



Adatom modified shape-controlled platinum nanoparticles towards ethanol oxidation



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ABSTRACT

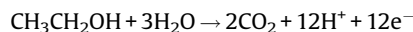
Different adatom modified shape-controlled Pt nanoparticles have been prepared and their electrocatalytic properties have been evaluated toward ethanol electrooxidation. Based on previous findings with Pt model surfaces, Sn, Rh, Ru and Pb adatoms have been selected as promising surface modifiers. The different adatoms have been gradually incorporated on the surface of the preferentially oriented (100) and (111) Pt nanoparticles under electrochemical conditions. The results obtained in 0.5 M H₂SO₄ indicated that, among the selected adatoms, Sn-modified nanoparticles displayed not only a significant shift to negative values on the onset potential of the ethanol oxidation, but also an important decrease on the hysteresis between the positive and negative sweeps. Interestingly, in chronoamperometric measurements at 0.6 V, the oxidation enhancement factors have been found to be dependent on the surface structure of the Pt nanoparticles. On the other hand, Ru and Pb-modified Pt nanoparticles only presented a rather small oxidation enhancement, whereas the activity of the Rh-modified Pt nanoparticles clearly diminished. In alkaline solutions, the oxidation mechanism changes, and the adsorption of Rh, Sn and Pb on the platinum surfaces just displays small catalytic effect at lower coverage for the potential onset in the voltammetric experiments. Ru adsorption does not present any positive effect over the reaction.

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1. Introduction

Nowadays, the studies about new energy sources are gaining momentum due to the depletion of fossil fuels. One of these alternative energy sources is the development of fuel cells, which can obtain energy simply from the reaction between a fuel and an oxidant species (usually oxygen). Fundamental research in fuel cells is usually centered in the material used for manufacturing the catalyst and its electrocatalytic response to the desired reaction on the cathode or on the anode [1]. As a catalyst, platinum is a good choice due to its well-known catalytic properties. Different chemicals have been selected as possible candidates for using as a fuel in the anode, from the most typical hydrogen to some small organic molecules such as formic acid, methanol or ethanol. Among these organic molecules, ethanol is one of the most studied fuels [2], because it presents some advantages as the easiness for obtaining it from biomass in addition to its low toxicity or its high

energy density for the complete oxidation to CO₂, where 12 electrons are exchanged according with the reaction:

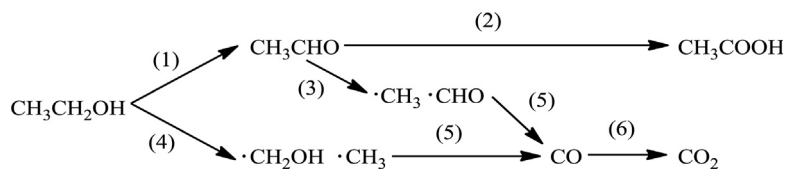


Nevertheless, this reaction is not as simple as appears in the general equation presented above, because parallel reactions can occur, decreasing the efficiency of the complete oxidation, the desired route. When using platinum as catalyst, this reaction has shown to be structure sensitive [3], that is, depending on the arrangement of the platinum atoms on the surface of the electrode, the reactivity changes. On this electrode, ethanol oxidation mechanism has a dual-path mechanism:

Step (1) of the scheme corresponds to the ethanol oxidation to acetaldehyde, whereas step (2) is the acetaldehyde oxidation to acetic acid. These two reactions compose the route known as ethanol incomplete oxidation. Step (3) and step (4) show the C-C bond scission from acetaldehyde and ethanol respectively, needed to achieve CO₂ formation. However, previous to the complete oxidation, CO is formed and poisons the catalyst surface. At high potentials, this CO is finally oxidized to CO₂. On Pt (111) electrodes, only acetic acid is formed without poison formation. However, on Pt (100) and Pt (110) electrodes, C-C bond scission is observed and

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CO is formed, blocking the surface for further reaction at low potentials [3,4]. On the other hand, the oxidation in alkaline solutions leads to the almost exclusive production of acetate and negligible amounts of CO and CO₂ (carbonate at higher pH values) [5].

The problem of using platinum is its high price. One option for reducing the cost of platinum is to use it in the form of nanoparticles, with high active area, thus allowing the use of lower amounts of platinum. In addition, most of the reactions in fuel cell applications are structure sensitive. Thus, a careful selection of the surface structure of the nanoparticle can lead to an increase in the electrocatalysis. This can be achieved by synthesizing shape-controlled platinum nanoparticles, as has been done for the oxidation of interesting molecules (formic acid, methanol, ethanol, glycerol and ammonia [6–9]) or oxygen reduction [10–12]. An additional increase in the catalytic activity of the Pt can be obtained by the modification of the electronic properties by forming alloys.

Focusing on ethanol oxidation, alloys composed of platinum and other metals, such as Sn, Ru, Rh, Mo or Cu, show improved selectivity to the C–C bond scission and/or enhanced activity for the oxidation of CO, so that the total electrocatalytic activity is increased [13–19]. However, for a better understanding of the actuation mechanism of the additional element in the Pt alloys, the controlled deposition of foreign adatoms on platinum with a well-known surface structure is considered as a suitable approach for this study. With this approach, a large amount of different modified platinum surfaces can be tested due to the easiness of preparation of electrodes with variable composition [20]. Additionally, the test of the different modifications can be carried out in similar conditions, which allows a better comparison between different modifiers.

The metals chosen for depositing on Pt surface and study their electrocatalytic effect towards ethanol oxidation were tin, rhodium, ruthenium and lead. In previous studies, Sn and Ru deposition on stepped surfaces showed some enhancement for the oxidation to CO₂ [21,22], whereas Pt deposited on Rh electrodes also shows increased activity for the C–C bond scission [23]. In addition, some works have demonstrated the improvement in the carbonate formation when Pb atoms are adsorbed on polycrystalline Pt surfaces in alkaline solutions [24,25].

In this work, fundamental studies about the electroactivity of the Sn, Rh, Ru and Pb-modified platinum nanoparticles, specifically in (100) and (111) Pt nanoparticles, for ethanol oxidation are reported in two different pH values (acidic and alkaline solutions). These two types of nanoparticles have been selected because they represent two different paradigms for the ethanol oxidation reaction. As aforementioned, the (111) plane of Pt is inactive for the cleavage of the C–C bond, yielding acetic acid/acetate both in acid and alkaline solutions, whereas the (100) plane is active for this process in acidic conditions. Thus, the effect of the adatoms on both reaction paths can be analyzed. The studies will be carried out using voltammetric and chronoamperometric techniques, which will allow the best conditions to achieve the highest electrocatalytic activity (pH and composition) to be determined for the studied reaction.

2. Experimental

Preferential cubic and octahedral Pt nanoparticles were used in this study. According to the observed shape by TEM, these nanoparticles should contain a high fraction of (100) and (111) domains, respectively [6,26]. For that reason, they have been named (100) Pt nanoparticles and (111) Pt nanoparticles. These Pt nanoparticles were prepared according to the colloidal method [27]. In brief, solutions containing K₂PtCl₄ for (100) nanoparticles and H₂PtCl₆ for (111) Pt nanoparticles were reduced using H₂ in controlled conditions to form nanoparticles. After that, nanoparticles were cleaned with NaOH pellets and dispersed in water. Additional details on the synthesis can be found in ref. [7,26].

Pt nanoparticles were deposited on a glassy carbon support, and dried during 15–20 minutes in Ar atmosphere. After the drying, Pt nanoparticle samples were cleaned using CO adsorption and stripping, but avoiding the use of high potential values to preserve the surface structure order. Cyclic voltammetry was used to assure the correct cleaning of the platinum nanoparticles. The active area was measured from the hydrogen adsorption charge after double layer subtraction using the reported reference value of 0.23 mC cm⁻² [28].

The deposition of Sn, Rh, Ru, and Pb on the nanoparticles was carried out from solutions containing SnSO₄ (Merck[®]), hydrated RhCl₃ (Aldrich[®]), hydrated RuCl₃ (Fluka[®]) and Pb(NO₃)₂ (Aldrich[®]), all of them with a purity higher than 99.8%. A very low concentration of the metal precursor was used (10⁻⁵–10⁻⁶ M in 0.5 M H₂SO₄), so that the deposition of the metal is slow and diffusion controlled. This allows the change of the adatom coverage on the surface to be followed by using the cyclic voltammogram recorded between 0.06 and 0.8 V at 0.05 V s⁻¹. The increase in the adatom coverage leads to the decrease in the hydrogen adsorption charge, as shown in previous experiments with Pd, Sb, Bi or Ti [29–32]. Thus, the coverage can be determined using the following expression:

$$\theta_x = 1 - \theta_H = \frac{q_H^0 - q_H^x}{q_H^0}$$

where q_H^0 and q_H^x are the hydrogen adsorption charges for bare and adatom modified Pt nanoparticles. This method for measuring the adatom coverage is valid for all the metals used in this work except for Rh, where new peaks appear in the voltammetric profile in the hydrogen adsorption region, due to hydrogen adsorption on rhodium. This prevents an accurate determination of the Rh coverage and for that reason an increasing order of coverage is only indicated.

Once completed the preparation of the modified electrodes, a cyclic voltammogram or a chronoamperogram were recorded in 0.2 M CH₃CH₂OH in 0.5 M H₂SO₄ or 0.1 M NaOH as supporting electrolyte, depending on the desired pH conditions. Ethanol absolute (Merck[®] p.a.), H₂SO₄ (Merck[®] Suprapur 96%) and NaOH monohydrate (99.99%, Merck[®] Suprapur) were used for preparing the solutions together with ultrapure water (Elga Purelab Ultra 18.2 MΩ cm).

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