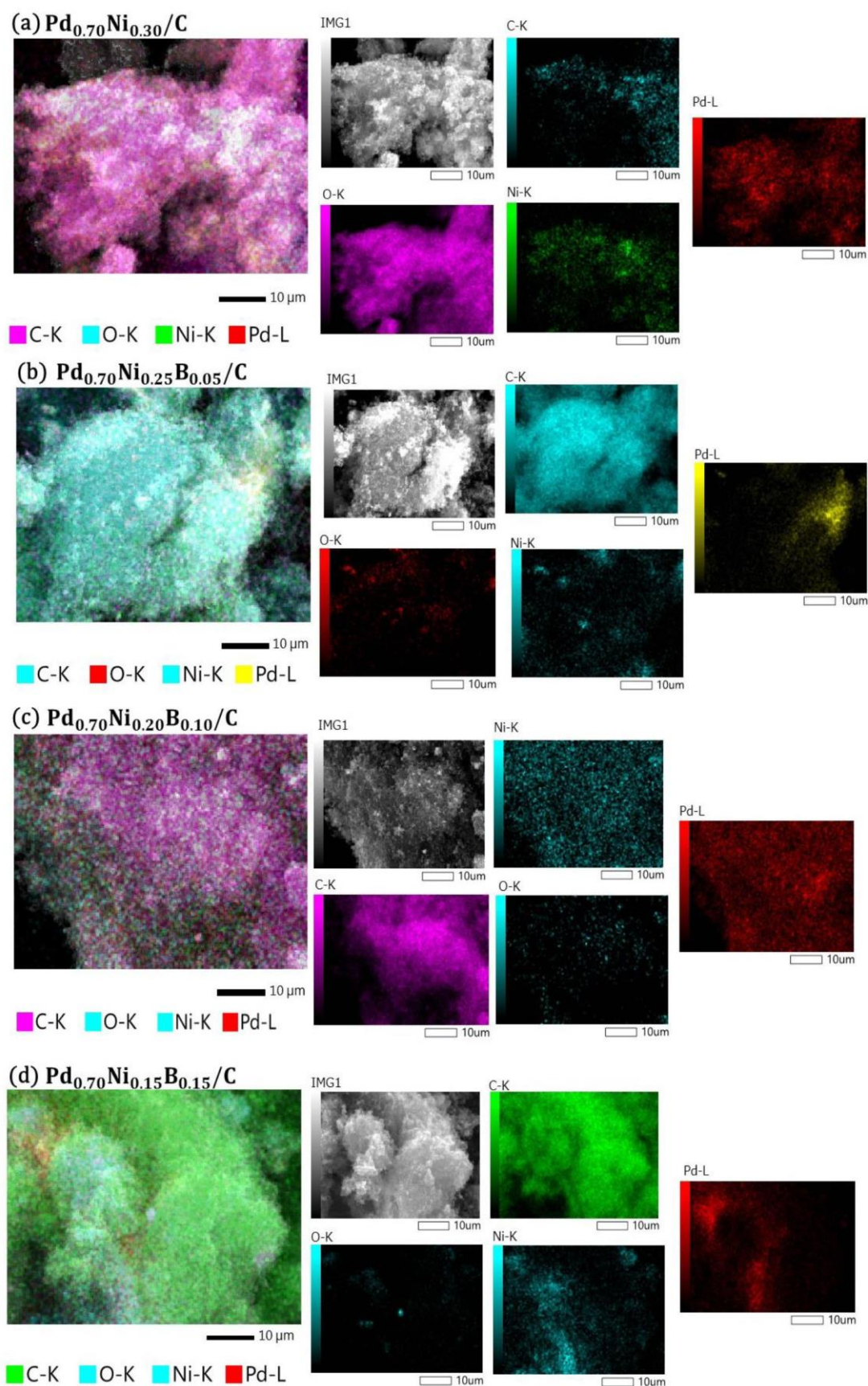


Figure 2 MEV-EDX patterns obtained from the Pd/C , $\text{Pd}_{0.7}\text{Ni}_{0.3}/\text{C}$, $\text{Pd}_{0.7}\text{B}_{0.3}/\text{C}$, $\text{Pd}_{0.7}\text{Ni}_{0.2}\text{B}_{0.1}/\text{C}$, $\text{Pd}_{0.7}\text{Ni}_{0.15}\text{B}_{0.15}/\text{C}$, and $\text{Pd}_{0.7}\text{Ni}_{0.1}\text{B}_{0.2}/\text{C}$ catalysts.

Table 2 Chemical composition data obtained by SEM-EDX and average particle size and diameter, and standard deviation obtained from the histogram of TEM images for all synthesized catalysts supported on carbon.

Catalysts	Nominal (%)	Atomic proportion identified by MEV-EDX			Carbon to metallic loading ratio (%)	Average particle size (nm)
	Pd:Ni:B	Pd	Ni	B		
Pd _{0.7} Ni _{0.3} /C	70:30:0	73 ± 1:	26.9 ± 0.4	---	88.5:11.5	3.4 ± 1.1
Pd _{0.7} Ni _{0.25} B _{0.05} /C	70:25:5	77.4 ± 0.1	17.6 ± 0.5	---	92.3:7.7	3.6 ± 1.0
Pd _{0.7} Ni _{0.2} B _{0.1} /C	70:20:10	72.0 ± 0.3	18 ± 1	---	91.9:8.1	3.3 ± 0.9
Pd _{0.7} Ni _{0.15} B _{0.15} /C	70:15:15	69.2 ± 0.7	15.8 ± 0.4	---	91.3:8.7	3.4 ± 0.5

Table 2 shows the elemental ratios and the metallic loading to carbon ratio, all taken from SEM-EDX measurements for the Pd_{0.7}Ni_{0.3}/C, Pd_{0.7}Ni_{0.25}B_{0.05}/C, Pd_{0.7}Ni_{0.2}B_{0.1}/C, and Pd_{0.7}Ni_{0.15}B_{0.15}/C catalysts. Notably, the metallic loading identified by EDX agreed with the nominal values (90% of carbon and 10% of metals). Moreover, the ratio between Pd and Ni in the samples is close to the nominal compositions for each catalyst.

Figure 3 shows the thermogravimetric curves for Pd/C, Pd_{0.7}B_{0.3}/C, and Pd_{0.7}Ni_{0.15}B_{0.15}/C. Initially, the first mass loss is observed in the range from 30 to 100°C, which is related to the evaporation of water adsorbed on the catalysts [34], showing a more significant loss for the Pd/C catalyst. Furthermore, the Pd/C catalyst showed different curve trends with mass loss at about 350°C (~60% by weight), which could be due to the synthesis shift [35], due to not adding the NaBH₄ precursor, which can also be influenced as a reducing agent in binary and ternary catalysts [36]. Between 500°C and 630°C, an intense mass loss is attributed to the complete oxidation of the carbon support, leaving only metals in the sample [37]. At 900°C, the remaining mass corresponds to the catalyst present on the carbon support, which was 12.2%, 10.6%, and 9.3% for Pd/C, Pd_{0.7}B_{0.3}/C, and Pd_{0.7}Ni_{0.15}B_{0.15}/C catalysts, respectively. These values are close to the calculated weight of the catalysts (10% by weight).

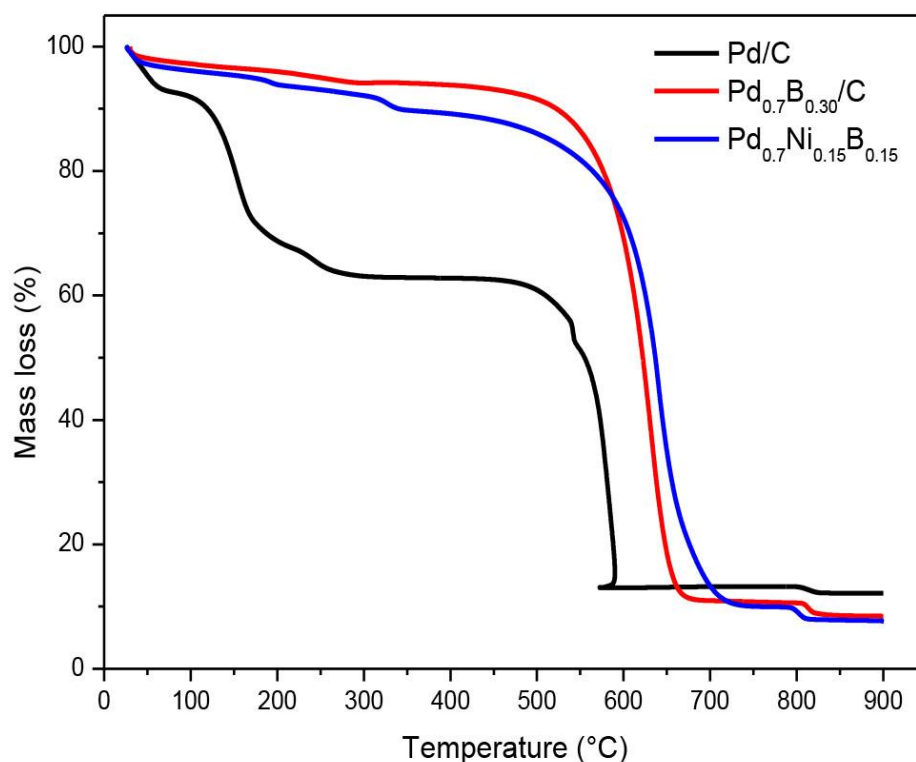


Figure 3 Thermogravimetric measurements for (a) Pd/C, (b) Pd_{0.7}B_{0.3}/C, and (c) Pd_{0.7}Ni_{0.15}B_{0.15}/C catalysts supported on carbon. The analysis was performed at 10°C min⁻¹ from 25 to 900°C under synthetic air flow.

The morphology of the Pd_{0.7}Ni_{0.3}/C, Pd_{0.7}Ni_{0.25}B_{0.05}/C, Pd_{0.7}Ni_{0.2}B_{0.1}/C, and Pd_{0.7}Ni_{0.15}B_{0.15}/C catalysts was investigated by TEM images (Figure 4). Nanoparticles of spherical shape and highly distributed on the carbon support are observed in the micrographs, thus demonstrating the feasibility of the adopted synthesis method. The average particle size and particle size distribution are shown in Table 1. These values were determined from the Gaussian fit and the full-width at half maximum (FWHM) and are shown in Figure 4. All catalysts have an average particle size of around 3.5 nm and narrow size distribution.

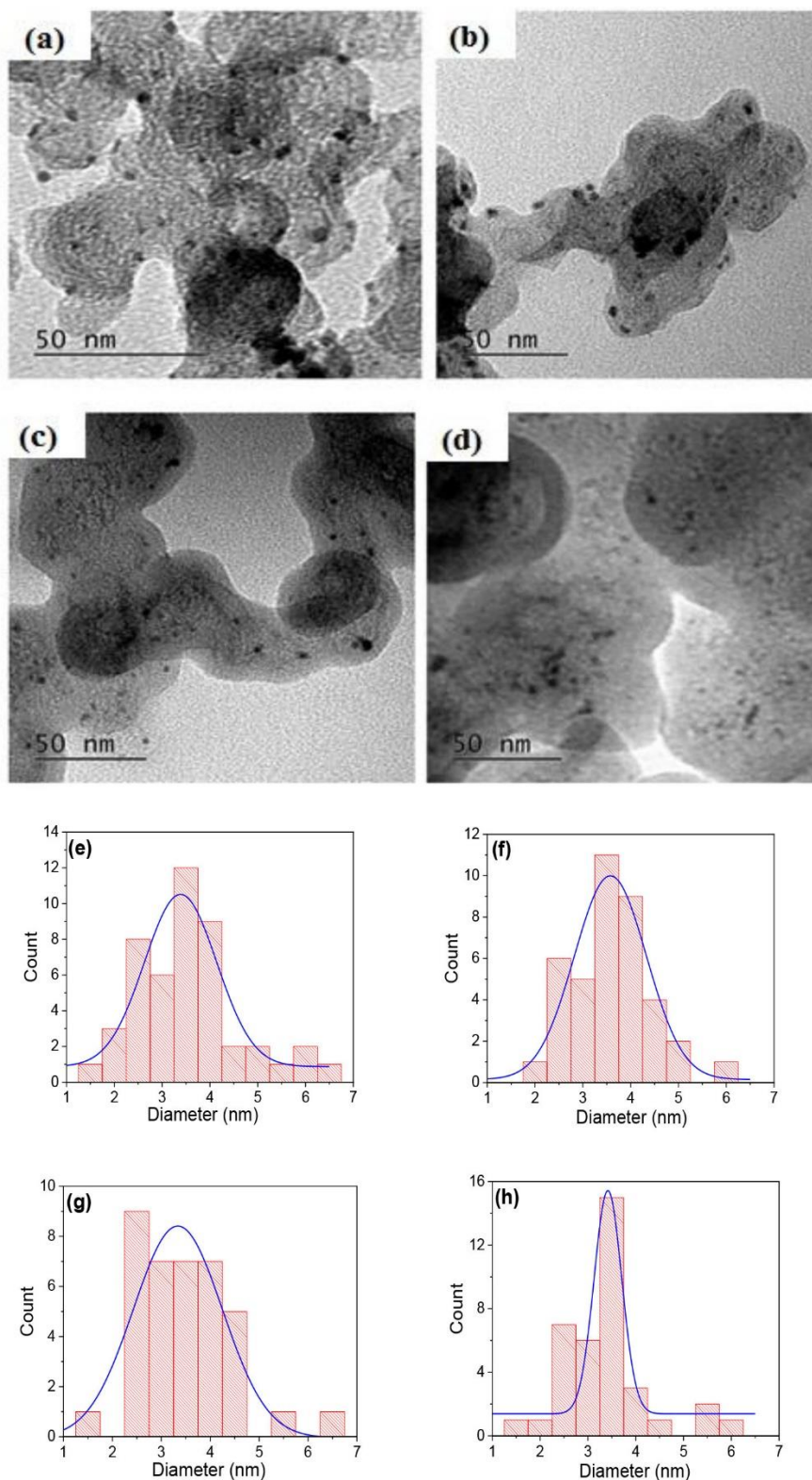


Figure 4 TEM images of the synthesized catalysts supported on carbon (a) $\text{Pd}_{0.7}\text{Ni}_{0.3}/\text{C}$, (b) $\text{Pd}_{0.7}\text{Ni}_{0.25}\text{B}_{0.05}/\text{C}$, (c) $\text{Pd}_{0.7}\text{Ni}_{0.2}\text{B}_{0.1}/\text{C}$, and (d) $\text{Pd}_{0.7}\text{Ni}_{0.15}\text{B}_{0.15}/\text{C}$ and histograms of the particle size with Gaussian fit. (e) $\text{Pd}_{0.7}\text{Ni}_{0.3}/\text{C}$, (f) $\text{Pd}_{0.7}\text{Ni}_{0.25}\text{B}_{0.05}/\text{C}$, (g) $\text{Pd}_{0.7}\text{Ni}_{0.2}\text{B}_{0.1}/\text{C}$, and (h) $\text{Pd}_{0.7}\text{Ni}_{0.15}\text{B}_{0.15}/\text{C}$. Fifty nanoparticles were counted for each catalyst.

3.2 Electrochemical Measurements

Figure 5 (a) shows cyclic voltammograms of the oxidative desorption of CO for the developed catalysts obtained in 1.0 mol L⁻¹ KOH aqueous solutions. The voltammetry of the oxidative desorption of a CO monolayer is essential to get information on the tolerance of catalysts to CO poisoning. CO is an intermediate produced during EOR and is responsible for electrode surface poisoning [32].

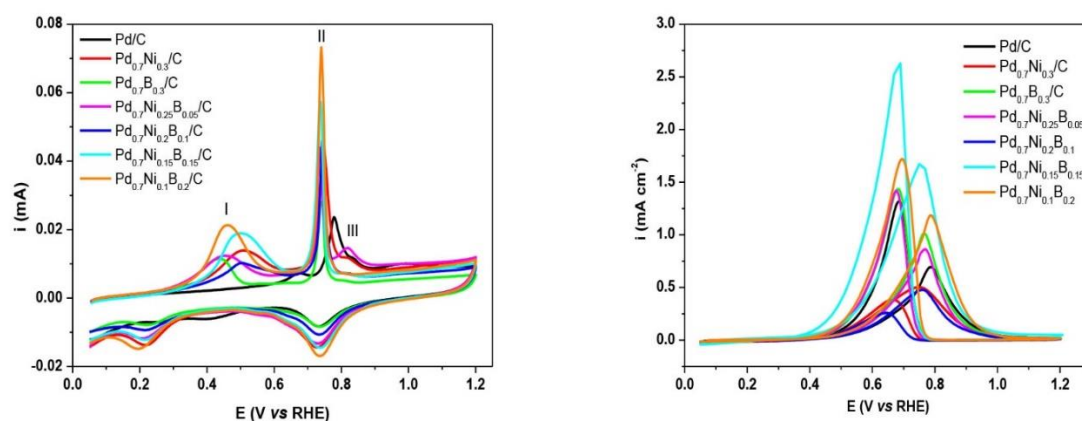


Figure 5 Cyclic voltammograms obtained for the oxidative desorption of CO in a 1.0 mol L⁻¹ KOH solution (a). Cyclic voltammograms (second cycle) for the electrochemical oxidation of 1.0 mol L⁻¹ ethanol dissolved in a 1.0 mol L⁻¹ KOH solution (b) Experiments performed for the Pd/C, Pd_{0.7}Ni_{0.3}/C, Pd_{0.7}B_{0.3}/C, Pd_{0.7}Ni_{0.25}B_{0.05}/C, Pd_{0.7}Ni_{0.2}B_{0.1}/C, Pd_{0.7}Ni_{0.15}B_{0.15}/C, and Pd_{0.7}Ni_{0.1}B_{0.2}/C catalysts. $\nu = 20 \text{ mV s}^{-1}$ and $T = 25^\circ\text{C}$.

Furthermore, Watanabe et al. [22] proved that the oxidative desorption of CO is an efficient technique for estimating the ECA of catalysts. The ECA is obtained from the voltammetric charge surrounding the region in which the oxidation of the adsorbed CO monolayer occurs over the palladium atoms of the catalysts. This region is identified from the intersection between the first cycle, related to CO oxidation, and the second cycle (or background), in which the complete removal of CO from the surface and the electrolytic medium occurred [22]. CO oxidation curves are shown in Figure 5 (a).

The three peaks in Figure 5 (a) strongly depend on the surface composition of the catalyst. The first peak (I) that occurs for all synthesized binary and ternary catalysts, between 0.30 and 0.50 V, refers to the oxidation of CO at Pd sites containing Ni and B species that can promote the bifunctional effect. Since the synthesized catalyst Pd/C is located at 0.68 V, it can be attributed to the strong adsorption of hydrogen on the surface of Pd, inhibiting CO adsorption [14]. The shift of the peak (I) to more negative potentials indicates that the catalysts Pd_{0.7}B_{0.3}/C, Pd_{0.7}Ni_{0.25}B_{0.05}/C, and Pd_{0.7}Ni_{0.1}B_{0.2}/C start before the oxidation reaction and have greater tolerance to CO. The second peak (II), which occurs at approximately 0.75 V for the binary and ternary catalysts with current values higher than the other peaks, is related to the oxidative removal of CO in places of low coordination in the crystallographic plane of the Pd surface. Notably, the higher the B content, the greater the peak II. For Pd/C, this peak is located around 0.78 V. The peak (III) appears for the catalysts Pd_{0.7}Ni_{0.3}/C and Pd_{0.7}Ni_{0.25}B_{0.05}/C. This peak may be related to the agglomeration of the

nanoparticles (Figure 4) and the presence of different crystalline facets on the catalyst surface [38-40].

The values of the CO oxidation onset potentials and ECA for all catalysts are shown in Table 3. The incorporation of B yielded a high electroactive area compared to that of the binary catalyst. The lowest onset potential for CO oxidation on binary and ternary catalysts may be related to the decrease in the adsorption force between Pd and CO, leading to faster oxidation of the CO monolayer, which improves oxidation through a bifunctional mechanism and the electronic effect that occurs with the addition of B [41] and Ni [14]. The ECA values for bimetallic and trimetallic catalysts are higher than those for Pd/C, revealing a greater use of Pd active sites.

Table 3 CO and ethanol oxidation onset potentials, peak current densities, Tafel slopes, and electrochemical surface area (obtained by CO-stripping) for all catalysts synthesized in this study.

Catalyst	CO oxidation onset potential (V)	Ethanol oxidation onset potential (V) ^a	Peak current density (mA cm ⁻²)	ECA (cm ²)	Oxidation onset potential (V vs. RHE) ^b
Pd/C	0.63	0.64	1.17	0.56	0.51
Pd _{0.7} Ni _{0.3} /C	0.39	0.59	0.45	0.84	0.42
Pd _{0.7} B _{0.3} /C	0.35	0.60	1.81	0.78	0.53
Pd _{0.7} Ni _{0.25} B _{0.05} /C	0.34	0.61	0.99	0.71	0.49
Pd _{0.7} Ni _{0.2} B _{0.1} /C	0.40	0.63	0.65	0.82	0.48
Pd _{0.7} Ni _{0.15} B _{0.15} /C	0.37	0.51	1.99	0.70	0.44
Pd _{0.7} Ni _{0.1} B _{0.2} /C	0.35	0.60	1.22	0.80	0.46

^a Values obtained via ethanol oxidation in Figure 5 (b)

^b Values obtained from the Tafel plot in Figure 7 (b)

In order to evaluate the electrochemical activities of the catalysts, an attempt was made to compare them with other binary and ternary Pd-based catalysts reported in the literature. However, the direct comparison of the results is inaccurate because there are differences in the experimental conditions. As shown in Table 4, the Pd_{0.7}Ni_{0.15}B_{0.15}/C catalyst showed high catalytic activity for ethanol oxidation, with the lowest onset potential. Moreover, our catalyst displays the second-highest specific activity, which is only lower than the Pd₁Ni₁/C catalyst that is composed of nanoparticles with a small average diameter (2.4e3.2 nm), narrow size distribution (1-6 nm), and large electrochemical surface areas (i.e., 67.3 m²/g).

Table 4 Comparative data of studies with some Pd-based binary catalysts for ethanol oxidation.

Catalyst	Supporting electrolyte	Concentration of ethanol (mol L ⁻¹)	Ethanol oxidation onset potential (V) ^a	Specific activity (mA cm ⁻²)	Ref
Pd _{0.7} Ni _{0.15} B _{0.15} /C	KOH 1.0 M	1.0	0.51	1.99	This work
Pd ₅₀ Ni ₅₀ /C	KOH 1.0 M	1.0	0.52	1.09	[14]
Pd ₁ Ni ₁ /C	NaOH 1.0 M	1.0	0.85	3.52	[42]
Pd ₇₀ Ni ₁₅ Fe ₁₅ /C	KOH 1.0 M	1.0	-	0.93	[43]

Pd₃Ni₁/C	NaOH 0.1 M	0.5	0.83	1.50	[44]
PdNi/C	NaOH 0.1 M	1.0	0.70	-	[45]

Figure S2 shows the cyclic voltammograms of the developed catalysts taken in the supporting electrolyte at 20 mV s⁻¹. The potential window was chosen in the potential range from 0.05 to 1.20 V to characterize the electrode surface throughout the region of interest.

The first anodic peak (I) that occurs from 0.1 to 0.15 V is related to hydrogen desorption on the surface of the catalysts [40]. The second peak (II) occurs between 0.38, 0.41, 0.45, 0.40, 0.42, and 0.43 V for the Pd/C, Pd_{0.7}Ni_{0.3}/C, Pd_{0.7}Ni_{0.25}B_{0.05}/C, Pd_{0.7}Ni_{0.2}B_{0.1}/C, Pd_{0.7}Ni_{0.15}B_{0.15}/C, and Pd_{0.7}Ni_{0.1}B_{0.2}/C, respectively. This peak comes from the adsorption process of OH⁻ ions on Pd, which partially overlaps the hydrogen desorption peak [41]. The Pd_{0.7}Ni_{0.25}B_{0.05}/C catalyst presented the highest peak current (peak II) among the other ternary catalysts. This behavior is due to the lower amount of B in this composition. This peak is the smallest for the Pd_{0.7}B_{0.3}/C catalyst, which could be due to the overlapping of the Pd–H signal with the B–H signal [46].

The third region (III), at approximately 0.65 and 0.85 V for binary and ternary catalysts, can be attributed to the reduction of Pd(II) oxide during cathodic scanning [47]. The fourth peak (IV) that appears at approximately 0.2 V for all catalysts results in hydrogen absorption in the Pd crystal lattice [37, 47]. The cathodic sweep's fifth peak (V) comes from the hydrogen evolution reaction. As the proportion of palladium is fixed, the peak potential value remains practically the same; however, the catalyst Pd_{0.7}Ni_{0.25}B_{0.05}/C showed higher peak current values than other catalysts containing B.

Figure 5 (b) shows cyclic voltammograms (second cycle) for the electrochemical oxidation of 1.0 mol L⁻¹ ethanol dissolved in 1.0 mol L⁻¹ KOH solution for the Pd/C, Pd_{0.7}Ni_{0.3}/C, Pd_{0.7}B_{0.3}/C, Pd_{0.7}Ni_{0.25}B_{0.05}/C, Pd_{0.7}Ni_{0.2}B_{0.1}/C, Pd_{0.7}Ni_{0.15}B_{0.15}/C, and Pd_{0.7}Ni_{0.1}B_{0.2}/C catalysts. In all of the catalysts, two oxidation peaks are observed. The anodic oxidation peak in the forward scan is attributed to the oxidation of chemically adsorbed species by ethanol adsorption. The oxidation peak in the backward scan is related to the oxidation of carbonaceous species, such as CO and CH₃CO_{ads}, partially oxidized in the forward (anodic) scan [47]. These species can accumulate on the surface of catalysts and affect the catalytic efficiency [40, 47]. Note that the hydrogen desorption/adsorption region (0.10–0.20 V) is suppressed in the presence of ethanol in the solution. The anodic peak in the forward scan occurs between 0.78 and 0.81, while the reverse peak occurs between 0.63 and 0.70 for all catalysts.

The current density value was set at 0.20 mA cm⁻² to establish the onset potentials for ethanol oxidation at all catalysts. The values of the onset oxidation potential and maximum-specific activity in the forward scan for the catalysts are shown in Table 3. The catalyst Pd_{0.7}Ni_{0.15}B_{0.15}/C started ethanol oxidation at lower potentials (0.51 V), demonstrating a high catalytic activity and a higher peak current density than the other catalysts. This proportion's synergy between Pd, Ni, and B species is significant. Furthermore, according to the ICP results (Table 2), adding B decreased the elemental composition of Ni in the catalyst, which changed the catalytic activity of the catalysts. It seems that the boron atoms have entered into the structure of the catalysts substituting Ni. However, the increasing amount of boron does not result in a positive tendency since the most catalytic catalyst was the one with the intermediary content of boron (Pd_{0.70}Ni_{0.15}B_{0.15}/C). Therefore, achieving the ideal ratio between the components of the catalyst and analyzing their influence on the catalytic performance is important to obtain efficient catalysts. According to Sun et al. [48], the interstitial insertion of B in PdCu nanocatalysts promoted positive synergies that increase the

ethanol oxidation reaction, such as (i) the electronic effect, (ii) the bifunctional effect, and (iii) a structural effect in which a smaller B is interstitially inserted into Pd-based nanocrystals.

Furthermore, Almeida et al. [35] demonstrated that the catalytic activity of the binary Pd₇₀/Ni(OH)₂₍₃₀₎/C catalyst exhibited the highest catalytic activity for ethanol oxidation in alkaline media, reaching a current density 4.7 times higher than that of the pure Pd catalyst. In this sense, Ren et al. [35] synthesized ternary PdPtNi nanostructures to reduce 40% of the Pt content and increase the catalytic activity against ethanol oxidation in an alkaline medium. The experimental results indicated that the PdPtNi catalysts showed better electrochemical activity and stability. The specific and mass activities of PdPtNi toward the EOR were 206.93 mA cm⁻² and 1195.81 mA mg⁻¹, which were higher than those of the binary PdNi, PdPt, and commercial Pt catalysts. The mass activity was estimated by normalizing the current intensity to the Pt mass and Pd in the nanocatalysts. This fact occurs because the composition of this ternary alloy has a large specific surface area, abundant reactive sites, and synergistic effects of the different metals.

It is worth mentioning that the improvement in the catalytic activity of the Pd_{0.70}Ni_{0.15}B_{0.15}/C catalyst toward the EOR may be related to several factors. Among them, we can list (i) the greater electroactive area compared to binary catalysts, (ii) the bifunctional mechanism, which facilitates the oxidation of CO to CO₂, and (iii) the electronic effect generated in this alloy due to an interaction between the metals Pd, Ni, and B, which modifies their electronic structures, reducing the activation energy required for EOR [9], the addition of a second metal results in changes in its electronic structure.

Chronoamperometry is a technique used to investigate a catalyst's electrochemical activity and stability. The results are presented in chronoamperometric curves (current density as a function of time). This technique is essential because some catalysts perform satisfactorily in voltammetry studies; however, they undergo deactivation when subjected to longer operating times. Figure 6 shows the chronoamperometric curves obtained of the synthesized catalysts with the polarized electrode at 0.5 V for 3600 s in a solution containing 1.0 mol L⁻¹ KOH + 1.0 mol L⁻¹ ethanol.

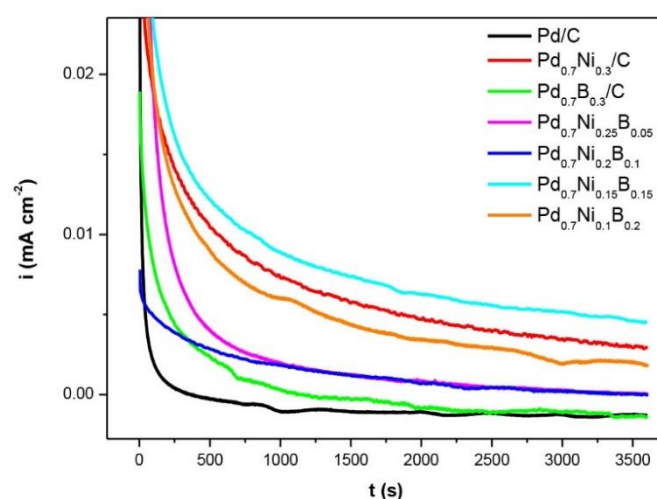


Figure 6 Chronoamperometric curves obtained for the Pd/C, Pd_{0.7}Ni_{0.3}/C, Pd_{0.7}B_{0.3}/C, Pd_{0.7}Ni_{0.25}B_{0.05}/C, Pd_{0.7}Ni_{0.2}B_{0.1}/C, Pd_{0.7}Ni_{0.15}B_{0.15}/C and Pd_{0.7}Ni_{0.1}B_{0.2}/C catalysts in 1.0 mol L⁻¹ in KOH solution + 1.0 mol L⁻¹ ethanol solution for 15 min. The electrodes were polarized at 0.5 V. T = 25°C.

After the potential application, there is a sudden drop in the oxidation current of ethanol, and later, an almost steady state is reached. The current drop is probably due to the electrode surface's blocking by adsorbed organic molecules' fragments [9]. Tan et al. [7] stated that this current drop is due to the initial oxidation of ethanol and the adsorption of CO-like species in Pd catalysts, which poison the catalysts. Eliminating surface impurities resulting from incomplete oxidation of ethanol leads to the stability of current density at the end of the established time [7].

The current density values (Figure 6) obtained for the Pd/C, Pd_{0.7}Ni_{0.3}/C, Pd_{0.7}B_{0.3}/C, Pd_{0.7}Ni_{0.25}B_{0.05}/C, Pd_{0.7}Ni_{0.2}B_{0.1}/C, Pd_{0.7}Ni_{0.15}B_{0.15}/C, and Pd_{0.7}Ni_{0.1}B_{0.2}/C catalysts were -0.00127, 0.00302, -0.00139, 0.00002, -0.00006, 0.00450, and 0.00177 mA cm⁻², respectively, at the end of 3600 s. The catalysts obtained negative current density values because oxidation still does not occur at the chosen potential of 0.5 V. The Pd_{0.7}Ni_{0.15}B_{0.15}/C catalyst had the lowest degree of decay, and the highest current density (0.00450 mA cm⁻²) after 3600 s compared with the other catalysts and showed a current density about four times higher compared to the Pd/C catalyst. Thus, this catalyst is less poisoned by intermediate species and has more free active sites for ethanol oxidation [49].

The catalyst with 15% B showed a lower current density loss and higher catalytic stability. The more stable behavior in chronoamperometry indicates better catalytic performance for ethanol oxidation, leading to oxidation at low potentials (as seen in Figure 5 (b)). This outcome suggests the need for further research on the effects of the 15% B composition on the electrocatalysis of the ethanol oxidation reaction.

We also evaluated the catalytic performance of the catalysts using polarization curves in a quasi-stationary state (Figure 7 (a) and Tafel plots 7 (b)) in a solution containing 1 mol L⁻¹ KOH + 1.0 mol L⁻¹ ethanol. A potential sweep from 0.05 V to 0.8 V was performed at a sweep speed of 1 mV s⁻¹. This procedure reduces the contribution of the capacitive current, and only the faradic current responses are obtained. Polarization curves exhibit peak current density values around 0.27 mA cm⁻², 0.09 mA cm⁻², 0.38 mA cm⁻², 0.45 mA cm⁻², 0.27 mA cm⁻², 0.51 mA cm⁻², and 0.59 mA cm⁻² for Pd/C, Pd_{0.7}Ni_{0.3}/C, Pd_{0.7}B_{0.3}/C, Pd_{0.7}Ni_{0.25}B_{0.05}/C, Pd_{0.7}Ni_{0.2}B_{0.1}/C, Pd_{0.7}Ni_{0.15}B_{0.15}/C, and Pd_{0.7}Ni_{0.1}B_{0.2}/C, respectively. Table 3 presents the electrochemical parameters obtained from the Tafel diagrams (Figure 7 (b)) for Pd_{0.7}Ni_{0.3}/C, Pd_{0.7}Ni_{0.25}B_{0.05}/C, Pd_{0.7}Ni_{0.2}B_{0.1}/C, and Pd_{0.7}Ni_{0.15}B_{0.15}/C catalysts, indicating good linearity with R² values between 0.9993 and 0.9880.

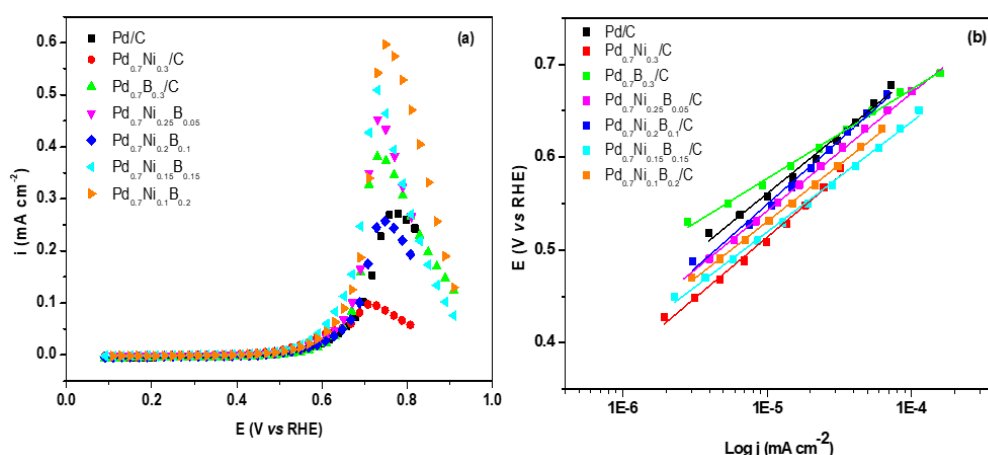


Figure 7 Linear sweep voltammograms at steady-state polarization (a) and Tafel plots (b) for the Pd/C, Pd_{0.7}Ni_{0.3}/C, Pd_{0.7}B_{0.3}/C, Pd_{0.7}Ni_{0.25}B_{0.05}/C, Pd_{0.7}Ni_{0.2}B_{0.1}/C, Pd_{0.7}Ni_{0.15}B_{0.15}/C, and Pd_{0.7}Ni_{0.1}B_{0.2}/C catalysts measured in 1.0 mol L⁻¹ KOH solution + 1.0 mol L⁻¹ ethanol.

Furthermore, the catalysts were investigated by polarization curves (Figure 7 (a)) and Tafel diagrams (Figure 7 (b)) to obtain more accurate results to clarify the CV results of the electrochemical oxidation of ethanol. The onset potential decreased in the order of $\text{Pd}_{0.7}\text{Ni}_{0.3}/\text{C} > \text{Pd}/\text{C} > \text{Pd}_{0.7}\text{Ni}_{0.25}\text{B}_{0.05}/\text{C} > \text{Pd}_{0.7}\text{Ni}_{0.2}\text{B}_{0.1}/\text{C} > \text{Pd}_{0.7}\text{Ni}_{0.1}\text{B}_{0.2}/\text{C} > \text{Pd}_{0.7}\text{Ni}_{0.15}\text{B}_{0.15}/\text{C}$. Thus, the $\text{Pd}_{0.70}\text{Ni}_{0.15}\text{B}_{0.15}/\text{C}$ catalyst obtained a better catalytic activity toward ethanol oxidation compared with the ternary catalysts, presenting the lowest values of onset potential of oxidation, at 0.44 V (Table 2), which is in good agreement with the catalytic behavior of CV for the oxidation of ethanol in alkaline media as seen in Figure 5 (b). These results also confirm the trends observed for the chronoamperometry tests in Figure 6. All electrochemical data (CV, AC, and steady-state polarization curves) indicate that the $\text{Pd}_{0.70}\text{Ni}_{0.15}\text{B}_{0.15}/\text{C}$ catalyst displays the lowest onset potential of ethanol oxidation.

4. Conclusions

This study evaluates the influence of the composition of the $\text{Pd}_{0.7}\text{Ni}_{0.3}/\text{C}$, $\text{Pd}_{0.7}\text{Ni}_{0.25}\text{B}_{0.05}/\text{C}$, $\text{Pd}_{0.7}\text{Ni}_{0.2}\text{B}_{0.1}/\text{C}$, and $\text{Pd}_{0.7}\text{Ni}_{0.15}\text{B}_{0.15}/\text{C}$ catalysts on their catalytic activity toward ethanol oxidation. Using ethylene glycol as the reducing agent, the chemical reduction method effectively produced carbon-supported Pd-Ni-B nanoparticles.

Physical characterizations of the catalysts confirmed the formation of nanoparticles in the carbon support, confirmed the presence of the synthesized metals, and demonstrated that the metal composition is close to the nominal composition. According to electrochemical tests, the $\text{Pd}_{0.70}\text{Ni}_{0.15}\text{B}_{0.15}/\text{C}$ catalyst is the most active toward ethanol oxidation among the ternary catalysts, presenting lower onset potentials for CO and ethanol oxidation, 0.37 V and 0.51 V, respectively. Furthermore, it gave the highest specific activity (1.99 mA cm^{-2}).

The addition of B to the binary PdNi catalyst probably caused electronic and geometric changes in the $\text{Pd}_{0.70}\text{Ni}_{0.15}\text{B}_{0.15}/\text{C}$ catalyst, reducing the onset potential for ethanol oxidation and facilitating the removal of intermediate species from the catalyst surface. Therefore, this study confirms that $\text{Pd}_{0.70}\text{Ni}_{0.15}\text{B}_{0.15}/\text{C}$ nanoparticles are a promising anodic catalyst for DEFC applications.

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Author Contributions

Jamylle Y.C. Ribeiro: Methodology, Validation, Investigation, Writing - Original Draft, Visualization. Ronaldo S. Silva: Validation, Investigation, Writing - Review & Editing. Giancarlo R. Salazar-Banda: Supervision, Conceptualization, Validation, Writing - Review & Editing, Visualization. Katlin I.B. Eguiluz: Supervision, Conceptualization, Validation, Writing - Review & Editing, Visualization.

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Competing Interests

The authors declare that they have competing interests.

Additional Materials

The following additional materials have been uploaded to the page of this paper.

1. Table S1: Crystallite size (t) was obtained using equation 1 and the (111) diffraction peak for all synthesized catalysts
2. Figure S1: EDX spectra of (a) Pd_{0.7}Ni_{0.3}/C, (b) Pd_{0.7}Ni_{0.25}B_{0.05}/C, (c) Pd_{0.7}Ni_{0.2}B_{0.1}/C, and (d) Pd_{0.7}Ni_{0.15}B_{0.15}/C catalysts.
3. Figure S2: Cyclic voltammograms (second cycle) obtained on Pd/C, Pd_{0.7}Ni_{0.30}/C, Pd_{0.7}B_{0.30}/C, Pd_{0.7}Ni_{0.25}B_{0.05}/C, Pd_{0.7}Ni_{0.2}B_{0.1}/C, Pd_{0.7}Ni_{0.15}B_{0.15}/C and Pd_{0.7}Ni_{0.1}B_{0.2}/C catalysts in a 1.0 mol L⁻¹ KOH solution; $v = 20 \text{ mV s}^{-1}$; $T = 25^\circ\text{C}$, ($\rightarrow$) anodic scan, ($\leftarrow$) cathodic scan.

References

1. Wnuk P, Lewera A. On-line analysis of ethanol electrochemical oxidation process in a low-temperature direct ethanol fuel cell. *Electrochim Acta*. 2020; 330: 135256.
2. Antolini E. Catalysts for direct ethanol fuel cells. *J Power Sources*. 2007; 170: 1-12.
3. Akhairi MA, Kamarudin SK. Catalysts in direct ethanol fuel cell (DEFC): An overview. *Int J Hydrog Energy*. 2016; 41: 4214-4228.
4. An L, Zhao TS. Transport phenomena in alkaline direct ethanol fuel cells for sustainable energy production. *J Power Sources*. 2017; 341: 199-211.
5. Beyhan S, Coutanceau C, Léger JM, Napporn TW, Kadirgan F. Promising anode candidates for direct ethanol fuel cell: Carbon supported PtSn-based trimetallic catalysts prepared by Bönemann method. *Int J Hydrog Energy*. 2013; 38: 6830-6841.
6. Wang D, Xin HL, Yu Y, Wang H, Rus E, Muller DA, et al. Pt-decorated PdCo@Pd/C core-shell nanoparticles with enhanced stability and electrocatalytic activity for the oxygen reduction reaction. *J Am Chem Soc*. 2010; 132: 17664-17666.
7. Tan JL, De Jesus AM, Chua SL, Sanetuntikul J, Shanmugam S, Tongol BJ, et al. Preparation and characterization of palladium-nickel on graphene oxide support as anode catalyst for alkaline direct ethanol fuel cell. *Appl Catal A Gen*. 2017; 531: 29-35.
8. Song T, Gao F, Jin L, Zhang Y, Wang C, Li S, et al. From bimetallic PdCu nanowires to ternary PdCu-SnO₂ nanowires: Interface control for efficient ethanol electrooxidation. *J Colloid Interface Sci*. 2020; 560: 802-810.
9. Liu X, Bu Y, Cheng T, Gao W, Jiang Q. Flower-like carbon supported Pd-Ni bimetal nanoparticles catalyst for formic acid electrooxidation. *Electrochim Acta*. 2019; 324: 134816.
10. Caglar A, Cogenli MS, Yurtcan AB, Kivrak H. Effective carbon nanotube supported metal (M = Au, Ag, Co, Mn, Ni, V, Zn) core Pd shell bimetallic anode catalysts for formic acid fuel cells. *Renew Energ*. 2020; 150: 78-90.

11. Roth C, Benker N, Theissmann R, Nichols RJ, Schiffrin DJ. Bifunctional electrocatalysis in Pt–Ru nanoparticle systems. *Langmuir*. 2008; 24: 2191-2199.
12. Siwal SS, Thakur S, Zhang Q, Thakur VK. Electrocatalysts for electrooxidation of direct alcohol fuel cell: Chemistry and applications. *Mater Today Chem*. 2019; 14: 100182.
13. Kottayintavida R, Gopalan NK. Pd modified Ni nanowire as an efficient electro-catalyst for alcohol oxidation reaction. *Int J Hydrog Energy*. 2020; 45: 8396-8404.
14. Almeida CV, Tremiliosi-Filho G, Eguiluz KI, Salazar-Banda GR. Improved ethanol electro-oxidation at Ni@Pd/C and Ni@PdRh/C core–Shell catalysts. *J Catal*. 2020; 391: 175-189.
15. Jeon MK, Zhang Y, McGinn PJ. A comparative study of PtCo, PtCr, and PtCoCr catalysts for oxygen electro-reduction reaction. *Electrochim Acta*. 2010; 55: 5318-5325.
16. Yin X, Wang Q, Duan D, Liu S, Wang Y. Amorphous NiB alloy decorated by Cu as the anode catalyst for a direct borohydride fuel cell. *Int J Hydrog Energy*. 2019; 44: 10971-10981.
17. Wang Y, Lv H, Sun L, Guo X, Xu D, Liu B. Ultrathin and wavy PdB alloy nanowires with controlled surface defects for enhanced ethanol oxidation electrocatalysis. *ACS Appl Mater Interfaces*. 2021; 13: 17599-17607.
18. Lu L, Gu Y, Guo W, Lu F, Li Y. Extrasmall ligand-free Pt nanoparticles as dual-function catalysts for methanol-assisted water splitting systems. *ACS Appl Nano Mater*. 2022; 5: 4222-4229.
19. Lu L, Zheng H, Li Y, Zhou Y, Fang B. Ligand-free synthesis of noble metal nanocatalysts for electrocatalysis. *Chem Eng J*. 2022; 451: 138668.
20. Burton PD, Boyle TJ, Datye AK. Facile, surfactant-free synthesis of Pd nanoparticles for heterogeneous catalysts. *J Catal*. 2011; 280: 145-149.
21. Kim P, Joo JB, Kim W, Kim J, Song IK, Yi J. NaBH₄-assisted ethylene glycol reduction for preparation of carbon-supported Pt catalyst for methanol electro-oxidation. *J Power Sources*. 2006; 160: 987-990.
22. Watanabe, M, Motoo S. Chemisorbed CO on a polycrystalline platinum electrode the effect of conditioning of the surface and of partial pressure of CO. *J Electroanal Chem Interfacial Electrochem*. 1986; 206: 197-208.
23. Schindelin J, Arganda-Carreras I, Frise E, Kaynig V, Longair M, Pietzsch T, et al. Fiji: An open-source platform for biological-image analysis. *Nat Methods*. 2012; 9: 676-682.
24. Fang LL, Tao Q, Li MF, Liao LW, Chen D, Chen YX. Determination of the real surface area of palladium electrode. *Chinese J Chem Phys*. 2010; 23: 543-548.
25. Wang YF, Zhu C, Yang YY, Zhao ZG. Surface-clean low-doped PdB/C as superior electrocatalysts toward ethanol oxidation in alkaline media. *J Energy Chem*. 2018; 27: 389-394.
26. Harraz FA, El-Hout SE, Killa HM, Ibrahim IA. Palladium nanoparticles stabilized by polyethylene glycol: Efficient, recyclable catalyst for hydrogenation of styrene and nitrobenzene. *J Catal*. 2012; 286: 184-192.
27. Chen T, Ellis I, Hooper TJ, Liberti E, Ye L, Lo BT, et al. Interstitial boron atoms in the palladium lattice of an industrial type of nanocatalyst: Properties and structural modifications. *J Am Chem Soc*. 2019; 141: 19616-19624.
28. Cermenek B, Ranninger J, Feketeföldi B, Letofsky-Papst I, Kienzl N, Bitschnau B, et al. Novel highly active carbon supported ternary PdNiBi nanoparticles as anode catalyst for the alkaline direct ethanol fuel cell. *Nano Res*. 2019; 12: 683-693.

29. Wang XB, Yang SQ, Xu C, Ma HD, Zhang ZH, Du ZY, et al. Effect of boron doping on the performance of Ni/Biochar catalysts for steam reforming of toluene as a tar model compound. *J Anal Appl Pyrolysis*. 2021; 155: 105033.
30. Shakir MD, Sengupta S, Sinhamahapatra A, Liu S, Vuthaluru H. B-Ni/MgAl₂O₄ catalyzed dry reforming of methane: The role of boron to resist the formation of graphitic carbon. *Fuel*. 2022; 320: 123950.
31. Xu J, Chen L, Tan KF, Borgna A, Saeys M. Effect of boron on the stability of Ni catalysts during steam methane reforming. *J Catal*. 2009; 261: 158-165.
32. Zhang Z, Penev E, Yakobson B. Two-dimensional boron: Structures, properties and applications. *Chem Soc Rev*. 2017; 46: 6746-6763.
33. Cermenek B, Genorio B, Winter T, Wolf S, Connell JG, Roschger M, et al. Alkaline ethanol oxidation reaction on carbon supported ternary PdNiBi nanocatalyst using modified instant reduction synthesis method. *Electrocatalysis*. 2020; 11: 203-214.
34. Shi D, Ouyang Z, Zhao Y, Xiong J, Shi X. Catalytic reduction of hexavalent chromium using iron/palladium bimetallic nanoparticle-assembled filter paper. *Nanomaterials*. 2019; 9: 1183.
35. Jadhav SN, Kumbhar AS, Mali SS, Hong CK, Salunkhe RS. A Merrifield resin supported Pd-NHC complex with a spacer (Pd-NHC@SP-PS) for the Sonogashira coupling reaction under copper- and solvent-free conditions. *New J Chem*. 2015; 39: 2333-2341.
36. Yang Y, Zhuang L, Lin R, Li M, Xu X, Rufford TE, et al. A facile method to synthesize boron-doped Ni/Fe alloy nano-chains as electrocatalyst for water oxidation. *J Power Sources*. 2017; 349: 68-74.
37. Ortiz-Ortega E, Carrera-Cerritos R, Arjona N, Guerra-Balcázar M, Cuevas-Muñiz FM, Arriaga LG, et al. Pd nanostructures with high tolerance to CO poisoning in the formic acid electrooxidation reaction. *Procedia Chem*. 2014; 12: 9-18.
38. Lee MJ, Kang JS, Kang YS, Chung DY, Shin H, Ahn CY, et al. Understanding the bifunctional effect for removal of CO poisoning: Blend of a platinum nanocatalyst and hydrous ruthenium oxide as a model system. *Acs Catal*. 2016; 6: 2398-2407.
39. Yang H, Wang H, Li H, Ji S, Davids MW, Wang R. Effect of stabilizers on the synthesis of palladium-Nickel nanoparticles supported on carbon for ethanol oxidation in alkaline medium. *J Power Sources*. 2014; 260: 12-18.
40. Urchaga P, Baranton S, Coutanceau C, Jerkiewicz G. Electro-oxidation of CO_{chem} on Pt nanosurfaces: Solution of the peak multiplicity puzzle. *Langmuir*. 2012; 28: 3658-3663.
41. Almeida CV, Eguiluz KI, Salazar-Banda GR. Superior ethanol electrooxidation activity of Pd supported on Ni(OH)₂/C. The effect of Ni(OH)₂ nanosheets content. *J Electroanal Chem*. 2020; 878: 114683.
42. Zhang Z, Xin L, Sun K, Li W. Pd-Ni electrocatalysts for efficient ethanol oxidation reaction in alkaline electrolyte. *Int J Hydrog Energy*. 2011; 36: 12686-12697.
43. Clímaco FR, Almeida CV, Aristides SS, Eguiluz KI, Salazar-Banda GR. Influence of the composition and morphology of PdNiFe/C nanocatalysts toward ethanol oxidation. *Chem Phys Lett*. 2022; 801: 139745.
44. Obradović MD, Stančić ZM, Lačnjevac UČ, Radmilović VV, Gavrilović-Wohlmuther A, Radmilović VR, et al. Electrochemical oxidation of ethanol on palladium-nickel nanocatalyst in alkaline media. *Appl Catal B*. 2016; 189: 110-118.

45. Martin-Yerga D, Henriksson G, Cornell A. Insights on the ethanol oxidation reaction at electrodeposited PdNi catalysts under conditions of increased mass transport. *Int J Hydrog Energy*. 2021; 46: 1615-1626.
46. Tsuzuki K, Natsir M, Inoue N, Sagara A, Noda N, Motojima O, et al. Behavior of hydrogen atoms in boron films during H₂ and He glow discharge and thermal desorption. *Vacuum*. 1996; 47: 931-934.
47. Bianchini C, Shen PK. Palladium-based electrocatalysts for alcohol oxidation in half cells and in direct alcohol fuel cells. *Chem Rev*. 2009; 109: 4183-4206.
48. Sun L, Lv H, Wang Y, Xu D, Liu B. Unveiling synergistic effects of interstitial boron in palladium-based nanocatalysts for ethanol oxidation electrocatalysis. *J Phys Chem Lett*. 2020; 11: 6632-6639.
49. Singh S, Datta J. Influence of Nafion template on the kinetics of anodic Pt based pluri-metallic catalyst for ethanol electro-oxidation. *J Electroanal Chem*. 2021; 882: 114974.