

Subsurface Oxygen Formation during H₂ Oxidation over Rh, Pt and Pt-Rh Model Nanoparticles.

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Metal catalysts may undergo adsorbate-induced alterations which may range from local reconstructions to overall 3D morphological shape transformations. Such structural alterations are inherently associated with changes in the chemical composition of the catalysts and therefore influence the catalytic performance. In case of *bulk* chemical and structural transformations, subsurface diffusion of atomic species is a necessary prerequisite. However, the penetration of the surface will depend on the local metal atom configurations and therefore cannot be expected to occur with a unique rate across the surface of a 3D metal particle. Ultimately, such local surface modifications may be involved in the emergence of non-linear dynamics [1]. The details of the interdependence between the structure and the reactivity and a fundamental understanding of these processes can be studied through a molecular scale investigation with model nanoparticles. In this context, we studied the O₂ dissociative adsorption over single nanoparticles of Rh, Pt and Pt-Rh (17at.% Rh) surfaces, as well as the interaction of atomic O(ads) species with H₂. The samples were prepared as sharp tips with apices of similar size and shape as those of a single nanoparticle of catalyst exposing a wide variety of crystallographic surface facets. These apices can be imaged by Field Ion and Emission Microscopies (FIM and FEM) at the nanoscale (FEM) and even with atomic lateral resolution (FIM). FEM images are formed by field-emitted electrons, the current of which depends on the local work function. The latter is influenced by the local structures as well as by the chemical nature of surface and subsurface species. Therefore, the FEM patterns for an ongoing reaction reflect the variations of local chemical and structural transformations and can be used to monitor the surface reaction while it proceeds.

O₂ dissociative adsorption and subsequent subsurface oxygen diffusion are observed at 700 K under pressures ranging between 10⁻⁴ and 10⁻⁵ Pa. Starting from clean metallic surfaces, the FEM patterns of Rh, Pt and Pt-Rh depict the local lowest work function areas corresponding to {012} facets. Once the sample is exposed to O₂, the brightness of these {012} regions decreases and remains dark, testifying the occurrence of local O₂ dissociative adsorption. As matter of fact, the presence of O(ads) notoriously increases the work function on both Rh and Pt. While {012} facets darken, the local brightness of {113} regions drastically increases (**Figure 1.a**). This counterintuitive observation can be explained by the diffusion of oxygen atoms into subsurface positions - denoted O(sub) - of the {113} facets. Photo Emission Electron Microscopy (PEEM) experiments have shown that the migration of O-species below the surface induces an inversion of the electric dipole formed with Rh and Pt atoms, causing a decrease of the local work function [2,3].

In another set of experiments, oxygen gas pressure is kept constant and hydrogen is introduced in the

chamber. This addition triggers a surface reaction observed via a drastic brightness increase of the {012} facets. This phenomenon reflects O(ads) removal from the surface in form of H₂O(g) following its reaction with H(ads). By maintaining a constant pressure of H₂ while varying the O₂ pressure, a dynamic phase diagram can be plotted to define the regions of reactivity. These diagrams reveal a region of bistability for P_{H₂}/P_{O₂} ratios between 0.5 and 2.5.

Within the same pressure range, on Pt-Rh, non-linear dynamics are observed in the form of periodic oscillations over {012} regions (**Figure 1.b-c**), for an O₂ pressure between 2.0×10⁻³ Pa and 4.0×10⁻³ Pa and a H₂ pressure between 2.0×10⁻³ Pa and 3.0×10⁻³ Pa. This type of phenomenon has been previously reported by in the NO₂+H₂ system over Rh, Pt and Pt-Rh [4,5]. The observation of changes in the {113} regions of Pt-Rh suggests that O(sub) and inter-facets dynamics are fully involved in this periodic process [6].

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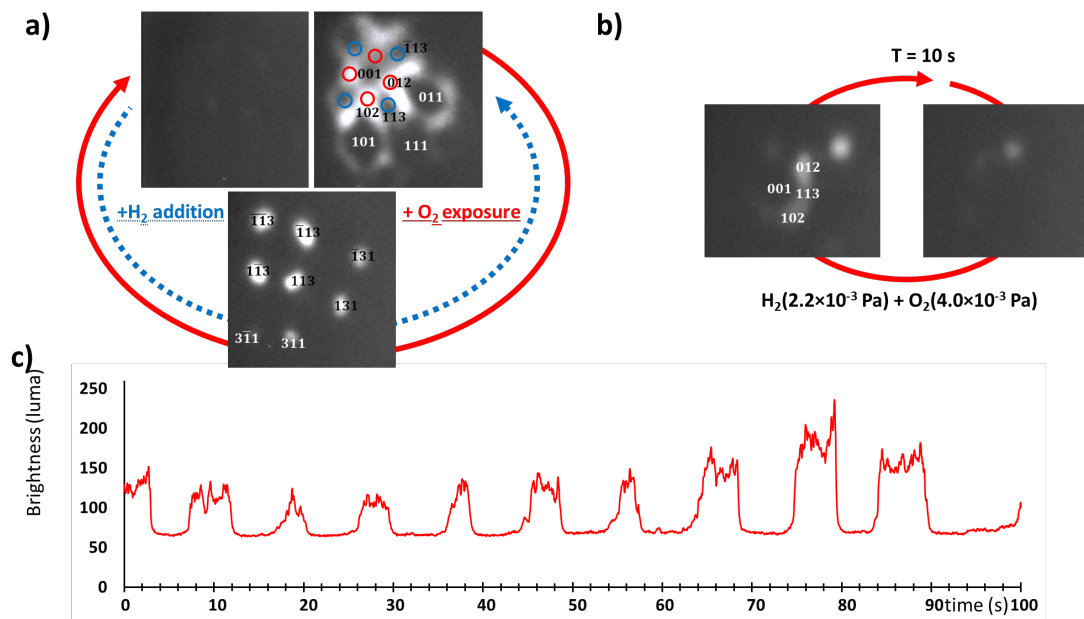


Figure 1. a) FEM pattern evolution during O₂ exposure on Rh catalysts at 700 K. The observed transition is reversible under exposure to H₂ gas. The same trend is observed for Pt and Pt-Rh; b) FEM patterns appearing periodically during the H₂+O₂ reaction at 700 K (respectively with 2.2×10⁻³ Pa and 4.0×10⁻³ Pa); c) Time series of the average brightness probed for the {012} regions during a H₂+O₂ exposure at 700 K, exhibiting oscillations with a period of 10 s.