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Influence of metallic oxides on ethanol oxidation



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ABSTRACT

An improvement in ethanol oxidation electrocatalysis is possible with multifunctional Pt-based combinations. Thus, the addition to Pt of Sn, Ir or Ni enhances the ethanol oxidation reaction (EO) and shifts the onset oxidation potential to lower values. It has been suggested that metallic oxides in the vicinity of Pt have the capacity of promoting the oxidation of residues coming from alcohol oxidative adsorption. In order to get a deeper knowledge on the ethanol oxidation catalysis, supported catalysts prepared either by thermal decomposition of polymeric precursors (PP) or by microwave assisted poliol reduction (MW) methodology are studied to determine the role of the catalyst components and its oxides on the improvement of ethanol oxidation. The catalysts are physically and electrochemically characterized. According to the synthesis method, the amount of SnO₂ in the catalyst varies. Faceted particle structures for the microwave-synthesized catalysts are observed. By employing electrochemical techniques it is concluded that the catalyst with the highest amount of SnO₂ has the best catalytic behaviour for EO.

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1. Introduction

Fuel cells that employ alcohols, such as direct ethanol fuel cells (DEFCs) are attractive to power portable devices because their theoretical cell voltage is similar to that obtained when hydrogen is oxidized [1,2]. Ethanol is a liquid easy to handle, transport and store and its complete electro-oxidation involves a 12-electron process. Nevertheless, the DEFC undergoes slow kinetics of alcohol oxidation on electrode surfaces. Efficiency is currently quite low for that fuel cell [3].

To achieve the maximum chemical energy from ethanol, it has to be completely oxidized to CO₂. Consequently, an acceptable ethanol catalysts need to have a great capability to convert it into CO₂ and water. It appears that an improvement in ethanol oxidation electrocatalysis is possible with multifunctional Pt-based combinations [4]. Thus, the binary PtSn/C or the ternary PtSnIr/C and PtSnNi/C supported catalysts enhance the EO and shift the onset oxidation potential to values lower than that on Pt/C supported catalyst [5–8]. The effect of Sn addition to Pt is related, to a certain extent, to alloy formation and a controversy is established regarding tin oxide

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in the vicinity of Pt nanoparticles. Some researchers found that the activity of PtSn catalysts for the ethanol oxidation reaction seems to be dependent on the amount of both non-alloyed and alloyed Sn [9].

It has been suggested that metallic oxides in the vicinity of Pt have the ability to promote the oxidation of residues resulting from alcohol oxidative adsorption [10,11]. According to Jiang et al. [11], SnO₂ can supply surface oxygen-containing species for the removal of strongly adsorbed residues on adjacent Pt active sites, considering the bifunctional mechanism.

The SnO₂ amount may depend on the catalysts preparation method, and on the presence of other precursors [12].

The aim of the work is to highlight the role of the multi-components catalysts and to evaluate if the synthesis method could favour the formation of different amounts of SnO₂ in the catalyst and modify the particle morphology.

To achieve the goal, PtSnM/C catalysts with M = Ir or Ni have been prepared either by thermal decomposition of polymeric precursors, (PP) or by microwave assisted polyol reduction (MW) and tested for ethanol oxidation reaction.

2. Experimental

2.1. Catalysts synthesis

Metal nanoparticles are mostly prepared by the growth of particles starting from metal atoms, which are obtained from the chemical interaction between ionic precursors and a reductor agent. The methodology is suitable to obtain small and uniform nanoparticles. And controlling the atom aggregation is the most important step to manage the size and uniformity of the metal nanoparticles [13,14].

In accordance with the Pechini methodology, a PtSnIr/C (PP) catalyst with a fixed total metal loading on carbon (Vulcan XC-72R) of 40 wt% was synthesized employing ethylene glycol as a reactant and reducing agent together with citric acid [15]. The method is based on the thermal decomposition of a polymeric precursor obtained by the polymerization reaction between citric acid, the metallic ions and ethylene glycol to form an esterified chelate.

Briefly, Pt, Ir and Sn polymeric precursors were prepared separately by employing metallic salts namely, H₂PtCl₆, IrCl₃·xH₂O and Sn citrate, dissolved in a mixture of ethylene glycol and citric acid at 60 °C. The molar ratio among citric acid, ethylene glycol and metallic salt was set as 4:16:1 for all the polymeric precursors. The mixture of the three polymer precursors was unified and the temperature was raised to 90 °C and kept under vigorous stirring for 3 h composing a polyester network that keeps the metallic ions homogeneously distributed. A calculated amount of the functionalized carbon black support was added. Finally, the mixture precursor solution/carbon was homogenized in an ultrasonic bath and then calcinated at different temperatures under an air atmosphere, using a temperature program reaching 350 °C to get rid of organic residues.

Employing chemical reduction by ethylene glycol, assisted by microwave heating, PtSnIr/C(MW), PtSnNi/C(MW), and PtSn/C(MW), catalysts have been prepared following [16,17]. In brief, a calculated amount of the different precursors were added to 25 mL of ethylene glycol. The mixture was stirred for

5 min in ultrasonic bath, and sufficient carbon Vulcan XC-72 powder was then added, in order to obtain a metal catalyst load of 40 wt%. The mixture was kept under ultrasound stirring for 30 min, until a homogeneous suspension was obtained. This suspension was then placed in a common household microwave oven (Likon, 2.45 GHz, 700 W) for 70 s. Finally, the suspension was filtered and washed repeatedly with water, and then dried in an oven at 80 °C for 24 h.

2.2. Characterization methodology

The physical characterization of the materials was accomplished by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS).

For the electrochemical characterization linear voltammetry (LV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) were employed.

A conventional three-electrode cell was employed, the working electrode consisted of a glassy carbon disk (0.071 cm² geometric area) covered by a thin layer of catalyst (28 μg cm⁻² Pt loading) embedded in a Nafion polymer electrolyte film (0.1 μm thick) [18]. A Pt foil of ca 1 cm² geometric area was used as counterelectrode and a saturated calomel electrode as reference electrode. In this work, the potentials refer to that of the reversible hydrogen electrode (RHE).

The supporting electrolyte was 0.5 M H₂SO₄ and the working solution was 1 M C₂H₅OH + 0.5 M H₂SO₄. After the assembly, the composite catalytic disk electrode was cycled in 0.5 M H₂SO₄ for 5 min at 0.10 V s⁻¹ between 0.05 and 1.24 V to clean the surface. Real areas were determined by considering the anodic charge corresponding to the CO-stripping peak and assuming that CO is linearly adsorbed on one Pt site and taking into account that 420 μC is equivalent to 1 cm².

To establish the catalytic activity of the synthesized materials, current–potential curves for EO were recorded at 0.01 V s⁻¹. The alcohol was added to the supporting electrolyte at 0.05 V and its oxidation was measured. The temporal stability of the electrode at 0.5 V was determined by chronoamperometry. The current densities refer to the CO calculated real area. Electrochemical impedance spectroscopy (EIS) was also employed to identify the materials with the best EO performance. The impedance spectra were recorded by polarizing in a constant voltage mode at 0.5 V at frequencies from 100 kHz to 10 mHz. The amplitude of the applied potential perturbation was 0.010 V. All electrochemical measurements were performed at 60 °C.

Prior to each EIS measurement, the electrolyte was replaced by fresh solution and the electrode was cycled to get a clean and reproducible surface. A 30 min holding time was applied at each potential to approach a near steady state before the data were collected.

3. Results and discussion

3.1. Physical characterization

In Fig. 1 TEM images of all the synthesized catalysts are shown: Fig. 1a, PtSnIr/C (PP), Fig. 1b, c and d, PtSnIr/C (MW),

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