



# Oxygen assisted reconstructions of rhodium and platinum nanocrystals and their effects on local catalytic activity of hydrogenation reactions



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## ABSTRACT

The reconstruction of rhodium and platinum crystals of some tens of nanometres diameter was investigated during the ongoing hydrogenation of oxygen atoms resulting from the dissociation of O<sub>2</sub> and NO<sub>2</sub> species. Field ion and field emission electron microscopies (FIM and FEM) were used to characterise the apex of tip samples before, during and after the catalytic reactions. On rhodium samples, the exposure of less than 10 Langmuir of O<sub>2</sub> is sufficient to induce significant morphological changes. At higher exposures, the presence of subsurface oxygen causes surface reconstructions illustrated with atomic resolution by FIM at 50 K. The same pattern is also visible at 505 K in the presence of H<sub>2</sub> and O<sub>2</sub> during water production. Upon the decrease of H<sub>2</sub> pressure, surface oxidation shows a strong sensitivity to the local surface initiated along the {001} zone lines.

On platinum, the kinetic instabilities of the NO<sub>2</sub>–H<sub>2</sub> reaction are followed by FEM at 390 K starting from a hemispherical tip sample. The instabilities are expressed as surface explosions occurring randomly in time, but synchronised over {011} facets. These instabilities expand along the {001} lines over the {001} pole and exhibit self-sustained kinetic oscillations. The analysis of the tips by FIM after the reaction shows dark regions over the {113} facets, suggesting the extension of those to the detriment of vicinal ones. A well-controlled field evaporation procedure reveals that these regions appear dark due to the presence of surface oxygen. Structural reconstructions are observed but do not lead to the drastic morphological changes suggested by the FIM and FEM patterns. Nanoparticle dynamics must be accounted in models describing the non-linear features of catalytic reactions and more generally included in the description of catalytic properties of nanosized particles.

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## 1. Introduction

Catalytic reactions often take place on surfaces conditioned in the form of nanoparticles to increase the surface/volume ratio. These particles frequently undergo structural modifications during adsorption and/or reaction. Due to their size and shape, such crystals display a variety of different facets which may exhibit a different reactivity towards a given chemical reaction. On a single 3D-crystal, every single crystal facet has its own surface free energy that contributes to the total free energy. As pointed out by Gibbs [1] for macroscopic systems, the equilibrium shape corresponds to a minimum of total free energy. As corollary, Wulff [2] introduced a simple relationship allowing easy predictions of crystal shapes when specific surface free energies are known, as well as the calculation of the relative free energies of the various crystallographic

faces when the equilibrium crystal shape is known. However on the nanometric scale, Wulff's predictions become questionable since the model does not consider the increasing importance of corner and edge atoms. On the basis of a number of theoretical models, Marks calculated that Wulff constructions are effective for crystals down to 20 nm diameter [3]. In the presence of reactive environments, the heat of adsorption of species often depends on the local structure [4,5]. Adsorption can modify not only the local surface energy but also the metal–metal interaction in such way that the mobility of some atoms may lead to new morphologies. As the latter may influence the catalytic process, operando reconstructions must be assessed experimentally in catalysis studies over supported formulations. One striking example is the reconstructions observed in the *in situ* transmission electron microscopy of supported copper nanocrystals [6]. In that work, hydrogen and water have antagonist effects over the crystal shapes which can then be fine-tuned. With the aim at bridging the gap between surface science studies and the applied world of catalysis, the investigation of these morphological/structural transformations during the reaction and

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their influences over the local catalytic activity is one step beyond the studies over single crystal planes [7]. Moreover, the very first atomic layers can undergo changes in their chemical nature (the presence of an oxidation layer [8,9], and the presence of subsurface oxygen [10] are some examples) and dramatically influence the reactivity and/or selectivity [11,12].

Field ion and field emission electron microscopies (FIM, FEM) allow the study of reconstructions of nanocrystals before, during and after the reaction with nanoscale lateral resolution. The very apex of the tip is imaged and closely approaches the structure of one single nanoparticle. Both methods provide a way to investigate the influence of these changes over the catalytic activity.

From a quasi-hemispheric nanoparticle, reconstructions may be thermally activated [13], and/or assisted by the addition of reactive gas species at the surface of the catalyst [14]. In some cases, one adsorbate species is sufficient to increase the mobility of the surface atoms, whereas in other cases, the reaction between two species forms the surface compound responsible for surface reconstructions [15]. These reconstructions may be reversible or not [16]. In most cases, it is a subtle combination of the applied temperature and gas exposure that leads to a variety of reconstructed particle shapes, making theoretical predictions of the latter difficult. The synergistic effects of the temperature, gas composition, local surface reactivities and local surface energies variations upon adsorption require experimental techniques such as FIM and FEM used in this work or *in situ* high resolution microscopies such as scanning tunnelling [17], scanning electron or transmission electron microscopies [6] (STM, SEM; HRTEM). The aim of this work is to provide direct evidences of reconstructions during ongoing reactions between H(ads) and O(ads) species proceeding over Rh and Pt surfaces. Two case studies are put in contrast: the  $O_2$ – $H_2$  reaction over Rh and the  $NO_2$ – $H_2$  reaction over Pt.

## 2. Experimental setup

Field ion microscopy (FIM) and field electron emission microscopy (FEM) are methods suitable for the purpose of this work. Their principles are described in reference [18]. Two setups that have been described earlier are used for this study. The first one is a field ion/electron microscope mainly used as a flow reactor allowing operando observations of the kinetics of surface processes over the visible surface area of the sample [19]. The second device is a “catalytic atom probe” allowing FIM and atom probe studies of samples before and after exposures in a dedicated reaction cell enabling exposures in a reactive environment without further exposure to air [20]. Atom probe experiments allow the direct investigation of the depth of the oxidation layer in a metal tip sample, as well as segregations in alloys [21,22]. Only FIM studies will be discussed in the present paper.

Samples are prepared in the form of sharp tips and are used as model catalysts. Platinum and rhodium tips are etched from metal wire of high purity in a molten salt mixture of NaCl and  $NaNO_3$  (1:4, w/w). A voltage of 2.1 V<sub>DC</sub> is applied for ~12 s to obtain a sharp tip. The sample is cleaned with distilled water and its profile is checked by optical microscopy. After introduction in the main chamber, the sample is cleaned by cycles of *in situ* treatments which are summarised as follows. Thermal annealing to approximately 600 K is made to remove residual impurities and to smoothen residual protrusions and irregularities on the tip apex to reach a symmetric shape. Field evaporation is visually followed by FIM to develop the tip. It consists of the application of a high electric field so that the surface atoms which protrude the most are evaporated as ions. Since continuous field evaporation occurs layer by layer, it presents a convenient method for cleaning tip specimens. If field evaporation turns out to be insufficient to completely remove

unwanted impurities, ion sputtering by means of Ne ions has to be applied. After further field evaporation, the tip exhibits a so-called field evaporation end form which corresponds to the instant shape under the conditions of ongoing field evaporation. The diminishment of the electric field seizes that structure ( $P_{Ne} = 10^{-3}$  Pa,  $F_{tip} = 30$ – $35$  V nm<sup>-1</sup>,  $T = 50$ – $60$  K). This approximately corresponds to a hemispherically shaped nanocrystal where the crystallographic orientations are clearly visible. Although many authors have discussed the influence of field evaporation procedures over the tip profiles [23–25], control experiments by HRTEM proved that in the present work, a field evaporation end form closely – but not perfectly – fits to a hemispherical shape.

The determination of the radius of curvature is usually estimated by counting the number of atomic planes between two known orientations. The radius range of the samples is typically between 10 and 50 nm.

## 3. Results and discussions

### 3.1. $O_2$ /Rh and $O_2$ – $H_2$ /Rh

The reconstruction patterns over rhodium after exposure to oxygen gas ( $O_2$ ) (99.998% purity) imaged by FIM are presented here and compared to the field ion micrograph captured during  $O_2$ – $H_2$  reaction. Despite the different experimental conditions used for the two sets of experiments, the similarity of the pictures is quite remarkable. In an earlier work, Voss et al. used Rh field emitter tips to demonstrate the polyhedral reshaping in the presence of  $O_2$  at temperatures between 500 and 550 K under field-free conditions [26]. Fig. 1a shows a clean Rh sample after field evaporation following the procedure described in Section 2. As previously mentioned, a series of controlled characterisations of the field evaporation of end forms of tip samples has been undertaken by HRTEM. The results are summarised into one micrograph shown in Fig. 1b. This depicts a rather large Rh tip but the field ion image shows the same features as that of Fig. 1a. Starting from the sample shown in Fig. 1a, a dose of 10,000 Langmuir ( $1 L = 1.3 \times 10^{-4}$  Pa s) is introduced to the sample at 390 K. After oxygen dosing, the removal of some 30 Rh layers by field evaporation is sufficient to restore the nearly hemispherical sample morphology. The next step corresponds to heating for 30 s at  $T = 500$  K in the absence of gaseous oxygen, which causes the polyhedral reconstruction shown in Fig. 1c. This is taken as a direct indication of reversible oxygen subsurface diffusion since a clean Rh crystal does not suffer reshaping at this temperature. It is therefore ascertained that the dissolved oxygen atoms diffuse from the bulk to the surface and trigger the reported reconstruction. Moreover, a much lower dose of 0.5 L of  $O_2$  over a clean Rh tip at  $T = 500$  K in the absence of electric field is sufficient to reach the same result [8]. During the reconstruction process, the only high-index planes present in the reconstructed form are of  $\{1\ 3\ 7\}$  symmetry. They appear as twins on either side of the  $\langle 100 \rangle$  zones lines. Local reconstruction forms of the missing-row type are identified in  $\{0\ 1\ 1\}$  and  $\{1\ 1\ 3\}$  planes, which is similar to STM results obtained with extended single crystal surfaces [27,28]. The fact that the local reconstruction of the missing-row type can be clearly identified on field emitter tips is interesting from the viewpoint that planes do not exist independently but may communicate with each other via diffusing adsorbates. It is also interesting to note that in the context of adsorbates-induced restructuring, the  $O_2$ – $H_2$  reaction on Rh is observed to occur on a tip reshaped to a polyhedron. Fig. 1d shows a field ion micrograph captured during  $O_2$ – $H_2$  reaction over Rh at  $T = 505$  K. The  $H_2$  pressure is kept sufficiently high to avoid surface oxidation [29]. We mention that this picture has been acquired on a different tip sample and has been rotated so as to highlight the common features with Fig. 1c. Despite a lower

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