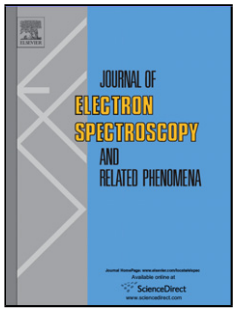

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PII: S0368-2048(17)30051-8
DOI: http://dx.doi.org/doi:10.1016/j.elspec.2017.06.005
Reference: ELSPEC 46684

To appear in: *Journal of Electron Spectroscopy and Related Phenomena*

Received date: 13-3-2017
Revised date: 31-5-2017
Accepted date: 22-6-2017

Please cite this article as: Attila Farkas, Donato Fantauzzi, Jonathan E.Mueller, Tianwei Zhu, Christian Papp, Hans-Peter Steinrück, Timo Jacob, On the Platinum-Oxide Formation under Gas-Phase and Electrochemical Conditions, Journal of Electron Spectroscopy and Related Phenomenahttp://dx.doi.org/10.1016/j.elspec.2017.06.005

On the Platinum-Oxide Formation under Gas-Phase and Electrochemical Conditions

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Highlights
We summarize our recent results on the oxidation of platinum surfaces, stressing the close connection between theory and experiment. The present theoretical approach is based on *ab-initio* quantum mechanics methods, such as density functional theory (DFT), *ab-initio* atomistic thermodynamics, Monte-Carlo methods and reactive molecular dynamics (RMD). Experimentally, photoelectron spectroscopy (XPS) under UHV and *in-situ* conditions (NAP-XPS) provides most of the discussed results. The oxidation of an extended variety of platinum surfaces is reviewed, starting from atomically flat Pt(111) to stepped surfaces to regularly shaped nanoparticles, under conditions ranging from UHV through ambient-pressures up to electrochemical interfaces. It turns out that in various cased platinum-oxides should form under reaction conditions, which should be taken into account when investigating catalytic and electrocatalytic reactions.

Abstract

We summarize our recent results on the oxidation of platinum surfaces, stressing the close connection between theory and experiment. The present theoretical approach is based on *ab-initio* quantum mechanics methods, such as density functional theory (DFT), *ab-initio* atomistic thermodynamics, Monte-Carlo methods and reactive molecular dynamics (RMD). Experimentally, photoelectron spectroscopy (XPS) under UHV and *in-situ* conditions (NAP-XPS) provides most of the discussed results. The oxidation of an extended variety of platinum surfaces is reviewed, starting from atomically flat Pt(111) to stepped surfaces to regularly shaped nanoparticles, under conditions ranging from UHV through ambient-pressures up to electrochemical interfaces.

Introduction

Recent years have witnessed an increased momentum in the extension of surface-sensitive electron spectroscopic techniques, such as X-ray photoelectron spectroscopy (XPS), originally limited to ultra-high vacuum (UHV) conditions, to a diversified range of catalytic systems with practical applications at near-ambient pressures [1–3] or in liquid and electrochemical environments [4–6]. These so-called *near ambient pressure* instruments and techniques (NAP-XPS) open the perspective of monitoring adsorbed species and oxidation states on the surface of an (electro-)catalyst in a quantitative way and in real time, even *in-situ* under relevant environmental conditions.

Platinum is a multi-facetted heterogeneous catalyst, its widespread practical applications ranging from the catalytic CO oxidation [7] and NO decomposition [8] in automobile exhaust, through the electro-catalytic reduction of CO_2 and the electro-oxidation of formic acid up to the reduction of O_2 in fuel cells [9]. In all these applications, the platinum catalyst surface is exposed to (electro-)oxidation in gaseous or in liquid environment, with far-reaching consequences for its catalytic performance. To understand the effects of surface oxidation on catalyst activity, experimental results and theoretical insight on the microscopic state of platinum surfaces under realistic *in-situ* conditions are necessary. It is notoriously difficult to experimentally analyze the oxidation state and the microscopic structure of a platinum catalyst under *in-situ* conditions, since powerful analysis methods of choice, such as XPS, are customarily limited to UHV conditions. However, XPS under ambient (gas phase) conditions is becoming increasingly accessible at synchrotron light sources [10,11] and even in the laboratory [12–14], whereas promising approaches to (quasi-)*in-situ* NAP-XPS electrochemical studies on aqueous metal/liquid interfaces have very recently been demonstrated [15–17].

There is a strong need to parallel the actual progress in experimental methods by the development of suited theoretical approaches, which would be in a position to suggest detailed microscopic interpretations of the experimental results being obtained. In the present work we summarize our recent theoretical studies based on *ab-initio* quantum mechanical methods such as density functional theory (DFT), *ab-initio* atomistic thermodynamics, Monte-Carlo methods and reactive molecular dynamics (RMD), stressing their close-knit connection with relevant experiments. The results reviewed here concern a wide range of platinum surfaces, starting from extended, atomically flat Pt(111) to stepped