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On the electrochemical properties of platinum stepped surfaces vicinal to the (100) pole. A computational study

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ABSTRACT

DFT studies on platinum stepped surfaces have been carried out in order to understand the differences in the electrochemical behavior between the surfaces with (111) and (100) terraces. Thus, adsorption energies of different species on selected surfaces have been computed. For the adsorption of Bi and Cu on the Pt(553) and Pt(711) surfaces, it has been found that the adsorption energy on the site corresponding to the step decoration for the Pt(553) surface is ca. 0.5 eV higher than that calculated on the (111) terrace sites. On the other hand, there is no preferential adsorption site for Cu or Bi on the Pt(711) surface, since the energy differences between the different sites on this stepped surface with (100) terraces are very small. CO and OH adsorption on the surfaces with (100) terraces, namely the Pt(100), the Pt(711) and the Pt(510) surfaces, has been also investigated. The energy differences between step sites and terrace sites for the surfaces are very small, ca. 0.2 eV for OH adsorption and <0.1 eV for CO adsorption. For OH, the preferred adsorption mode is a bridge mode, whereas the adsorption energy for the on top and bridge configurations of CO are similar on those surfaces. The comparison with previous DFT calculations indicates that the perturbation created by the step on the (100) terrace is significantly smaller than that created on the (111) terraces. Thus, the modification of the electrochemical properties produced by the presence of a step in the (100) terrace is minor, in agreement with the experimental results.

1. Introduction

Reactions rates in catalytic and electrocatalytic processes strongly depend on the nature of the interactions between reactants (or intermediates) and the surfaces exposed by catalysts, which, in turn, depend on the composition and structure thereof. This is clearly the case of the reactions involved in fuel cells. Both the oxidation of the possible fuels (hydrogen, methanol, formic acid, ethanol...) and the reduction of oxygen strongly depend on the composition and structure of the electrode materials.

For reactions in fuel cells, platinum is the pure metal with the overall highest catalytic activity. For that reason, its electrochemical behavior has been extensively studied [1–3]. When a detailed analysis of the effects of the surface structure in the electrochemical reactivity is pursued, platinum single crystal electrodes are normally used. This type of electrodes, with a very well defined structure, are very helpful to demonstrate how the surface structure affects the reactivity for a given reaction. From the pioneering works of Clavilier, it was clear that the electrochemical reactivity strongly depends on the surface structure of the platinum electrode [4–7]. In those studies, the so called low index planes were used, that is, Pt(111), Pt(110) and Pt(100) surfaces. Those surfaces contain only one type of site, which help in understanding the elementary steps of those reactions. The presence of only one type of site on the surface simplifies the complexity of the system and allows establishing qualitative and quantitative correlations between site and reactivity [8,9].

Although low index planes are very useful in fundamental studies, the surface structure of the real surfaces are far from the ideal low index planes. For practical electrodes, those composed by nanoparticles, their surfaces contain small ordered domains with a (100) or (111) symmetry separated by a series of atoms with a low coordination number. Although the behavior of the long-range ordered (100) or (111) domains can be assimilated to that of the (111) or (100) surfaces, the behavior of small domains and atoms with low coordination number cannot be directly correlated to the ideal basal planes. It is clear that more complex models are required to understand those practical electrodes. The use of stepped surfaces can help to bridge the gap between real surfaces and low index planes. Stepped surfaces contain terraces with a (111) or (100) symmetry separated by monoatomic rows of steps with a given symmetry. The terraces can be used to

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understand the electrochemical reactivity of the ordered domains in the nanoparticles. On the other hand, the step sites, which are composed by atoms with a low coordination number, serve as models for rest of the atoms in the surface of the nanoparticle. Thus, the different adsorption energy of hydrogen on the (100) and (111) terraces and the different step sites results in voltammetric peaks at different electrode potential. These signals have been used to elucidate the surface structure of the nanoparticles [10,11]

As in the case of the nanoparticles, the reactivity of the stepped surfaces is determined by the width and symmetry of the terrace and the symmetry of the step site. By changing the terrace width, the effect of the size of the ordered domain can be studied. For reactions very dependent on the symmetry of the terrace site, significant effects of the ordered domain size have been found. For instance, the ammonia oxidation reaction in alkaline media only occurs at a significant rate on well-ordered Pt(100) electrodes [12]. This fact explains the reactivity of the nanoparticle electrodes for this reaction, so that the highest activity is found for platinum nanoparticles with a significant ratio of large (100) domains on the surface of the nanoparticles [13]. The presence of the steps also modifies the reactivity of the electrode. For the surfaces vicinal to the (111) stereographic pole, that is, those containing terraces with (111) symmetry, significant effects in reactivity of the surface have been found. For those surfaces, the step sites are the active sites on these surfaces for the oxidation of adsorbed CO [14], the cleavage of the C-C bond in the ethanol oxidation reaction [15–18], or the formation of CO in the formic acid oxidation reaction [19–21], whereas the (111) terrace sites have a negligible activity for those processes. On the other hand, for the surfaces vicinal to the (100) pole, the reactivity of the (100) domains is much less affected by the presence of the steps. The only significant exceptions are the ammonia oxidation reaction [12] or the nitrite/nitrate reduction reaction [22]. For those reactions, an ensemble of sites with (100) symmetry is probably required, as in the case of dimethyl ether oxidation [23]. For instance, the currents for formic acid oxidation [24], methanol oxidation [25], ethanol [23], dimethyl ether [23] or oxygen reduction [26–28] are almost unaffected by the presence of steps on the (100) terraces, especially for surfaces with long terraces.

In order to understand the aforementioned differences in reactivity, experiements and DFT calculations were carried out. Four processes were considered, because they can serve as models to understand more complex reactions: the deposition of Bi or Cu, and the adsorption of CO and OH, on different platinum stepped surfaces with (100) and (111) terraces. OH and CO adsorptions are probes that can be used to determine adsorption properties of different sites, and are intermediates in fuel cell reactions, and Bi or Cu deposition can be used as a probe of the modification of the properties on the terrace created by the appearance of a step. For the surfaces with (111) symmetry terraces the surface Pt(553) was selected. This surface has five atom-wide terraces separated by (111) monoatomic steps and can be named as Pt(s)[5(111) × (111)]. Since the (111) step on a (111) terrace site defines a (110) symmetry site, this surface can also termed a Pt(s)[4(111) × (110)]. Two different surfaces, also with 4 atom wide terraces, have been chosen to study (100) stepped surfaces with (111) and (110) monoatomic steps: Pt(711) = Pt(s)[4(100) × (111)] and Pt(510) = Pt(s)[4(100) × (110)].

2. Methods

2.1. Experimental methods

Platinum single crystal electrodes were oriented, cut and polished from small single crystal beads (2.5 mm diameter) following the procedure described by Clavilier and co-workers [29]. The electrodes were cleaned by flame annealing, cooled down in H_2/Ar and protected with water in equilibrium with this gas mixture to prevent contamination before immersion in the electrochemical cell, as described elsewhere [30]. Experiments were carried out in a classical two-compartment electrochemical cell deaerated by using Ar (N50, Air Liquide in all gases used), including a large platinum counter electrode and a reversible hydrogen (N50) electrode (RHE) as reference.

The potential program for the transients was generated with an arbitrary function generator (Rigol, DG3061A) together with a potentiostat (eDAQ EA161) and a digital recorder (eDAQ, ED401). To avoid any interference of the diffusion of formic acid in the reaction rate, stationary experiments were carried out using a hanging meniscus rotating disk configuration at 900 rpm (controlled by a Radiometer CTV 101).

2.2. Computational methods.

Bi and Cu adsorption energies on different surface sites have been calculated for the stepped surfaces Pt(553) and Pt(711), whereas the low index surface Pt(100) and the stepped surfaces Pt(510) and Pt(711) have been used for calculating the adsorption energy on different sites for CO and OH. Running Dmol3 [31], adsorption energies were estimated using DFT under numerical basis sets of double-numerical quality plus polarization functions [32], DFT semi-core pseudo-potentials (which include scalar relativistic effects) [33] and the GGA-RPBE functional (which was specifically developed for catalysis applications) [34]. Brillouin zones were sampled, under the Monkhorst-Pack method [35], using grids corresponding to distances, in the reciprocal space, of the order of 0.04 1/Å. Convergence was facilitated by introducing 0.005 Ha of thermal smearing, although energies were extrapolated to 0 K. The effects of non-zero dipole moments in the supercells were cancelled by means of external fields [36].

The Pt(553), Pt(711), Pt(100) and Pt(510) surfaces were modeled by means of periodic supercells comprising 38, 30, 16 and 42 Pt atoms, respectively, corresponding to metal layer thicknesses of 9.45, 7.90, 6.04 and 7.90 Å, also respectively, and vacuum slabs of 14 Å (Fig. 1). During optimizations, the bottom 18, 14, 8 and 20 Pt atoms, respectively, were frozen in their bulk crystal locations, meanwhile the remaining 20, 16, 8 and 22 Pt atoms, respectively, were completely relaxed with the adsorbates. The shortest distances between adsorbate images were 5.70, 5.70, 5.70 and 8.06 Å, respectively. Adsorption energies were calculated as the energy difference between that corresponding to the adsorbent-adsorbate complex, after adsorption, and those corresponding to absorbent and adsorbate, before adsorption. Given that all the investigated supercells are large enough to minimize the interaction between adsorbate images (the shortest distance between adsorbate images being 5.70 Å), adsorbate energies were estimated in gas phase, and the obtained results used as a fixed reference in each corresponding adsorption energy calculation. For each adsorption site, the position of each adsorbate atom was optimized during the calculation.

3. Results

3.1. Adatom adsorption on (111) steps on (100) terraces and (100) steps on (111) terraces.

The first important difference found in the experimental behavior between the stepped surfaces with (111) and (100) terraces is the possibility of decoration of the step with a foreign adatom. It has been shown that some adatoms are able to decorate the step of a (111) terrace both in electrochemical [37–40] and UHV