Surface/Subsurface Interactions During Rh Oxidation Revealed by Atom Probe Tomography and Microscopy

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Metal catalysts may undergo a series of surface and subsurface structural and chemical transformations during a chemical reaction, which inevitably change the surface properties. Understanding such dynamics from a fundamental science standpoint is important to build rational links between chemical/structural surface properties and the desired catalytic performance. The research presented here addresses, the dynamics of early oxide formation on rhodium (Rh) single nanoparticle during O_2 exposures revealing the important role that the subsurface plays. O_2 dissociative adsorption, as well as its reaction with H_2 mainly imply the Rh{012} regions and is directly observable on Rh nanoparticles with the use of Field Ion and Emission Microscopies (FIM/FEM). Adsorbed oxygen atoms (O(ads)) resulting of the O_2 dissociative adsorption can migrate to the bulk through the surface. The combination of our observations by FEM and our observations using Atom Probe Tomography (APT) reveals an inter-facet cooperation between Rh{012} and Rh{113} during this process.

FIM and FEM are capable to image the apex of very sharp needles with nanometric lateral resolution. At the nanoscale, this apex appears as hemisphere exposing a variety of atomic planes and facets that can simultaneously probed. The shape of this sample mimics a single metal nanoparticle by its size and shape. Surfaces structures of this nanoparticle is accurately imaged by FIM. FEM analyses of the same orientations exhibit image contrast which is mainly determined by crystallographic plane-dependent variations of the work function. Consequently, a cleaned Rh surface exhibit bright {012} regions while other regions remain dark for the same conditions of image acquisition (Fig. 1a, left). Local work function variations, observed as local brightness variation in FEM, may result of the presence of adsorbates such as adsorbed oxygen atoms (O(ads)), which are known to increase the Rh surface work function [1]. O_2 adsorption, desorption and its reaction with H_2 can be monitored by following the real-time local brightness variations in video-FEM and provides insight into surface reaction kinetics. The APT is capable to provide a 3D map of the whole apex volume with atomic scale and chemical identification. Thus, APT is used to explore the nature of oxygen atom penetration in the bulk, by mapping the 3D distribution of Rh oxide and the morphology of the oxide/metal interface within the bulk after a controlled $O_2(g)$ exposure. FEM and APT observations are combined to reveal the complete path of the oxygen atoms from their formation, after O_2 dissociative adsorption on the surface, to their penetration inside of the bulk.

Experiments are initiated by imaging the Rh surface by FEM at 700 K which show local brightness over the {012} regions (Fig. 1a, left); the degree of brightness is directly proportional to the local work function. However, the progressive addition of $O_2(g)$ in the analytical chamber causes a drastic decreasing of the local brightness over the {012} regions, which is an expected behavior since that O(ads) should increase the Rh surface work function. Surprisingly, this transformation is simultaneously accompanied by the

local brightness increasing over the vicinal {113} regions (Fig.1a, right). This FEM pattern transformation can be explained by surface O(ads) diffusion into the subsurface region (O(sub)) and further into the bulk (O(bulk)), which is similarly observed on platinum surfaces by Photo Electron Emission Microscopy (PEEM) [1-2]. The subsurface bonding position of an oxygen atom can reverse the orientation of the electric dipole and thus can decrease the local work function. This anisotropic surface penetration, along with O(sub) formation on Rh{113} regions, thus can be described as the first step of Rh surface oxidation, ultimately leading to an anisotropic formation of the bulk oxide. $O_2(g)$ dissociative adsorption occurs over Rh{012} regions, but the oxygen penetration into the Rh bulk occurs under the {113} regions: the first steps of Rh oxidation result of an inter-facet cooperation process. Finally, APT is used to follow the oxygen atoms path inside of the bulk. Following a 600 s exposure of O_2 (2.0×10^{-2}Pa) at 700K of a pristine Rh needle (i.e. no native surface oxide), APT analysis reveals the anisotropic distribution of Rh oxides (RhO$_X$) and the complex morphology of the oxide/metal interface. An enhanced density of RhO_X^{n+} (x = 1 or 2 and n = 1 or 2) species are found both under the (111) central plane and along only one of the two three-fold symmetric crystal zones comprising the {113} facets (Fig.1b). The 3D reconstructions highlight a deep penetration of the oxygen under the central (111) for the most advanced oxidation states (Fig.1c). With an angle of 29.5° between (111) and its vicinal {113} facets, oxygen atoms are able to penetrate deeper inside the bulk along this direction and enhance accumulation under the (111) facet.

The combination of FEM and APT analysis delivers new insight into the Rh oxide formation. We find the O_2 dissociative adsorption mainly occurs over the Rh{012}, and the resulting O(ads) penetrate the metallic layer through {113} and {111} forming both O(sub) and subsequently higher coordinated positions inside the bulk. This work offers exciting perspectives leading a better and more fundamental understanding of the heterogenous catalysis as well as corrosion dynamics [3].

References:
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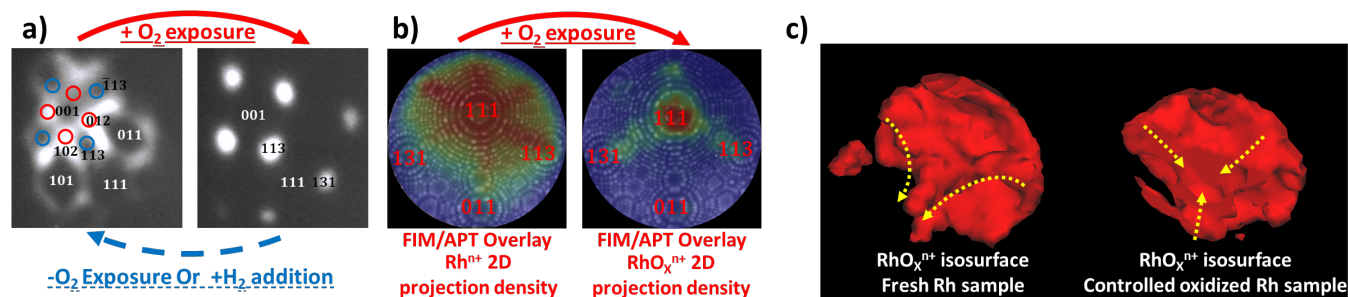
Figure 1. (a) FEM images of a Rh (001) oriented surface before and after O_2 exposure at 700 K (P(O_2)=1.0×10^{-5} Pa, F=2.0 V.nm^{-1}). Original FEM pattern can be retrieved with the simultaneous addition of H_2 (P(H_2)=3.6×10^{-3} Pa). (b) 2D atomically-resolved FIM surface projection of (111) apex-oriented Rh (blue) with an overlay 2D APT density projection of Rh ions (Rh^{n+}; left) and Rh-oxide (RhO_x^{n+}; right) after O_2 exposure. Note the enhanced RhO$_X$ density along only *one* of the 2×3-fold symmetries along the the {113} facets. (c) RhO_X^{n+} APT isodensity surfaces of a naturally-oxidize Rh specimen (left) and same specimen after removal of natural oxide and controlled oxidizing treatment (right).