Surface restructuring of Pt monolayers on vicinal Au(hkl) surfaces

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Introduction

Stepped surfaces of transition-metals have been employed as model systems to investigate several chemical and physical processes of technological interest [1, 2]. One of the main advantages of those surface models is the possibility to study the correlation between chemical and physical properties with the surface atom coordination. For example, it has been well known that under-coordinated atoms located in steps have different reactivity than atoms located in the terraces of the vicinal surfaces, which has been correlated with the shift of the electronic states of the under-coordinated atoms towards the Fermi level, and hence, enhances the reactivity. Thus, it can be concluded that stepped surface reconstruction, which occurs to lower the energy of the surface, can affects drastically the reactivity of stepped transition-metal surfaces. The restructuring of vicinal transition-metal surfaces can be induced by the adsorption of molecular species and/or the deposition of different transition-metal species [3], in which the strength of the binding energy of the adsorbate-metal and meta-metal interactions play an important role. Therefore, there is a great interest to improve our understanding of the mechanism that leads to the reconstruction of stepped surfaces. In this study, we will report an investigation of the structure reorganization of platinum films deposited on stepped surfaces of gold belonging to the [n(111)x(111)] family, employing experimental and computational techniques.

Methodology

Experimental
A RHE prepared in the base electrolyte solution was used in all experiments as the reference electrode and a gold foil as counter electrode. Electrolyte solutions were prepared from Milli-Q water and high purity reagents and Pt films were obtained from galvanic replacement of a previously deposited Cu monolayer. CO stripping experiments were performed in 0.1 mol dm^{-3} $HClO_4$ solution using a 50 mV s^{-1} sweep rate. First, high purity CO was adsorbed at 0.1 V. Ethanol electro-oxidation experiments were performed in 0.5 mol dm^{-3} ethanol + 0.1 mol dm^{-3} $HClO_4$ solution. In situ FTIR experiments were performed in a Nicolet Nexus 680 spectrometer using a planar ZnSe window to achieve frequencies down to 600 cm^{-1}. The resolution used in all spectroscopic experiments was set to 8 cm^{-1} and all spectra were taken as the average of 60 interferograms

Computational details
To investigate the possible structure of Pt layer on Au(332), different types of overlayers such as Pt/Au, PtAu/PtAu and Au/Pt were deposited on the stepped Au(332) surface using (1×2) surface unit cell as the repeated slab geometry with 54 atoms per unit cell, separated by a vacuum region of about 12 Å. During the optimization procedure all layers were allowed to relax, except for the lowest layer of Au(332) that was frozen. For

the Brillouin zone integration, we applied a 6×2×1 k-point mesh. For all optimizations, the equilibrium geometries are obtained when the atomic forces are smaller than 0.025 eV/Å on each atom, and employing a total energy convergence of 10−4 eV.

Results and Discussion

Voltammograms obtained for Pt/Au(hkl), hold some discrepancies in the hydrogen adsorption/desorption region of the voltammograms compared to results in the literature for pure Pt(554), Pt(775) and Pt(332). This suggests that Pt film do not follow the crystal orientation of the gold substrate. However, full coverage of Au substrate is inferred from the absence of Au_yO_x reduction peak in the range 1.0-1.4 V. These observations are in agreement with the fact that Pt layers should be strained since lattice parameter for Pt is slightly smaller than for Au (ca. 4% smaller). Consequently, experimental results indicate that the formation of a continuous film of Pt on an Au surface induces the reorganization of the underlying atomic layers, leading to a removal of the monoatomic steps originally present on the gold substrate. This is supported by our DFT calculations, which found that a Pt monolayer deposited on the Au(332) surface forms an almost flat (111) surface and this reconstruction contributes strongly to lower the energy of the Pt/Au(332) surface.

Regarding CO adsorption/oxidation, simulations predict a reorganization of the topmost atomic layers of the Pt/Au(332) surface due to CO adsorption, leading to the formation of a film of mixed composition. This reorganization is evidenced by a loss in Pt electroactive area after CO ad-layer oxidation. Since anodic potential cut is low, the possibility Pt dissolution is discarded. Instead, we find the situation predicted by simulations is more plausible. Hence, some Pt atoms would exchange position with the underlying Au layer forming a bimetallic film. Since energy difference between CO/Pt/Au/Au(332) and CO/Pt-Au/Pt-Au/Au(332) is relatively small, a midterm situation should prevail; i.e., surface being partially smothered by the presence of Pt and mixing of surface atoms occurs at some extent driven by CO adsorption and oxidation. In this case, smoother surface having a lower density of steps and Au ad-atoms exposed to the electrolyte would be a more accurate representation of the real surface.

Finally, change on product yields is observed for Pt/Au(775). This can be interpreted as a consequence of the surface modification underwent. In this sense, we found an increment in the amount of CO_2 produced, followed by a diminution in CH_3COOH levels. This suggests that the effect of the film reconstruction is not related to the ability of the Pt film to deal with the CO early produced, but to the ability of the new surface array to break the C-C bond of the ethanol molecule. For instance, the idea that Au domains formed on the surfaces due to Pt/Au exchange might assist the oxidation reaction has been considered in a previous paper for a polycrystalline system. Theoretical results also predict that adsorptive properties of Au and Pt are modified due to film reorganization; hence, it should be expected that reaction mechanism will be affected as well.

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