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# Catalytic Activity of Pt-Based Nanoparticles with Ni and Co for Ethanol and Acetaldehyde Electrooxidation in Alkaline Medium

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ABSTRACT

In this work, Pt-based nanoparticles with Ni and Co on carbon support were prepared and used as electrocatalysts in the oxidation reactions of ethanol and acetaldehyde in alkaline solution. The nanoparticles were prepared by chemical reduction with sodium borohydride and characterized by means of energy dispersive X-ray spectroscopy, X-ray powder diffraction, and transmission electron microscopy. The catalytic activity was determined from cyclic voltammetry and chronoamperometry measurements. Our results indicate that in our Pt-based catalysts, the presence of Ni promotes the initial steps of the oxidation process, while Co promotes later steps involving acetyl species. The catalytic behavior of the materials can be understood when considering factors as chemical composition and alloy degree in the prepared nanoalloys.



## 1. Introduction

Direct alcohol fuel cells (DAFCs) have potential applications as power generators in portable devices. These cells use methanol or ethanol as fuel due to their relatively high energetic densities of 6.09 and 8.05 kWh $kg^{-1}$, respectively [1], which are comparable to the energetic density of gasoline (10.5 kWh $kg^{-1}$) [1]. When compared to methanol, ethanol exhibits some advantages like a higher energetic density, lower toxicity, and the possibility of being produced from renewable sources like the sugar cane [2]. However, it is well known that the ethanol oxidation reaction (EOR) on Pt catalysts exhibits a selectivity towards $CO_2$ between 0.5% and 7.5% in acid media [3], which results in direct ethanol fuel cells (DEFCs) with insufficient power to be used in some applications. This is a consequence of the slow rate for the EOR due to the adsorption of intermediates as acetyl species [4,5] and carbon monoxide [6–8] and the fact that the C—C bond has to be broken.

Ethanol can be oxidized in acid and alkaline media, but the main advantage of using high pH is the readily available OH species required for subsequent oxidation steps with the concomitant enhancement in the global EOR rate [9]. This implies then, that these species are not required to be provided by the catalyst from water dissociation, as is the case in acid media.

Several studies have shown an improvement in the catalytic activity for the EOR on Pt-based materials when adding other metals as Ru [10,11], Sn [10–15], Rh [15–18], Fe [11], and Ni [11] due to modified geometrical and electronic properties of Pt. Among them, Pt-Ru and Pt-Sn are considered as the most efficient catalysts for the EOR [10,12,13,19], exhibiting higher currents densities mainly due to the fast rate towards acetaldehyde and acetic acid, as shown by *in situ* Fourier transform infrared spectroscopy and on-line differential electrochemical mass spectroscopy (DEMS) studies [10,20]. Other studies using *in situ* infrared reflection-absorption spectroscopy [21,22], have found that ternary materials as the Pt-Rh-$SnO_2$/C catalysts can break the C—C bond of the ethanol molecule efficiently at room temperature and acid media, being the highest activity obtained for the composition Pt:Rh:Sn = 3:1:4. Ternary materials of Pt-Sn-M (M = Fe, Ni, Pd, and Ru) were obtained by Almeida et al. [11] and evaluated by fluorescence to optimize the catalytic activity as a function of the catalyst composition. They found that the catalysts containing Fe exhibit

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the highest activity, followed by those containing Ni, which is consequent with the fact that alloys of Pt with highly oxophilic transition metals lead to the activation of the oxygenated species necessary in the EOR [1]. It has been reported that the activity of the Pt-Rh-Ni/C material for the EOR is higher than that of the Pt-Rh-Sn/C material in both, acid and alkaline media [23]. As expected for oxophilic transition metals, the improvement in the activity of Ni-containing materials is due to the fact that the surface Ni atoms provide oxygenated species for the ethanol oxidation [1]. Similar conclusions have been found for Pt-Co/C materials, where the catalytic activity increased with Co content between 0 and 75%, with Co providing anchor sites for the oxygenated species necessary for the oxidation of the EOR intermediates [24]. In particular, the use of materials containing Ni and Co is seen as an alternative to obtain cheaper catalysts.

In order to obtain a higher selectivity towards more oxidized products, it is desirable that the EOR electrocatalysts also favor the acetaldehyde oxidation reaction (AOR). In this sense, results obtained using DEMS [25] show that Pt-Ru/C and $Pt_3Sn$/C materials are the most efficient for the total acetaldehyde oxidation. However, their performance only reaches 10%, which is not much better than that obtained using Pt/C at room temperature, which indicates that, for all catalysts, the C—C bond breaking is insignificant at the evaluated conditions. On the other hand, for the oxidation of acetaldehyde in alkaline medium, it is known that the acetaldehyde can either react with adsorbed OH to form acetate by an Eley-Rideal mechanism or undergo an Aldol condensation, leading to a deactivation to any further reaction [26]. Therefore, it is pertinent to evaluate other metallic mixtures that are more active for the acetaldehyde electrooxidation. Looking for an improvement in the selectivity and the oxidation rate of the EOR and the AOR, in this work, the electrooxidation of ethanol and acetaldehyde in alkaline medium has been studied on bi- and trimetallic Pt-based catalysts containing Ni and Co with different metallic relations supported on carbon.

## 2. Experimental

### 2.1. Synthesis of the catalysts

Monometallic, bimetallic, and trimetallic catalysts, with the nominal compositions Pt/C, Ni/C, Co/C, $Ni_{50}Co_{50}$/C, $Pt_{50}Ni_{50}$/C, $Pt_{50}Co_{50}$/C, $Pt_{50}Ni_{25}Co_{25}$/C, $Pt_{25}Ni_{50}Co_{25}$/C, and $Pt_{25}Ni_{25}Co_{50}$/C, were synthesized by chemical reduction with sodium borohydride. The compounds $H_2PtCl_6.6H_2O$, $Ni(NO_3)_2.6H_2O$, and $Co(NO_3)_2.6H_2O$ were used to prepare precursor solutions, which in turn, were used to obtain the catalyst powder with 20% of metallic content. Aliquotes from the precursor solutions were diluted with water to a 25.0 mL total volume, then Vulcan carbon XC-72R and 25.0 mL of water were added. Finally, pH was adjusted to 9.0. The mixture was sonicated for 1 hour at 20 °C. Then, 25.0 mL of $NaBH_4$ 1.0 mg $mL^{-1}$ were added. The solution was filtered and the resulting solid was dried during 12 hours in a vacuum desiccator and then, 30 minutes at 90 °C.

### 2.2. Physical characterization of the catalysts

The crystalline structure of the catalysts was determined by X-ray diffraction (XRD) using a D2 Phaser-Bruker diffractometer with Cu Kα radiation (λ = 0.15406 nm) generated at 40 kV and 30 mA. The values for the lattice parameter and crystallite size, for each material, were obtained by means of the General Structure Analysis System (GSAS) program version 2004 [27–29] using the Rietveld method [29] being the X-ray pattern calculated a $RF^2$ unless a 20%. Transmission electron microscopy (TEM) micrographs were obtained in a Tecnai F20 Super Twin TMP microscope and used to determinate the mean diameter distribution and its average value using Image-Pro software considering unless 300 particles by sample. Chemical composition was obtained by using energy dispersive X-rays (EDX) in a JEOL JSM 5910 LV microscope.

### 2.3. Electrochemical measurements

Working electrodes were prepared as follow: 2.0 mg carbon supported catalyst was sonically mixed with 985 μL isopropanol and 15 μL Nafion solution (5.0 wt. %) to form a well-dispersed catalyst ink [30]. Then, 26.9 μL of the catalyst ink was uniformly spread on the surface of a glassy carbon disk (Ø7 mm). The auxiliary electrode was a glassy carbon bar. The reference electrode was a reversible hydrogen electrode (RHE) prepared in alkaline media. All reported potential values in this work are referred to this reference electrode.

Prepared materials were activated by successive cyclic voltammetry (CV) scans carried out in a 0.10 M NaOH solution between 0.05 and 0.90 V at a scan rate of 100 mV $s^{-1}$ until reproducible CV profiles were obtained. After activation, the surface was electrochemically characterized using two additional voltammetric cycles carried out at a scan rate of 10 mV $s^{-1}$. CV and chronoamperometry (CA) were used to evaluate the catalysts catalytic activity for both, acetaldehyde and ethanol electrooxidation using solutions of 0.10 M NaOH + 0.01 M acetaldehyde and 0.10 M NaOH + 1.0 M ethanol, respectively. CVs were carried out between 0.05 and 0.90 V at a scan rate of 10 mV $s^{-1}$. CAs were measured at a specified potential (between 0.20 and 0.70 V) sustained per 1800 s after applying a potential of 0.05 V during 300 s. All electrochemical

**Table 1**
Composition, mean particle size, crystallite size, lattice parameter, and alloy degree by EDX, XRD, and TEM.

| Catalyst | EDX | | | XRD | | | TEM |
|---|---|---|---|---|---|---|---|
| | Metal/C (wt. %) | Oxygen loading (wt. %) | Atomic ratio Pt:Ni:Co | Lattice parameter (nm) | Alloy degree (%) | Mean crystallite size (nm) | Mean particle size (nm) |
| Pt/C | 20.9 | 2.3 | 100:0:0 | 0.3926 | – | 4.4 | 4.4 |
| Ni/C | 18.7 | 15.4 | 0:100:0 | – | – | – | – |
| Co/C | 18.4 | 14.9 | 0:0:100 | – | – | – | – |
| $Pt_{50}Ni_{50}$/C | 18.8 | 3.5 | 60:40:0 | 0.3890 | 16.7 | 3.5 | 3.5 |
| $Pt_{50}Co_{50}$/C | 19.7 | 7.0 | 50:50:0 | 0.3898 | 8.7 | 3.9 | 2.0 |
| $Ni_{50}Co_{50}$/C | 22.2 | 21.8 | 0:46:54 | – | – | – | – |
| $Pt_{50}Ni_{25}Co_{25}$/C | 18.0 | 6.0 | 51:24:25 | 0.3897 | 9.0 | 4.1 | 2.9 |
| $Pt_{25}Ni_{50}Co_{25}$/C | 20.4 | 10.5 | 25:48:27 | 0.3900 | 2.5 | 4.2 | 2.6 |
| $Pt_{25}Ni_{25}Co_{50}$/C | 20.7 | 11.0 | 24:25:51 | 0.3907 | 1.7 | 3.5 | 3.8 |