



Ethanol electro-oxidation on carbon-supported Pt₃Sn/C, Pt₃Cu/C and PtSnCu/C catalysts: CV and in situ FTIR study

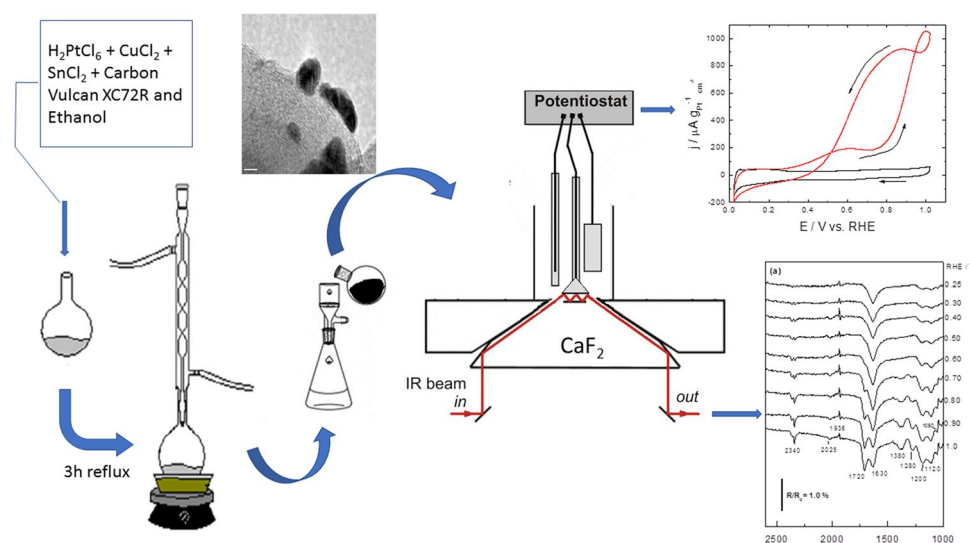
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Abstract

Carbon-supported PtSnCu/C, Pt₃Sn/C, Pt₃Cu/C and Pt/C electrocatalysts were synthesized by chemical reduction of metal precursors in ethanol reflux. These materials were characterized by energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), transmission electron microscopy (TEM) and applied to the ethanol electro-oxidation in acidic medium. The reaction kinetics was studied by cyclic voltammetry and the mechanism was explored by in situ Fourier transform infrared spectroscopy (FTIR). The investigated materials presented chemical composition close to the nominal ones. XRD results indicated the formation of solid solution of Pt and Cu and/or Sn in the bi and tri-metallic materials. The particle size distribution was narrow with mean particle size of around 3 nm. A homogeneous distribution of the nanoparticles over the carbon support was evidenced. The investigated catalysts were active towards the ethanol oxidation reaction in acidic medium and led to the formation of CO₂ and carbonyl compounds, as evidenced by FTIR. PtSnCu/C and Pt₃Cu/C started to produce CO₂ at 0.70 V vs. RHE, while this product was detected only at 0.75 V and 0.80 V vs. RHE on Pt and Pt₃Sn/C, respectively, suggesting that Cu improves the dissociative adsorption of ethanol.

Graphic abstract



Keywords Ethanol oxidation reaction · Direct ethanol fuel cell · FTIR · PtSn · PtSnCu

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1 Introduction

In recent years, there has been a steadily growing concern with the effect of pollutants, as nitrogen and sulfur oxides, CO, CO₂ and CH₄, on the environment and human health [1]. High levels of pollutants are produced from fossil fuels processing and combustion for energy generation. Therefore, the application of clean energy sources is an emergency need. In this scenario, ethanol is an attractive alternative to fossil fuels. Ethanol is a renewable fuel mainly produced from glucose fermentation. Its chemical energy can be directly converted into electrical energy in Direct Ethanol Fuel Cells (DEFC). These electrochemical devices typically comprise platinum (Pt)-based materials as cathode and anode-like catalysts in gas diffusion electrodes [2]. It operates at temperatures of around 80 °C, which are considered low [3]. Ethanol presents advantages as a fuel in low-temperature fuel cells because of its lower toxicity in comparison with other liquid fuel as methanol [4]. Although DEFC is regarded as a promising alternative to produce clean and renewable energy, the sluggish kinetics of ethanol oxidation reaction (EOR) on the anode, the low selectivity to CO₂, and the complete oxidation product are still challenging [5, 6].

Carbon-supported Pt nanoparticles are commonly used as anode catalyst in low-temperature fuel cells [7–10]. However, pure Pt is known to be rapidly poisoned on its surface by strongly adsorbed species, like CO, coming from the dissociative adsorption of ethanol [9, 10, 11]. Furthermore, Pt has limited ability for breaking down the C–C bond [9–13], leading to the formation of acetaldehyde and acetic acid (2-carbon atom chain products of ethanol oxidation) in addition to CO₂.

The mechanism of the EOR on Pt-based materials has been previously investigated by differential electrochemical mass spectroscopy (DEMS), Fourier Transform Infrared (FTIR) Spectroscopy and Electrochemical Thermal Desorption Mass Spectroscopy (ECTDMS) [14–19]. Based on these studies, some authors proposed the EOR to occur by the two following pathways [12, 18–20]: (i) with C–C bond breaking down and formation of CO₂; (ii) without C–C bond breaking down and with formation of acetic acid as the main product.

Modification of Pt catalysts by the addition of other metals improves its tolerance to poisoning at low potential in EOR [21, 22]. In particular, the catalytic performance of PtSn/C electrocatalysts towards the EOR was significantly better than that of Pt/C materials [23–27]. The performance of Pt catalysts was also improved by the addition of Cu and this behavior was associated with the formation of copper oxides, which may influence the bifunctional mechanism of EOR on PtCu/C materials [28]

and formation of stable PtCu/C alloys by the insertion of Cu in the crystalline lattice structure of Pt [29]. On the other hand, bimetallic Pt-based materials were reported to favor the acetic acid formation as a major product [30].

A possible strategy to overcome the difficulties concerning the EOR kinetics and selectivity is to modify Pt materials with more than one metal, producing PtM₁M₂ tri-metallic materials, where M₁ and M₂ are preferentially non-noble metals [31]. Beyhan et al. [12] added Ni, Co, Rh or Pd to PtSn/C and observed the formation of acetate, acetyl, carbonate, CO and CO₂, with substantial production of CO₂ when PtSn/C was modified by the addition of Pd or Ni [12]. Magalhães et al. [32] have shown that carbon-supported PtSnCu/C electrocatalysts are active and stable for EOR in sulfuric acid solution, making the reaction to start about 0.2 V earlier than on Pt₃Sn/C and Pt₃Cu/C. These results are in accord with previous studies [33]. Although the EOR kinetics is improved by the addition of Cu to Pt₃Sn/C catalysts, information about the corresponding products is still missing in the literature.

In the present work, carbon-supported PtSnCu/C, Pt₃Sn/C, Pt₃Cu/C and Pt/C electrocatalysts were prepared and characterized with respect to their physical and chemical properties. These materials were applied to EOR. Intermediates and reaction products were investigated by *in situ* FTIR spectroscopy.

2 Experimental

2.1 Electrocatalysts preparation

Pt/C, Pt₃Sn/C, Pt₃Cu/C and PtSnCu/C electrocatalysts, with 20 wt.% of metal loading on carbon support, were prepared in a single step by an alcohol-reduction process [34–36]. For the PtSnCu/C catalyst, an appropriate mass of carbon powder (Vulcan XC-72, Cabot, 240 m² g^{−1}) was suspended in a solution containing H₂PtCl₆ 6H₂O (Aldrich), SnCl₂ 2H₂O (Vetec), CuCl₂ (Vetec) and ethanol (Aldrich). This suspension was heated up to the boiling point and maintained in reflux for 3 h. Then the suspension was left to cool down to room temperature and the solid was filtered and dried in an oven at 60 °C for 1 h. The same procedure was applied to Pt/C, Pt₃Sn/C and Pt₃Cu/C, employing a solution containing the appropriate metallic precursors.

2.2 Energy dispersive X-ray spectroscopy (EDX)

The atomic ratio of the Pt₃Sn/C, Pt₃Cu/C and PtSnCu/C catalysts was determined using energy dispersive X-ray spectroscopy (EDX), an analytical technique, coupled with a scanning electron microscope, JSM-6610, JEOL, scientific. For these analyses, the sample was agglutinated with

Polytetrafluoroethylene (PTFE) and fixed at sample holder with silver stick; the sample holder was then introduced into microscope.

3 X-ray diffraction (XRD)

All materials were morphologically characterized by XRD in a Shimadzu XRD-6000 diffractometer. The scan rate was 2° min^{-1} between 20 and 120 degree in 2θ . For these analyses, a sample of catalyst was deposited on a sample holder and placed into the diffractometer.

The crystallite average diameters (d) were determined by using the Scherrer equation [37]:

$$d = \frac{k\lambda}{B\cos\theta},$$

where k is a particle shape-dependent constant (assuming spherical particles, $k=0.9$), λ is the wavelength of the X-ray radiation (for Cu $K\alpha$, $\lambda=1,540 \text{ \AA}$), θ is the angle of the diffraction peak and β is the width in radians of the diffraction peak at half-height.

The lattice parameters were calculated by Bragg's law [38]:

$$a = \frac{\lambda\sqrt{2}}{\sin\theta},$$

where a is the lattice parameter, λ is the wavelength of the X-ray radiation and θ is the angle of the diffraction peak.

3.1 Transmission electron microscopy (TEM)

These analyses were performed using a TEM microscope JEOL, JEM 2100, URP, operating at 200 kV and having a resolution of 0.2 nm . Samples for TEM were prepared by drop-casting an isopropilic alcohol suspension of the as-prepared catalysts over a carbon-coated copper grid (400 mesh and 3 mm diameter), followed by drying under ambient conditions. About 300 particles were measured to build the size distribution histograms. The mean particle diameter, d , was calculated using

$$d_i = \sum_i \frac{n_i d_i}{n}, \quad (2)$$

where n_i is the frequency of occurrence of a particle with size d_i .

3.2 Electrochemical measurements

Electrochemical experiments were carried out with an Omnimetra PG-39 potentiostat/galvanostat. They were conducted at room temperature ($\sim 27^\circ \text{C}$) in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$

(Aldrich) and at distinct ethanol concentrations. A conventional single compartment electrochemical cell with three electrodes was employed. The counter electrode was a Pt gauze. In this paper, all potentials are shown with respect to the reversible hydrogen electrode (RHE), used as the reference electrode. The working electrodes were Pt/C, $\text{Pt}_3\text{Sn/C}$, $\text{Pt}_3\text{Cu/C}$ and PtSnCu/C on glassy carbon. For the preparation of the working electrodes, a catalyst sample was suspended in aqueous isopropyl alcohol solution. An aliquot of this suspension was deposited on glassy carbon imbibed in a Teflon® rod. Before the deposition, the glassy carbon surface was polished to a mirror-like finish with $1 \mu\text{m}$ diamond paste. The electrodes consisted of $100 \mu\text{g}$ of Pt per cm^2 . The catalysts were characterized by cyclic voltammetry. The onset of EOR was defined as the potential in which the oxidation current was 5% higher than that corresponding to the baseline (in absence of ethanol).

3.3 Spectro-electrochemical measurements

The EOR product distribution was evaluated by in situ FTIR. A Nicolet Nexus 670 FTIR spectrometer equipped with a MCT detector cooled with liquid nitrogen was used for the analytical measurements. An in-house electrochemical cell with a CaF_2 window was employed, as described in a previous work [39]. Spectra were taken in the wavenumber region between 2500 cm^{-1} and 1000 cm^{-1} , in the potential range from 0.1 V to 1.0 V vs. RHE, in 0.05 V steps. Spectra were computed from the average of 128 interferograms. The spectral resolution was set to 8 cm^{-1} . Reflectance spectra were calculated as the ratio (R/R_0), where R represents a spectrum at the sample potential and R_0 is the reference spectrum collected at 0.05 V . Positive and negative going bands represent the consumption and the production of substances at the sample potential, respectively.

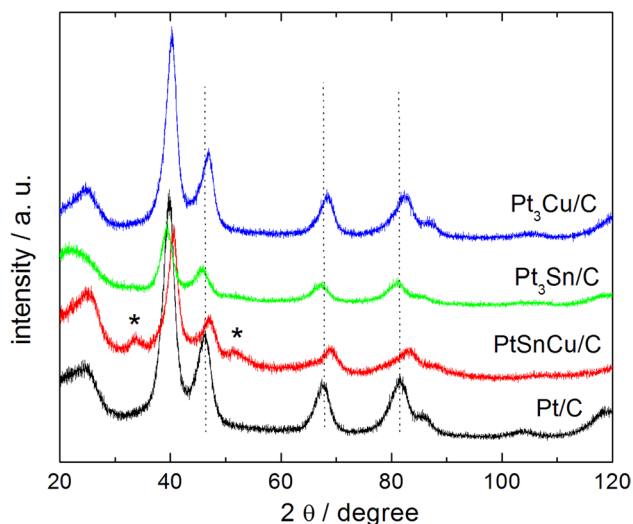
4 Results and discussion

The catalysts were characterized by EDX analyses and the chemical composition evidenced experimentally is shown in Table 1. The atomic ratios of the investigated materials are close to their nominal chemical compositions, attesting the accuracy of the employed method for the catalyst preparation.

Figure 1 shows XRD patterns of the carbon-supported $\text{Pt}_3\text{Cu/C}$, $\text{Pt}_3\text{Sn/C}$, PtSnCu/C and Pt/C catalysts. Diffraction peaks at around $2\theta = 25^\circ, 40^\circ, 47^\circ, 65^\circ, 82^\circ$, and 87° are observed. The peak at $2\theta = 25^\circ$ is related to the carbon support and the peaks at ca. $2\theta = 40^\circ, 47^\circ, 65^\circ, 82^\circ$, and 87° are, respectively, associated to the (111), (200), (220), (311) and (222) planes of Pt [40], which present face-centered cubic (fcc) structure. For the $\text{Pt}_3\text{Cu/C}$, $\text{Pt}_3\text{Sn/C}$ and PtSnCu/C

Table 1 Nominal and experimental chemical composition, crystallite average diameter, lattice parameter and average particle size of the investigated carbon-supported Pt-based materials

Material	Nominal chemical composition Atomic ratio/%	Experimental chemical composition Atomic ratio/%	Pt crystallite average diameter/nm	Lattice parameter/nm	Average particle size/nm
PtSnCu/C	33.34:33.33:33.33	36.52:37.49:25.99	2.3	0.3859	3.0
Pt ₃ Cu/C	75.00:25.00	75.69:24.31	2.6	0.3878	3.2
Pt ₃ Sn/C	75.00:25.00	69.64:30.36	2.1	0.3934	2.6
Pt/C	—	—	2.7	0.3911	2.9

**Fig. 1** XRD patterns of the carbon-supported Pt₃Cu/C, Pt₃Sn/C, PtSnCu/C and Pt/C catalysts. Dotted vertical lines indicate the position of the diffraction peaks corresponding to Pt crystalline planes and stress the shift of peak position observed for the Pt₃Cu/C, Pt₃Sn/C and PtSnCu/C materials with respect to the Pt/C catalyst. *Denotes the peaks related to SnO₂ (cassiterite)

catalysts, the diffraction peaks corresponding to Pt are shifted with respect to those of the Pt/C catalyst. Particularly for the Pt₃Sn/C catalyst, the peaks are shifted to lower degrees, while for the Pt₃Cu/C and PtSnCu/C catalyst the peaks are shifted to higher degrees. Both shifts suggest the insertion of the second metal into the Pt crystalline lattice and the divergence of shift way may be attributed to the difference between the Sn and Cu atom sizes. Sn is larger than Pt and its insertion into the Pt crystalline lattice promotes its expansion [41]. On the other hand, Cu is smaller than Pt and its insertion into the Pt crystalline lattice causes its contraction [42]. The expansion or contraction of the crystalline lattice of fcc structure carries in a shift in the diffraction peak position towards higher or lower diffraction degrees [43]. For the PtSnCu/C catalyst, it is possible to infer that a preferential insertion of Cu (with respect to that of Sn) into the Pt crystalline lattice has occurred. In addition to the peaks associated with Pt, peaks related to Sn oxides, more specifically SnO₂ (37°, 52°) (cassiterite) [31, 44] are also observed in the XRD profiles of the Pt₃Sn/C and PtSnCu/C catalysts,

indicating the presence of these species in the Sn-containing materials. More details were presented and discussed elsewhere [32]. No peaks related to the presence of Cu oxides, in particular CuO (36°, 38°) and Cu₂O (42°, 61°)[45], were observed in the DRX profiles of the Pt₃Cu/C and PtSnCu/C catalysts. Nevertheless, the occurrence of these species in the Cu-based materials cannot be disregarded, since these peaks may be present at small intensities or may be hidden.

The Pt crystallite average diameters, determined by using the Scherrer equation applied to the peak at $2\theta = 65^\circ$, are shown in Table 1. They varied from 2.1 to 2.7 nm. The lattice parameters, calculated by the Bragg's law applied to the peak at $2\theta = 65^\circ$, are shown in Table 1 also. The modification of the lattice parameter of Pt in Pt₃Cu/C, Pt₃Sn/C, PtSnCu/C catalysts with respect to that in the Pt/C catalyst indicates the formation of solid solution of Pt and Cu and/or Sn. These results are in agreement with those reported in previous studies [46].

Figure 2 shows TEM images of the investigated carbon-supported PtSnCu/C, Pt₃Sn/C, Pt₃Cu/C and Pt/C catalysts with the corresponding particle size distribution histograms (inset). TEM micrographs were obtained with magnifications of 200,000-fold. Homogeneous distribution of the nanoparticles over the carbon support was observed (no particle agglomeration was evidenced), as illustrated by the TEM images (Fig. 2). This is remarkably interesting for catalytic applications since particle agglomeration leads to a decrease in the surface area and consequently in the activity [7, 9].

As seen by the histograms of particle size distributions, shown in the insets of Fig. 2, metal particles presented a narrow Gaussian particle size distribution. Irrespective of the catalyst composition, the mean particle size was around 3 nm (Table 1). It is important to emphasize that the particle size distribution histograms were obtained from analyses of several different regions, i.e., not only the images showed here, and it quantitatively reflected the uniform size distribution of the catalysts.

The average particle size from TEM and the crystallite average diameter from XRD are close. In opposition to that, in studies about the effect of thermal treatment on Pt₇₅Sn₂₅/C [44] and Pt₅₀Sn₅₀/C [47], for materials submitted to thermal treatment at high temperatures ca. 500 °C, Colmati et al. observed discrepancies between the average particle

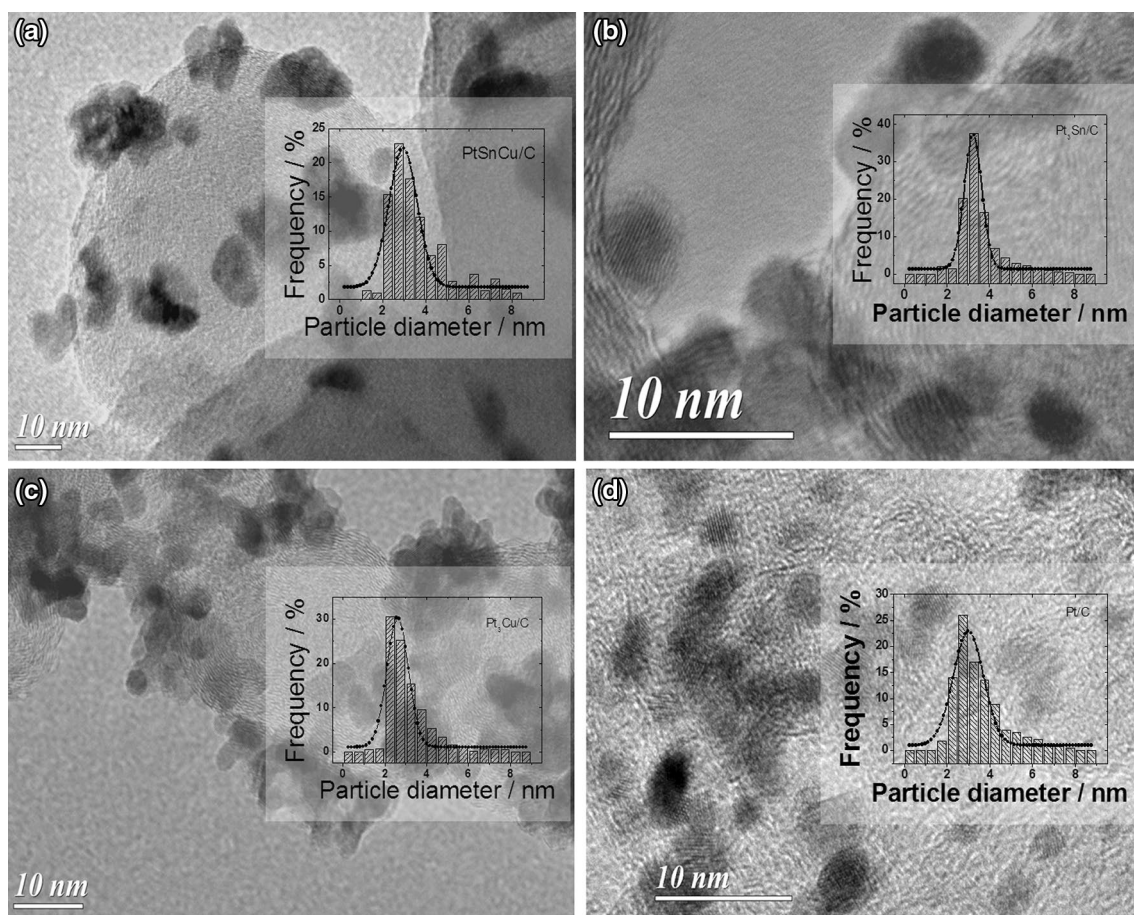


Fig. 2 Transmission electron microscopy images of the PtSnCu/C, Pt₃Sn/C, Pt₃Cu/C and Pt/C catalysts and the histograms of particle size distributions (inset)

size calculated from TEM and the crystallites size calculated from XRD. By XRD analyses, large particles were evidenced, while limiting count of particles in the TEM images resulted in an histogram of small particles with narrow size distribution. Therefore, the agreement between TEM and XRD results in the present work suggests the absence of large particles.

4.1 Electrochemical characterization

The cyclic voltammetry results of EOR on the Pt/C, Pt₃Cu/C, Pt₃Sn/C and PtSnCu/C catalysts in acidic medium are shown in Fig. 3. For comparison, a magnified view of respective cyclic voltammogram of the investigated material in acidic medium in the absence of ethanol is shown in Fig. 3a. In the absence of ethanol, the carbon-supported Pt-based materials presented the characteristic hydrogen adsorption/desorption region between 0.05 and 0.35 V vs. RHE and the double-layer and oxide regions from 0.35 to 1.0 V vs. RHE. For the ternary material, the double-layer capacitance grows (with respect to that of the

Pt/C catalyst) despite the presence of tin oxides. On the other hand, these results differ from those observed for the Pt₃Cu/C and Pt₃Sn/C materials, which shows the double-layer capacitance similar to that of the Pt/C catalyst. It can be explained by the interaction between Pt and the second metal that results in a slight oxide formation, in accord with previous studies [32, 46].

In the presence of ethanol, as it can be observed in Fig. 3b, the incorporation of Cu or Sn into the carbon-supported Pt catalyst leads to a reduction of the onset potential from 0.65 V to about 0.55–0.50 V vs. RHE. For the tri-metallic material, the onset potential reduced drastically to 0.3 V vs. RHE. This behavior can be assigned to a synergism among Pt, Cu and Sn, in which Cu modifies Pt by an electronic effect and Sn contributes to the bi-functional mechanism, once Pt and Cu form alloy easily at different atomic ratios [46] and Pt₃Sn/C present low alloy degree in this material, as seen by the XRD results (Fig. 1).

The formation of reaction intermediates and products was investigated by in situ FTIR and the corresponding results are presented in Fig. 4.

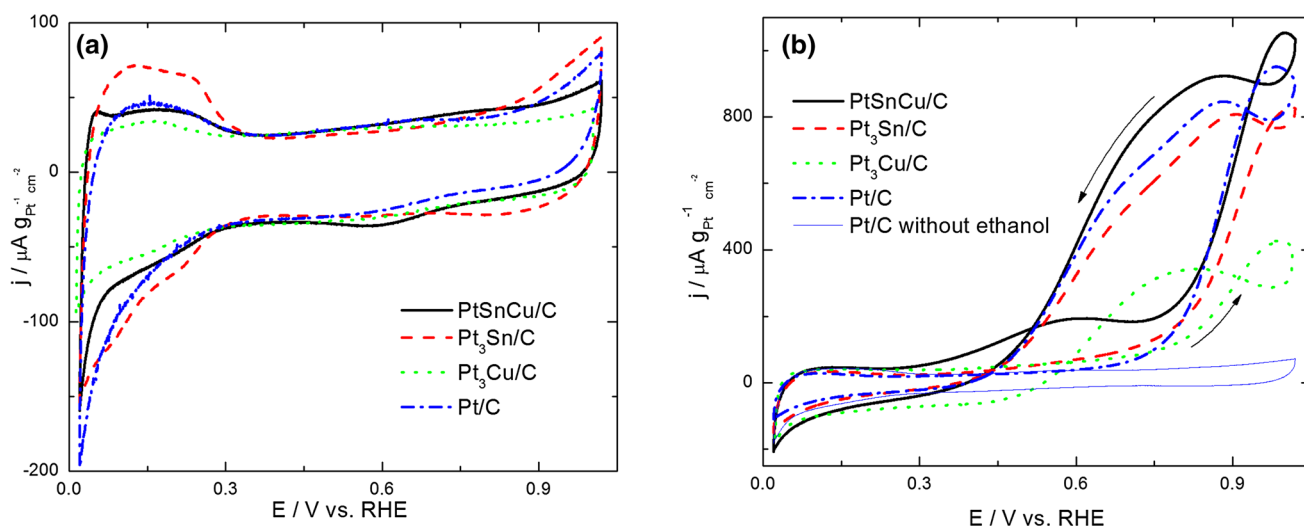


Fig. 3 Cyclic voltammograms of the PtSnCu/C, Pt₃Sn/C, Pt₃Cu/C and Pt/C catalysts (a) in 0.5 mol L⁻¹ H₂SO₄ and (b) in the presence of 0.1 mol L⁻¹ CH₃CH₂OH, $\nu = 0.05$ V s⁻¹, T = 27 °C. The cyclic

voltammogram of Pt in acidic medium is also shown in Fig. 3b as a baseline for the onset potential determination

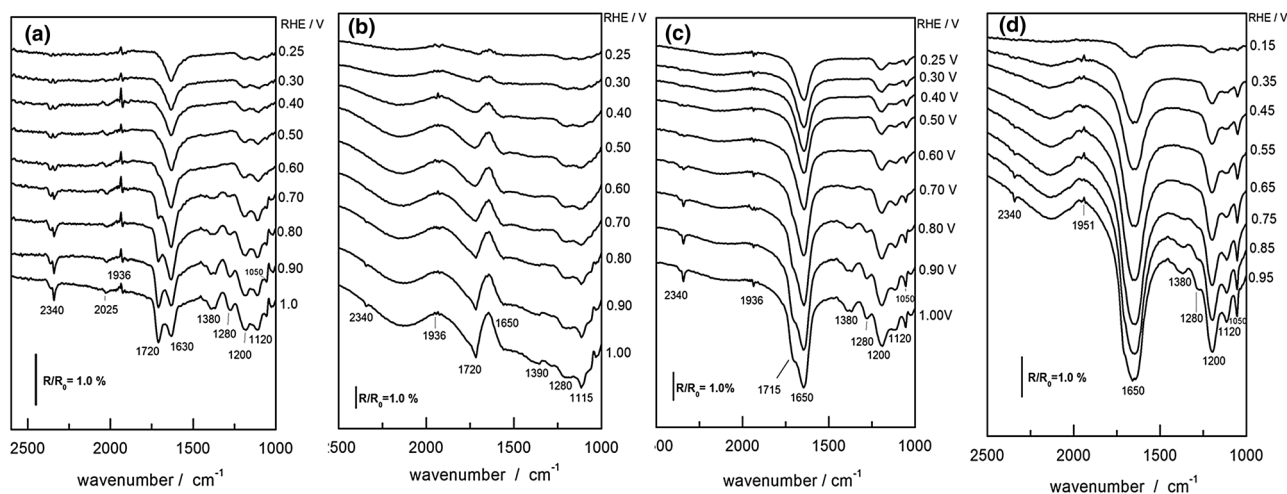
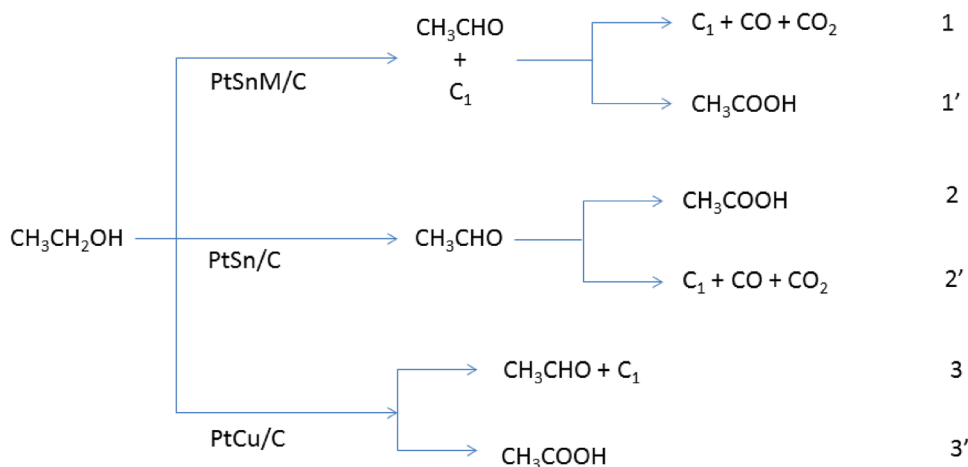


Fig. 4 In situ FTIR spectra of the PtSnCu/C (a), Pt₃Sn/C (b), Pt₃Cu/C (c) and Pt/C (d) in 0.5 mol L⁻¹ H₂SO₄ and 0.1 mol L⁻¹ CH₃CH₂OH. Spectra were computed from an average of 128 interferograms. The spectral resolution was 8 cm⁻¹

Figure 4 shows FTIR spectra of the PtSnCu/C, Pt₃Sn/C, Pt₃Cu/C and Pt/C in 0.5 mol L⁻¹ H₂SO₄ and 0.1 mol L⁻¹ CH₃CH₂OH. In these spectra, the main bands related to the ethanol oxidation in sulfuric acid solution were observed, namely a band at 2340 cm⁻¹, assigned to CO₂, bands at 2025 cm⁻¹ and 1935 cm⁻¹, attributed to linearly and bridge-bonded CO on Pt sites, respectively, bands at 1715–1720 cm⁻¹, related to CO stretching of carbonyl groups, a band at 1280 cm⁻¹, attributed to -COOH group of acetic acid, a band at 1360 cm⁻¹, corresponding to CH₃ symmetric bending of acetaldehyde molecules, bands at 1200 cm⁻¹ and 1120 cm⁻¹ associated with SO₄²⁻ and HSO₄⁻, respectively, a band at 1630 cm⁻¹, assigned to the

OH bending of water molecules in the thin layer, and the band at 1050 cm⁻¹, ascribed to CO stretching of ethanol molecules in solution [48–50]. CO₂ started to be formed on PtSnCu/C and Pt₃Cu/C at potentials close to 0.7 V, while Pt₃Sn/C and Pt/C produced CO₂ from 0.8 to 0.75 V, respectively. Carbonyl products (as seen by the band at 1720 cm⁻¹) were observed at 0.6 V for PtSnCu/C and 0.65 V for the bimetallic materials, although the bands at 1360 cm⁻¹ and 1280 cm⁻¹ (related to the formation of acetaldehyde and acetic acid, respectively) started to be evident only at 0.7 V for PtSnCu/C and Pt₃Cu/C, 0.80 V for Pt₃Sn/C and 0.75 V for Pt/C. Our results show that the addition of Cu to Pt or Pt₃Sn/C favors the CO₂ formation at lower potentials and

Fig. 5 Scheme of the ethanol oxidation reaction pathways. Pathways *i* are favored in comparison with pathways *i'*, C_1 is by-product with one carbon atom



suggests that Cu improves the dissociative adsorption of ethanol on the catalyst surface. In opposition to Cu, the addition of Sn to Pt did not have a positive impact on the CO_2 production. These results are in accord with those previously reported in the literature. Beyhan et al. [12] studied the oxidation of ethanol on PtSn/C catalysts and explored the effect of the addition of a third metal to the catalyst on the materials performance. CO_L was formed at low potential (0.1 V) on PtSnCo and PtSnRh, suggesting dissociative adsorption of ethanol on these surfaces. On the other hand, in the absence of Co or Rh, Sn had a minor effect on the C–C bond cleavage of ethanol. In another work, Delpeuch et al. [18] studied ethanol oxidation reaction on Pt, PtSn and PtSnRh and observed that, in the presence of Rh, CO_2 formation was improved, indicating an increase of the C–C bond cleavage. Furthermore, de Souza et al. [51] also showed that PtSn modified with Rh favors the CO_2 production. These data suggest that PtSn/C present fast kinetic towards ethanol oxidation reaction and deliver large current density in direct ethanol fuel cell, but the main by-product is acetic acid. Tin modifies Pt 5d band fill [52], which, in turn, impacts on the ethanol/acetic acid adsorption desorption process. On the other hand, the insertion of the Cu reduces the ethanol oxidation reaction kinetic and lower current is observed [47], although particle sizes are close (Table 1). Additionally, the insertion of Cu to PtSn favors the acetaldehyde formation, which can be oxidized to CO and CO_2 in lower amount. A scheme of these reactions is shown in Fig. 5.

5 Conclusion

Carbon-supported Pt-based materials investigated in the present work were active towards the ethanol oxidation in acidic media. Pt modified by Sn or Cu presented contraction and expansion on Pt lattice and it modified the electrochemical activity towards ethanol oxidation reaction. All materials

presented narrow nanoparticles size distribution and homogeneous distribution of particles on the carbon support. The PtSnCu/C presented lower onset potential for ethanol electro-oxidation in acid medium in comparison with Pt₃Sn/C and Pt₃Cu/C. FTIR analyses suggest that the addition of Cu to Pt-based catalysts improves the dissociative adsorption of ethanol and different pathways are favored depending on the Pt modification towards expansion or contraction of the Pt lattice. Our results show that multimetallic catalysts present improved performance towards the ethanol oxidation reaction.

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