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Addition of iron oxide to Pt-based catalyst to enhance the catalytic activity of ethanol electrooxidation

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ABSTRACT

Iron oxide is largely used as catalyst in many industrial processes such as the synthesis of ammonia, the conversion of carbon monoxide into carbon dioxide, and the dehydrogenation of different organic substrates. For this reason and based on previous results obtained with iron as co-catalyst for the electrooxidation of ethanol, we have investigated how iron oxide as support for Pt-based catalysts affects the oxidation of this alcohol. For this purpose, we deposited Pt and PtSn over iron oxide-C and compared the catalytic activity of these materials with the catalytic activity of Pt/C and PtSn/C. Iron oxide-C, mainly in the form of γ-Fe_2O_3-C, was obtained by thermal decomposition of polymeric precursors, which was followed by deposition of Pt and PtSn on the γ-Fe_2O_3-C substrate by the microwave-assisted method. γ-Fe_2O_3-C positively affected the activity of Pt/C and PtSn/C in the electrooxidation of ethanol. Therefore, the addition of γ-Fe_2O_3-C improves the activity of the well-known catalyst Pt_3Sn in the oxidation of ethanol

1. Introduction

The increasing world population has prompted global leaders, scientists, and environmentalists to implement actions that make the society aware of the need to develop new sources of energy and to prevent or reverse the environmental degradation caused by intense urbanization and industrialization [1–3]. In this context, electrochemical technology has emerged as a helpful tool.

Over the last few decades, the scientific community has been devoted to finding clean energy sources and highly efficient energy conversion systems with reduced environmental impact. In this scenario, researchers have investigated the Direct Ethanol Fuel Cell (DEFC), which can generate power efficiently without harming the environment. However, the prohibitive costs associated with fuel cell technology, including the price of materials and manufacturing processes, makes the commercial availability of fuel cells as energy converters difficult. For instance, to operate at low temperatures (50–90 °C) and to compensate the deficiency of the kinetic process, the DEFC requires materials with high catalytic activity and usually demands the use of a noble metal as the main catalyst in the system.

Many research groups that study the DEFC still face the challenge of developing an efficient material for the electrooxidation of ethanol [4–10]. Pt-based catalysts represent the main material for this purpose. However, Pt alone does not display good catalytic activity toward the oxidation of ethanol, so the addition of other metals that can act as co-catalyst is necessary [7,11–20]. Over the years, a range of binary and ternary Pt-based catalysts have been evaluated [16,21–25], mainly PtSn [26–30] and PtRu [31–34]. The proposed reaction mechanism for the electrooxidation of ethanol at a Pt-M catalyst is based on different techniques such, Differential Electrochemical Mass Spectrometry (DEMS) [33,35–38], *in situ* Fourier-Transform Infrared Spectroscopy (FTIR) [39–43], and High Performance Liquid Chromatography (HPLC) [16,44,45], which have helped to identify the reaction products. Acetaldehyde and acetic acid always emerge as the main products and reflect the stability of the C—C bond at lower DAFC operating temperatures 80–100 °C.

Pt-based catalysts containing iron and iron oxide are promising catalysts for the oxygen evolution reaction (OER) [46], and for the oxygen reduction reaction [47–49] when they are applied as cathode in the alcohol fuel cell. Iron and iron oxide have recently gained attention because they can be used as co-catalyst or conductive support during the oxidation of alcohols. Few researchers have employed these materials to oxidize methanol [50–53], ethanol [54–57], or glycerol [58]. Iron and Fe_2O_3 are advantageous co-catalysts or supports for Pt-based catalysts: they are inexpensive as compared to other metal oxides, and they present excellent physicochemical properties, such as high surface, porosity, and electropositivity, which enhance the activity of Pt-based catalysts and contributes to the occurrence of electronic and

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bifunctional mechanism over Pt.

Some of us have recently used combinatorial electrochemistry to assess the catalytic activity of some PtSn-based catalysts in the oxidation of ethanol [54]. The addition of iron to these materials resulted in good activity. For this reason, here we conducted a more systematic investigation into how iron, as a conductive support (γ-Fe_2O_3-C), influences the activity of Pt-based catalysts during the oxidation of ethanol.

2. Experimental

2.1. Preparation of iron oxide

The iron oxide-C support was prepared by thermal decomposition of polymeric precursors; the procedure described elsewhere [5,16,21] was followed. Briefly, $FeCl_3.6H_2O$ (Aldrich) was mixed with citric acid (CA) (Merck) and ethylene glycol (EG) (Merck) in a quartz crucible placed in a water bath at 65 °C; a 1:4:16 metal/CA/EG molar ratio was employed. After complete dissolution of the precursor salt, the temperature was raised to 90 °C, and the mixture was kept under vigorous stirring for 30 min. Then, 3 mL of ethanol and treated carbon Vulcan XC-72 powder (enough powder to achieve 20% wt. iron loading) was added to the mixture. Next, the mixture was homogenized in an ultrasonic bath for 10 min and returned to the water bath until ethanol was completely evaporated. Finally, the mixture was calcined under air atmosphere; the mixture was heated at a rate of 5 °C min^{-1} until 350 °C and kept at this temperature for 2 h.

2.2. Preparation of the electrocatalysts

Pt/C, Pt/Iron oxide-C, Pt_3Sn/Iron oxide-C were synthesized by the microwave-assisted method [54,59]. Microwave-assisted Pt_3Sn was characterized and reported previously [60].

To obtain the Pt/C and the Pt/Iron oxide-C catalysts, first 30 mL of propylene glycol (as reducing agent), 1.32 mL of $H_2PtCl_6.6H_2O$ (Aldrich) 0.077 M, and 41.8 mg of sodium acetate (as a stabilizing agent) were mixed in an orbital shaker under continuous stirring. After homogenization, the mixture was added with enough Fe_2O_3-C (catalyst support, 30 mg) to achieve catalysts with 40% wt. Pt loading. The mixture was kept under ultrasound stirring for 30 min, until a homogeneous suspension was obtained. Once again, the suspension was placed in an orbital shaker, where it remained for 24 h. After this period, the mixture was placed in a common household microwave oven (Panasonic NN-ST568WRU, 2450 Hz, 800 W) for 5 min, at a power of 200 W. Finally, the suspension was filtered and washed with acetone (Merck), and the solid product was dried in an oven at 120 °C for 2 h, under N_2 atmosphere.

Pt_3Sn/Iron oxide-C was synthesized by mixing 30 mL of propylene glycol, 1.14 mL of $SnCl_2$ (0.025 M), 1.11 mL of $H_2PtCl_6.6H_2O$ (0.077 M), and 46.6 mg of sodium acetate. The experimental procedure was the same as the one described above.

2.3. Physical characterization

The experimental catalyst metal loading on the carbon support was obtained by thermogravimetric analysis on an SDT 2960 Simultaneous DSC-TGA analyzer operating from 20 to 800 °C at a heating rate of 5 °C min^{-1}, under air atmosphere.

Catalyst composition was analyzed by energy dispersive X-ray spectroscopy (EDX) on a Leica microscope Zeiss LEO 440 model SEM coupled to an Oxford 7060 model analyzer.

The diffraction patterns were obtained on an X-ray diffractometer (D5005 Siemens) operating with Cu Kα radiation (λ = 1.5406 Å) generated at 40 kV and 40 mA. The following parameters were kept constant during the analysis: 2θ range = 20° – 90°, step = 0.03° s^{-1}, and total analysis time = 1.97 h. The crystallite size and the apparent lattice parameter were estimated by using the Scherrer's Eq. (1) and Eq. (2), respectively, considering the plane (220) as a reference:

$$D = \sqrt{2}\,\lambda / B\cos\theta_B \tag{1}$$

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

In the case of γ-Fe_3O_4, the lattice parameter was determined by the indexing method; the (311) plane was used as reference.

The morphology and the particle size distribution of the nanocatalysts were evaluated by Transmission Electron Microscopy, conducted on a TEM/STEM JEM-2100-JEOL microscope. The equipment contained a LaB6 filament and was operated in the UHR-mode, at 200 kV. Five hundred isolated particles were counted to estimate a statically appropriate value of the average size and size distribution of the electrocatalysts. The Gauss Model Equation (y = y0 + {A/[w*sqrt (PI/2)]}*exp.{ − 2*[(x-xc)/w]^2}) was employed to calculate the fit curve for the histogram of the nanoparticles. All the TEM images were processed with the ImageJ free-software.

2.3. Electrochemical measurements.

The electrochemical profile of the catalysts was obtained by cyclic voltammetry (CV) in N_2-purged H_2SO_4 (Mallinckrodt) 0.5 M solution. Measurements were conducted in a conventional electrochemical cell that included a reversible hydrogen electrode (RHE) and a platinum wire as reference and counter electrode, respectively. The working electrode was prepared by deposition of a catalyst ink prepared in isopropanol/Nafion® solution on a previously polished gold disk electrode (0.5 cm^2). In all the cases, the catalyst layer had a metal loading of 0.05 mg cm^{-2}. Activity and stability tests were carried out by cyclic voltammetry, chronoamperometry, and galvanostatic voltammetry in the presence of ethanol 1.0 M and H_2SO_4 0.5 M.

3. Results and discussion

3.1. Physical characterization

Thermogravimetric analysis revealed deposition of 21% wt. iron on carbon Vulcan, which was the desired amount of iron in the catalysts. Hence, thermal decomposition efficiently converted $FeCl_3$ into iron oxide. The catalysts Pt/C, Pt/γ-Fe_2O_3-C, and Pt_3Sn/γ-Fe_2O_3-C presented metal loading of 39.8%, 29%, and 33% wt., respectively. Only Pt/C had the metal loading close to the nominal percentage. Pt/γ-Fe_2O_3-C and Pt_3Sn/γ-Fe_2O_3-C had10% less metal deposited on the γ-Fe_2O_3-C support, but metal loadings were still considerably close to the nominal percentage.

The bulk composition of Pt_3Sn/γ-Fe_2O_3-C determined by EDX analysis showed the Pt:Sn molar ratio was Pt(65):Sn(35). Even though EDX just provides semi-quantitative data, the experimental and nominal compositions of Pt_3Sn/γ-Fe_2O_3-C agreed considerably.

Fig. 1 illustrates the diffraction patterns and the structural profiles of the catalysts obtained by XRD. The peak at 2θ = 25° referred to the crystallographic plane (002) of carbon. The Fe_2O_3-C support displayed six well-defined sharp peaks, at 30.22°, 35.60°, 43.28°, 53.74°, 57.74°, and 62.95°, which was characteristic of the crystalline cubic structure of γ-Fe_2O_3 (space group P4332), also known as maghemite, and corresponded to the reflection planes (221), (311), (173), (422), (511) and (353) (JCPDS # 01–089-5192), respectively. The crystallite size was about 20.0 nm, and the lattice parameter (8.3573 Å) did not differ significantly from the lattice parameter of pure γ-Fe_2O_3 (8.3457 Å).

Pt/C (Fig. 1B) exhibited the characteristic peaks of the crystalline structure of face-centered cubic (fcc) platinum. The peaks were related to the reflection planes (111), (200), (220), (311), and (222) (JCPDS # 00–004-0802). The crystallite size remained about 2.0 nm, which was 10 times smaller than the crystallite size of γ-Fe_2O_3. The experimental lattice parameter (3.920 Å) resembled the experimental lattice parameter of pure Pt (3.923 Å).

Addition of Pt and Pt_3Sn onto γ-Fe_2O_3-C suppressed all the peaks