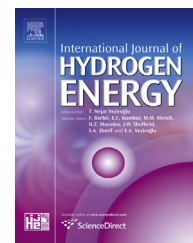




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Platinum border atoms as dominant active site during the carbon monoxide electrooxidation reaction

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ABSTRACT

In the current work the concept of the active site is analyzed. With this end, Pt was deposited on Au(111) electrode assisted by water in oil microemulsion, in which the micelles confine the formation of small Pt clusters. The presence of highly and lowly coordinated Pt atoms was finely tuned by controlling the annealing processes and confirmed by CO stripping voltammetry in conjunction with scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). This procedure allowed for the individuation of the effects of materials free and rich of catalytic defect sites on the CO electrochemical oxidation profile. Thus, a clear correlation between low-coordinated Pt atoms and the appearance of CO oxidation peaks at more negative potentials (peaks at 0.26 and 0.59 V vs. RHE) compared to high-coordinated Pt atoms (ca. 1.1 V vs. RHE) was identified.

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Introduction

One of the fundamental concepts widely applied in heterogeneous catalysis is that of “active site”. However, it is also one of the most difficult to be conceived for its experimental investigation [1]. On a catalytic metal surface, low-coordinated atoms, which are located in step, corner, and edge sites, are expected to be active sites for many catalytic

reactions. This hypothesis comes from their enhanced ability to bind catalytic intermediates respect to that of highly coordinated atoms, which are normally located in terrace sites [2].

A frequently adopted strategy for establishing the role of defects in heterogeneous catalysis is the study of the carbon monoxide electrooxidation reaction on stepped single-crystal surfaces in which the orientation of the step differs from that of the mostly close-packed (111)-type terrace [3]. Employing

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such approach, it has been demonstrated that steps of (110) orientation are the active sites in the electrooxidation of carbon monoxide adsorbed (CO_{ad}) on stepped platinum single-crystal electrodes in acidic media [4,5]. In alkaline media G. García et al. established a unique structure sensitivity for the CO_{ad} oxidation on stepped platinum single-crystal electrodes [2,6–12]. It was found that step sites of (110) orientation are more active than those of (100) orientation, whereas (111) terrace sites exhibit the lowest activity towards the CO oxidation reaction. In the same way, it was demonstrated that step site presents a “dual” role in the CO_{ads} electrooxidation reaction: CO approaching the step from the bottom is the most reactive, whereas CO sitting on top of the step is the least reactive and reacts only with adsorbed OH (OH_{ads}) on the terrace [9]. Additionally, kink, edge or step defects sites are believed to be the most active ones, and are involved in the oxidation of CO_{ads} at potentials as low as 0.3 V vs. RHE (usually called “pre-peak” potential region) [6,12]. All these different active sites (i.e. kink, step and terrace sites) could be, in principle, detected during a CO_{ads} stripping voltammogram by separate stripping peaks at corresponding characteristic potentials [12,13]. However, the study of a single process is hardly decoupled from others due to the surface mobility of reactive adsorbed species, i.e. CO [12,14].

Over the last few years, significant contributions have addressed the origin of CO preoxidation, “pre-peak”, which has been widely debated [2,4–12,15–20]. This reported enhanced catalytic activity has been attributed by electrochemistry, Fourier transform infrared spectroscopy (FTIRS) and density functional theory (DFT) to an easily water dissociation on low-coordinated Pt atoms. Currently, the most useful electrodes for this type of studies are Pt single crystal surfaces. However, single crystal electrodes contain *per se* undesirable defects (i.e. kink, edge or step defects sites) and, therefore, an unambiguous correlation of the catalytic activity with the active site is not so straightforward as desired [1–3,10].

It is remarkable that the origin of the so-called “pre-peak” is not only important from a fundamental point of view but also for applied science, since the pre-peak provides a reaction path for the CO electrooxidation reaction at low overpotentials. This phenomenon has a potential application in fuel cells due to the performance of these devices strongly depends on the surface catalytic activity [2,3,21]. In this regard, gold–platinum (Au–Pt) alloys are promising materials as electrocatalysts for fuel cells [22–24]. The interest of these materials (Au–Pt alloys) is mainly due to the fact that CO adsorbs strongly on Pt [2–5,15,16,18], but it does not adsorb on Au in acidic media [25–28]. Therefore, Au–Pt alloy materials are expected to exhibit synergic catalytic effects such as altering the electronic band structure to modify the surface adsorption strength of adsorbed species and in the best scenario suppressing the adsorption of poisonous species (e.g. CO).

In this paper a new approach involving Pt nanodisks (0.25 nm high and 5 nm wide) adsorbed on Au(111) surface as source of low-coordinated atoms to unveil their enhanced catalytic capabilities versus the CO oxidation is presented. Likewise, the goal of the present work is aimed to the conception of novel catalytic materials that can be

synthesized with a noticeable control on surface defect occurrence. Consequently, the catalytic activity of highly and lowly coordinated atoms can be discerned, and the “pre-peak” detected during the CO stripping voltammetry can be straightforwardly correlated with the presence of such structures.

Experiment measurement

Preparation of catalysts

Platinum planar clusters were prepared by the microemulsion method previously described by Guillén-Villafuerte et al. [29]. Thus, platinum clusters were obtained by reduction of H_2PtCl_6 (8% wt; Aldrich) with hydrazine monohydrate (99.0% Fluka) using a water/oil microemulsion of water/polyethyleneglycol-dodecylether (BRJ 30)/n-heptane. The size of the microemulsion droplet is determined by the molar ratio (R) of water to surfactant. In this work, R was fixed to six. The concentration of the surfactant was 16.54% w/w and that of the H_2PtCl_6 solution employed in the synthesis was 0.2 M (in the aqueous phase).

Briefly, synthesis of the Pt clusters proceeded as follows. First, two microemulsions were prepared, one of them containing hexachloroplatinic acid in the aqueous phase, and the second one containing 100% excess of hydrazine. Both microemulsions were left stirring during several hours until a clear homogeneous solution was obtained. After that, they were combined under stirring to form a single microemulsion. During the reduction process, the color of the microemulsion changed from yellow-orange to red-brown. Solid deposits were never detected, even for aged microemulsions of Pt clusters.

The procedure to synthesize the catalytic samples consists of the following steps:

A) *Sample I, defect-free catalytic surface*: 5 μL of micelles containing Pt clusters were deposited on a Au(111) surface (0.125 cm^2). In order to obtain a monolayer of micelles containing Pt onto the Au(111) surface the material was copiously washed with acetone. The last was corroborated by STM technique, in which a full monolayer of Pt disc-shaped nanoparticles of 0.25 nm high and 5 nm wide onto the Au(111) surface is discerned (Fig. 1) in agreement to that reported in ref. [29]. Afterward, the sample was heated at 300 °C under a reductive atmosphere.

B) *Sample II, high catalytic defect abundance on surface*: a second monolayer of micelles containing Pt was deposited on the Sample I. Then, the same procedure than described for the Sample I was carried out, and again the heating treatment was performed.

Electrochemical characterization

Electrochemical experiments were carried out in sulphuric acid solution prepared from high purity reagents (H_2SO_4 from Merck Suprapur) and ultra-pure water (Millipore MilliQ gradient A10 system, 18.2 M Ω cm, 2 ppb total organic carbon). Argon (N66) was used to deoxygenate all solutions and CO (N47) to dose CO. The catalytic activity of the samples was

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