

## Nanoscale Imaging of Subsurface Oxygen Formation on Rhodium Catalysts.

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During a catalytic process, a catalyst may undergo changes of its structure or morphology, as well as modifications of its local composition, which is due to oxidation/reduction processes, surface segregation, or even the presence of subsurface species [1]. All these modifications may affect the activity and the selectivity of the catalyst and contribute to the ageing of the catalyst. To develop catalysts with improved efficiency, a fundamental understanding of the catalytic process is needed. The shape of the nanoparticle, its size, its local chemical composition and the synergistic influences of these features on the catalytic activity must be determined, down to the molecular level, to unravel the details of this reaction. Such studies gain significance if they are performed during the ongoing process so as to highlight transient behaviors that cannot be observed before and after reactions.

In this work, we studied the adsorption O-containing molecules (CO<sub>2</sub>, N<sub>2</sub>O, O<sub>2</sub> and CO) at the surface of rhodium catalysts, as well as the interaction of O-containing molecules with H<sub>2</sub>. Experiments are performed using field emission techniques *i.e.* Field Emission Microscopy (FEM) and Field Ion Microscopy (FIM). Samples are prepared as sharp tips, the extremity of which is imaged at the nanoscale (FEM) and even with atomic lateral resolution (FIM). The size and the morphology of the apex part are well-suited to model a single catalytic grain, presenting a variety of crystallographic facets in communication. The brightness intensity of the FEM pattern depends on the amount of electrons locally emitted from the nanocrystal. The current density depends on the work function, which is influenced by the presence and nature of adsorbates. Probing the brightness signal thus allows to monitor surface reactions while they proceed.

CO<sub>2</sub> adsorption and dissociation are reported for temperatures ranging between 200 and 700 K under pressures ranging between  $1.0 \times 10^{-4}$  and  $5.0 \times 10^{-3}$  Pa. Starting from a clean sample and before any exposure, the FEM pattern corresponds to mainly the presence of {012} facets since their work function on Rh is the lowest (**Figure 1.a(left)**). When the sample is exposed to CO<sub>2</sub>, the brightness of these {012} facets drastically decreases and remains dark: this phenomenon reflects the CO<sub>2</sub> dissociative adsorption leading to the presence of O(ads) increasing the work function (thus decreasing the brightness). At the same time, the brightness from the {113} facets increases, leading to a typical FEM pattern that can be observed on **Figure 1.a(right)**. Since O(ads) increase the work function, this observation can be explained by the formation of subsurface oxygen O(sub) beneath the {113} facets. Comparative experiments were performed in similar conditions with N<sub>2</sub>O, O<sub>2</sub> and CO gases. The exposure to N<sub>2</sub>O and O<sub>2</sub> leads to the same pattern evolution, presumably due to their dissociative adsorption leading to the presence of O(ads) at the surface which migrates as O(sub). However, exposure to CO gas does not induce any changes in the pattern, except the expected general decrease in brightness due to the adsorption. This is a further proof that the presence of O(ads) is a prerequisite to

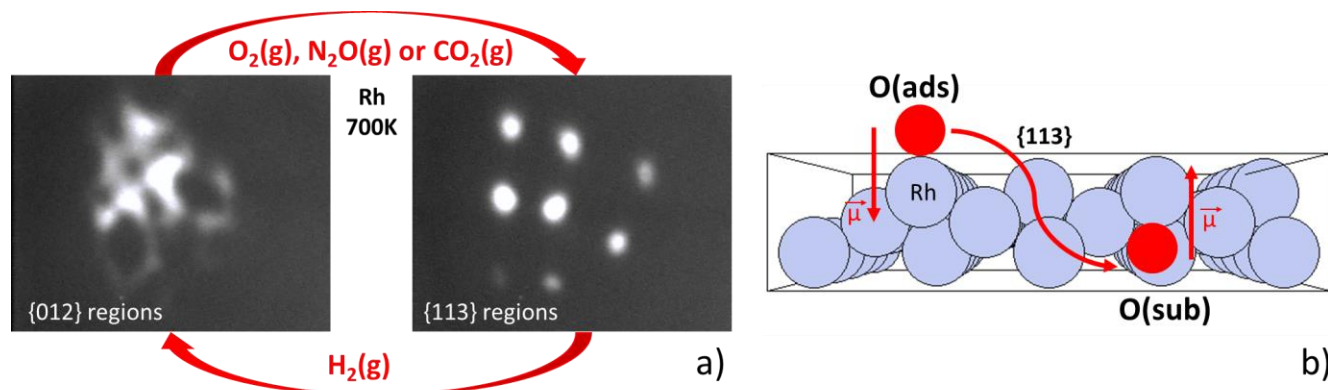
observe the pattern modification. The presence of surface oxygen notoriously increases the local work function of the surface. It is indeed known that the migration of O-species below the surface induces an inversion of the electric dipole  $\vec{\mu}$  formed with Rh atoms (**Figure 1.b**), which causes a decrease of the local work function [2,3].

The reversibility of the formation of subsurface oxygen has been tested by introducing H<sub>2</sub> gas in the reaction chamber while the CO<sub>2</sub> pressure is maintained. Reaction phenomena are observed, and the FEM pattern evolves back to its initial state, proving the occurrence of reaction between the H(ads) and the O(sub), which is supposed to migrate back to the surface to react. For the sake of comparison, reaction phenomena were also observed with N<sub>2</sub>O+H<sub>2</sub>/Rh and O<sub>2</sub>+H<sub>2</sub>/Rh systems in similar experimental conditions. However, the CO+H<sub>2</sub>/Rh system did not present any changes.

The dissociation adsorption of O-containing molecules has been studied by Field Emission Microscopy, leading to the presence of O(ads) and subsequent formation of subsurface species O(sub) with a drastic effect on the FEM pattern. Adding hydrogen in the reaction chamber allows to study the reversibility of the O(sub) formation. The presence of O(sub) is a transient phenomenon which only appears on some crystallographic orientations: this has to be taken into account to get a better understanding of the catalytic process and could not have been observed without real-time FEM experiments. [4]

#### References:

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**Figure 1. a)** Modifications of the FEM pattern during the exposure of O-containing molecules on Rh catalysts at 700 K: FEM pattern where (left) {012} facets are the brightest and (right) {113} facets appear brighter due to the formation of subsurface oxygen. This transition is reversible under exposure to hydrogen gas. **b)** Schematic representation of the mechanism leading to a different FEM pattern during the presence of subsurface oxygen.