# 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 $\mathrm{O}_{2}$ and $\mathrm{NO}_{2}$ 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 $\mathrm{O}_{2}$ 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 $\mathrm{H}_{2}$ and $\mathrm{O}_{2}$ during water production. Upon the decrease of $\mathrm{H}_{2}$ pressure, surface oxidation shows a strong sensitivity to the local surface initiated along the $\langle 001\rangle$ zone lines.

On platinum, the kinetic instabilities of the $\mathrm{NO}_{2}-\mathrm{H}_{2}$ 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 $\langle 001\rangle$ 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

[^0]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
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 $\mathrm{H}(\mathrm{ads})$ and O (ads) species proceeding over Rh and Pt surfaces. Two case studies are put in contrast: the $\mathrm{O}_{2}-\mathrm{H}_{2}$ reaction over Rh and the $\mathrm{NO}_{2}-\mathrm{H}_{2}$ 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 $\mathrm{NaNO}_{3}$ $(1: 4, \mathrm{w} / \mathrm{w})$. A voltage of $2.1 \mathrm{~V}_{\mathrm{DC}}$ is applied for $\sim 12 \mathrm{~s}$ 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 socalled 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 $\left(P_{\mathrm{Ne}}=10^{-3} \mathrm{~Pa}\right.$, $F_{\text {tip }}=30-35 \mathrm{Vnm}^{-1}, T=50-60 \mathrm{~K}$ ). 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. $\mathrm{O}_{2} / \mathrm{Rh}$ and $\mathrm{O}_{2}-\mathrm{H}_{2} / \mathrm{Rh}$

The reconstruction patterns over rhodium after exposure to oxygen gas $\left(\mathrm{O}_{2}\right)$ ( $99.998 \%$ purity) imaged by FIM are presented here and compared to the field ion micrograph captured during $\mathrm{O}_{2}-\mathrm{H}_{2}$ 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 $\mathrm{O}_{2}$ 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 ( $1 \mathrm{~L}=1.3 \times 10^{-4} \mathrm{Pas}$ ) 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 $T=500 \mathrm{~K}$ 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 $\mathrm{O}_{2}$ over a clean Rh tip at $T=500 \mathrm{~K}$ 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 $\{137\}$ 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 $\{011\}$ and $\{113\}$ 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 $\mathrm{O}_{2}-\mathrm{H}_{2}$ reaction on Rh is observed to occur on a tip reshaped to a polyhedron. Fig. 1d shows a field ion micrograph captured during $\mathrm{O}_{2}-\mathrm{H}_{2}$ reaction over Rh at $T=505 \mathrm{~K}$. The $\mathrm{H}_{2}$ 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


Fig. 1. (a) Field ion micrograph of a clean ( 001 )-oriented Rh tip (imaging conditions $T=60 \mathrm{~K}, F=37 \mathrm{~V} \mathrm{~nm}^{-1}, P_{\mathrm{Ne}}=10^{-3} \mathrm{~Pa}$ ). The arrow indicates a little stacking defect. (b) Control HRTEM picture of a field evaporation end form of a tip developed to a FIM pattern similar as in (a). (c) Same Rh sample as in (a) after exposure to oxygen ( $\sim 10,000 \mathrm{~L}$ at $10^{-4} \mathrm{~Pa}$ ) in the absence of field at $T=390 \mathrm{~K}$ followed by field evaporation leaving oxygen dissolved into the bulk. The image is taken after a subsequent heating of 30 s duration at $T=500 \mathrm{~K}$ of the field evaporated crystal (imaging conditions $T=63 \mathrm{~K}, F=35 \mathrm{~V} \mathrm{~nm}^{-1}, P_{\mathrm{Ne}}=10^{-3} \mathrm{~Pa}$ ). (d) Field ion micrograph of a Rh tip at $T=505 \mathrm{~K}$ exposed to a $\mathrm{O}_{2}-\mathrm{H}_{2}(1: 2)$ gas mixture at a total pressure of $4.5 \times 10^{-3} \mathrm{~Pa}$. The imaging species are $\mathrm{H}_{2} \mathrm{O}^{+}$ions resulting from the ionisation of the reaction product.
(Panel dis reprinted with kind permission from Springer Science and Business Media).
resolution as compared to Fig. 1c, it is recognised that the tip has undergone a transformation to coarser and polyhedral structure. Reduced resolution does not allow here for a possible missing-row type reconstructions of the $\{011\}$ and $\{113\}$ facets. However, the extension of the $\{137\}$ twin facets is clearly visible as dark regions of both sides of the $\langle 100\rangle$ zone lines. Obtaining a relatively well resolved micrograph in the presence of hydrogen raises questions about the instant surface composition and species responsible for image formation. The removal of oxygen from the analysis chamber - but leaving the hydrogen present - causes the picture to darken immediately. We carry out the experiments at a modest field value of $12 \mathrm{Vnm}^{-1}$. Because of its low ionisation potential ( 12.1 eV ), $\mathrm{O}_{2}{ }^{+}$ can then be expected to contribute at least partially to the image formation. One-dimensional atom probe confirmed that it is indeed the case [29]. The same method has also highlighted intense mass signals at $M / Z$ ratio of 18 and 19 , which is why we assume that the water ions $\left(\mathrm{H}_{2} \mathrm{O}^{+}, \mathrm{H}_{3} \mathrm{O}^{+}\right)$resulting from the reaction between the reactants are the imaging species. The formation of water under these conditions over Rh is the subject of a well-documented literature [30-32].

Reconstructions observed under reaction conditions (Fig. 1d) are undoubtedly assisted by oxygen. A morphological change to a polyhedral shape is never observed in experiments with hydrogen alone, neither in the presence of an electric field, nor in its absence. This conclusion is reinforced by a series of blank experiments where freshly developed tips are heated to $500-550 \mathrm{~K}$ prior
to various chemical treatments under ultra-high vacuum in the presence of a field of $9-10 \mathrm{Vnm}^{-1}$. These experiments do not lead to reconstructions as those reported in this work. At most, after heat treatments of some 10 min , a slight modification in size is detected for the topmost ( 001 ) plane. Similarly, a small displacement of atoms is observed over the rough surfaces as $\{012\}$ facets but this is dissimilar to well-defined structures shown in Fig. 1c.

Extended $\{137\}$ facets remain stable within a temperature range between 480 K and 530 K . This is visualised by comparing the morphology of the sample at three different temperatures. Fig. 2 shows the morphological evolution of the same tip sample exposed to the same gas mixtures at increasing temperatures: 505 K (Fig. 2a), 550 K (Fig. 2b) and 600 K (Fig. 2c). Without any modification of the experimental parameters, the picture of Fig. 2a remains unchanged and shows the extension of $\{137\}$ twin faces. Fig. $2 \mathrm{~b}(T=550 \mathrm{~K})$ shows a somewhat different structure which also persists within the duration of the experiment. For the results reported here, micrographs captured at one chosen temperature are persistent for some tens of minutes. In this case, the dark regions near the centre correspond to the $\{113\}$ facets, located between the central pole and the four $\{111\}$ peripheral poles. The extension of $\{113\}$ facets is accomplished to the detriment of their vicinal orientations at higher temperature. The same applies for the drastic extension of the $\{011\}$ facets, located over the $\langle 011\rangle$ zone lines that interconnect the most stable peripheral $\{111\}$ planes.


Fig. 2. Field ion micrographs of a Rh tip exposed to a $\mathrm{O}_{2}-\mathrm{H}_{2}(1: 2)$ gas mixture at a total pressure of $4.5 \times 10^{-3} \mathrm{~Pa}$ at increasing temperatures. The viewing field is estimated to $\sim 10 \mathrm{~V} \mathrm{~nm}^{-1}$. (a) $T=505 \mathrm{~K}$, (b) $T=550 \mathrm{~K}$ and (c) $T=600 \mathrm{~K}$.

Fig. 2 c is recorded at 600 K and shows the further extension of $\{011\}$ and $\{111\}$ faces at the periphery of the tip. Interestingly, the $\{113\}$ faces that are extended at an intermediate temperature of 550 K are reduced in size in favour of $\{011\}$ and $\{111\}$ faces. It should be noted that at 550 K , the morphological transformation of the tip is sufficiently advanced to allow a direct communication between the $\{011\}$ and $\{113\}$ faces. As compared to the pattern of Fig. 2a, the tip apex undergoes a major morphological transformation that would require the field evaporation of many layers before the restoration of the quasi-hemispherical shape. A further
increase of the temperature to 650 K can be tried but the FIM pattern shows signs of a significant field evaporation made visible through the shrinkage of dense $\{111\}$ and ( 001 ) poles. Meaningful interpretation of the morphological changes in the presence of evaporation becomes difficult and probably of a lower scientific relevance. Despite the occurrence of this process, the apex maintains its polyhedral morphology instead of moving back towards a hemispherical structure. In this context, it is reasonable to assume that the mobility of rhodium atoms is sufficiently important in the presence of oxygen to ensure a stable polyhedral 3D morphology.


Fig. 3. (a) Field ion micrographs of a Rh tip at 550 K during exposure to a $\mathrm{O}_{2}-\mathrm{H}_{2}$ (1:2) gas mixture at a total pressure of $4.5 \times 10^{-3} \mathrm{~Pa}$. (b) same sample imaged under neon gas $\left(10^{-3} \mathrm{~Pa}\right.$ ) at $T=51 \mathrm{~K}$ with a viewing field of $\sim 32 \mathrm{Vnm}^{-1}$. (c) Same as in (b) during field evaporation of rhodium atoms at $F \sim 40 \mathrm{~V} \mathrm{~nm}^{-1}$. (d) Field evaporation end form after the removal of several tens of atomic layers.

 ( $T=390 \mathrm{~K}, F=4 \mathrm{Vnm}^{-1}, P_{\mathrm{H}_{2}}=1.85 \times 10^{-4} \mathrm{~Pa}, P_{\mathrm{NO}_{2}}=5.4 \times 10^{-6} \mathrm{~Pa}$ ). (a) 200 ms before the maximum intensity of the surface explosion. (b) At the highest intensity and (c) 400 ms after explosion. (d) Brightness signal over a few cycles of reaction for the ( 011 ) and ( 001 ) facets, showing the qualitative activity of both facets. Probed regions correspond to red and blue circles respectively shown on (a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

Visual information of the mobility of atoms along the surface is however not reached at this resolution. We note that FEM patterns of the same system are very similar to FIM ones. This is due to the poor resolution of the FIM method under these conditions and the relatively high electric field present on edge and corners sites of the crystal. If the resolution of the images taken at high temperatures is low but satisfactory, the origin of the contrasts can still give rise to discussions. Fig. 3a is the rhodium tip imaged at 550 K already presented in Fig. 2b. The morphological change seems obvious, but this reconstruction needs to be assessed at low temperature, and therefore with high-resolution, to confirm the interpretation and conclusions drawn from pictures taken under the reaction conditions. This assessment is well illustrated in Fig. 3b that shows the micrograph of the same tip at 51 K after having replaced the reactive gas mixture by neon gas. Remarkably, the conclusions that can be extracted from viewing the tip at high temperature are confirmed by a more detailed analysis at atomic lateral resolution. In this case, the transformation resulted in a significant extension of the faces with small Miller indices as previously discussed. This is manifested by the presence of dark extended areas. The lack of brightness in these regions is an indication of their major extension: the movement of rhodium atoms - probably in the form of mobile $\mathrm{Rh}_{x} \mathrm{O}_{y}$ species - to sites of greater stability caused the appearance of flat areas where the electric field becomes lower. Fig. 3c shows the structure visible shortly after the beginning of field evaporation: the dark regions are reduced in size and still do not show any structural detail. This is in line with the interpretation of a
drastic morphological transformation. The evaporation of several tens of atomic layers is mandatory here to recover the classical quasi-hemispherical shape (Fig. 3d). As we will see it in the next section, this relatively simple interpretation unfortunately does not apply for the case of the $\mathrm{NO}_{2}-\mathrm{H}_{2}$ over platinum tips despite similar patterns.

We address the question of the sensitivity of the surface oxidation of Rh to the local structure at different temperatures. As mentioned, all the field ion patterns of Rh observed in the presence of a reactive gas mixture have been intentionally acquired under reducing conditions allowing the observation of a surface in a metallic state. Previous works from our group have described in details the effects of the variation of the $\mathrm{H}_{2}$ pressure while keeping the $\mathrm{O}_{2}$ pressure constant [29]. To summarise these results, the decrease of the $\mathrm{H}_{2}$ pressure leads to a surface oxidation. At temperatures ranging from 400 K to 500 K , the latter occurs first along the $\langle 001\rangle$ zone lines and leads to a typical cross-like pattern that corresponds to a local surface oxidation. The quadrants defined by the cross remain in a metallic state. At even lower $\mathrm{H}_{2}$ pressure, the quadrants undergo surface oxidation within a fraction of a second, independently and in random order [33]. Raising the temperature up to 550 K diminishes the structure sensitivity towards surface oxidation which then occurs in a quasi-isotropic way, from the top to the outskirts of the tip apex with only a little preference for $\langle 001\rangle$ lines [34]. Ultimately, well-defined and fixed experimental conditions allow for the observation of alternating oxidation of the whole visible surface area, followed by fast removal of the




 referred to the web version of the article.)
oxide layer in a self-sustained oscillatory way [35]. The outcome of these data indicate that at temperatures above 550 K , the drastic morphological changes of the tip apex have a limited influence over the relative rates of surface oxidation of the different reconstructed facets made visible by FIM. At lower temperatures -505 K and lower - the reported reconstructions imply a lower number of displaced Rh atoms. However, the structure sensitivity of the surface oxidation process is clear over the $\langle 001\rangle$ zones. Expressed in a different way, the effects of an increasing temperature on the local structure sensitivity to surface oxidation are dominating the effects of morphological transformations.

## 3.2. $\mathrm{NO}_{2}-\mathrm{H}_{2} /$ Pt and $\mathrm{O}_{2} / \mathrm{Pt}$

This section reports on the occurrence of cyclic kinetic instabilities during the $\mathrm{NO}_{2}-\mathrm{H}_{2}$ interaction over Pt tip samples. Focus is put on the transient period starting from a freshly developed quasi-hemispherical Pt tip to a supposedly polyhedral shape. The transition from the first to the second is expressed by the evolving reactivity of some planes (Figs. 4 and 5).

The field evaporation end form of the catalyst is imaged with high resolution by FIM before and after the reaction. The reaction itself and related patterns during the ongoing reaction are followed by FEM. Whereas the details of the dynamics won't be discussed in this paper but will be presented elsewhere [36], emphasis is put here on the transient behaviour of kinetic instabilities, starting from a clean Pt sample exposed to reactive gases to the observation of
synchronised self-sustained kinetic oscillations over well-defined regions along the visible surface area. The main observations that can be made in FEM mode during the ongoing process are presented. The reaction between $\mathrm{NO}_{2}$ and $\mathrm{H}_{2}$ on Pt samples shows self-sustained kinetic instabilities that are expressed as peaks of brightness around the $\{011\}$ facets. Interestingly, their ignition is synchronised within the time resolution of our video recording device ( 40 ms ). This suggests the presence of a strong diffusional coupling, the details of which are not fully understood today. During the first minutes of the interaction, only $\{012\}$ and $\{011\}$ facets are active for the given reaction. After a time delay of some 15 min , facets located along the $\langle 100\rangle$ zone lines become active, as well as the ( 001 ) centre. Finally, during the whole process, the $\{113\}$ and $\{111\}$ facets remain totally inactive for the reaction.

In the first case, at the beginning of the reaction, the tip apex is freshly developed and exhibits a quasi-hemispherical shape already illustrated by Fig. 1b. The interaction starts by the occurrence of kinetic instabilities that are most active over the $\{012\}$ and $\{011\}$ facets. The monitoring of the brightness signal intensity provides a qualitative estimation of the catalytic activity. Fig. 4a-c shows snapshots of the field emission patterns during the catalytic reduction of $\mathrm{NO}_{2}$; before, during and after a peak of brightness. For clarity, FEM micrographs have been processed to enhance the contrast between active and non-active facets. The treatments are equally applied to all the FEM micrographs presented in Figs. 4a-c and 5a-c. The time series that monitor the brightness during 15 to 25 s are acquired on raw video digitised


Fig. 6. Field ion micrographs of a (001)-oriented platinum tip sample (expect b). (a) Clean sample, field evaporation end form (imaging conditions: $T=29 \mathrm{~K}, F=44 \mathrm{~V} \mathrm{~nm}^{-1}$, $P_{\mathrm{He}}=2 \times 10^{-3} \mathrm{~Pa}$ ). (b) Field electron micrograph of a ( 001 )-oriented platinum tip sample. (c) After treatment to oxygen gas ( $P_{\mathrm{O}_{2}}=2 \times 10^{-3} \mathrm{~Pa}$ at 300 K during 180 s ; imaging conditions $T=170 \mathrm{~K}, F=22 \mathrm{Vnm}^{-1}, P_{\mathrm{H}_{2}}=2 \times 10^{-3} \mathrm{~Pa}$ ). (d) same as in (c) with $T=145 \mathrm{~K}$. (e) After replacement of the imaging gas from $\mathrm{H}_{2}$ to helium; imaging conditions ( $T=29 \mathrm{~K}, F=37 \mathrm{~V} \mathrm{~nm}^{-1}, P_{\mathrm{He}}=2 \times 10^{-3} \mathrm{~Pa}$ ). (f) Same as in (e) with $F=43 \mathrm{~V} \mathrm{~nm}^{-1}$.
files without prior image processing (Figs. 4d and 5d). Only a few reaction cycles are shown out of video sequences of usually several tens of minutes for fixed control parameters. The topmost ( 001 ) and peripheral ( 011 ) probed regions are indicated by circles in Figs. 4a and 5a. The mean brightness within these circles is measured using an open source programme [37]. The values are expressed in greyscale levels in the 8 bits dynamic range of the digitization, from 0 (black) to 255 (white or signal saturation). For easier visualisation, the brightness signal of the (011) facet has been shifted upwards by 20 levels of brightness to easily distinguish the two different signals. Although a brightness signal cannot be linearly related to the instant local catalytic activity, one can
however qualitatively assume that catalytic activity on the ( 001 ) pole is significantly lower than on the $\{011\}$ peripheral facets. The corresponding curves in Fig. 4d clearly highlight the difference in activity between the ( 001 ) and ( 011 ) facets.

The sequence of Fig. 5 has been captured 15 min after that of Fig. 4. After this time delay, the activity of the catalytic grain becomes visible along the $\langle 100\rangle$ zones and on the topmost (001) centre, as illustrated in Fig. 5b. As in the previous case, Fig. 5a-c depicts field emission patterns during a surface explosion. It is shown on those snapshots that the ( 001 ) centre is now an active facet of the catalyst. This evolution results from the progressive reconstruction of the Pt tip sample. The brightness signal of Fig. 5d
highlights the relative catalytic activity of (001) and (011) facets. Although the brightness on (001) is lower than that of (011) in Figs. 4 and 5 , it is obvious that the intensity of $(001)$ is increasing with time. In the present case, we will see that the extension of the active areas is in accordance with the control experiments described in Fig. 6. The inactivity of $\{113\}$ and $\{111\}$ facets is visible on both Figs. 4 and 5. Although enlarged dark regions suppose their extension to the detriment of surrounding high Miller-index planes, we suggest that the lack of brightness is due to the presence of chemisorbed oxygen atoms which inhibit local field emission. On the basis of earlier works [38], the temperature of 390 K is too low to cause surface oxidation, i.e. the subsurface diffusion of oxygen atoms and the formation of an oxide layer. The oxidation of platinum nanoparticles in the presence of $\mathrm{NO}_{x}$ is only observed at higher temperature ( $\sim 573 \mathrm{~K}$ ) [38]. During the hydrogenation process, $\mathrm{NO}_{2}$ gas species adsorb and dissociate to $\mathrm{NO}(\mathrm{ads})$ and O (ads). The latter is an active species which reacts with fast diffusing $\mathrm{H}(\mathrm{ads})$ atoms to form water [39]. From the reported field emission patterns, the surface explosions indicate the location of an ongoing catalytic conversion. This is supported by the fact that between surface explosions, adsorbed oxygen is present and notoriously increases the work function [40]. The local current density of emitted electrons is lowered accordingly. The reaction of O (ads) with H (ads) causes the local work function to decrease within some 200 ms . This phenomenon is translated to a sudden peak of the local brightness which actually images surface regions that are transiently metallic. Subsequent adsorption of $\mathrm{NO}_{2}$ and its dissociation over these areas causes the field emission patterns to darken. A particular attention is paid to the $\{113\}$ facets which do not show brightness peaks. Moreover, these regions extend with time. This can be attributed either to an important extension of these regions which are less reactive towards the $\mathrm{NO}_{2}-\mathrm{H}_{2}$ reaction, or to the occurrence of a more complex adsorption process which acts on the local field emission. Previous studies show that the dissociative adsorption of $\mathrm{NO}_{2}$ is hindered on surfaces that are pre-covered by oxygen [41]. This raises the question of the exact role of NO (ads) in the reported data. The local surface composition of the tip samples during ongoing processes can be determined by one dimensional atom-probe. The question of the instant surface concentration of NO (ads) on different regions of the tip is unfortunately not solved today. However, it is suggested that the adsorbed oxygen is less active than on the $\langle 100\rangle$ zone lines and inhibits the dissociative adsorption of $\mathrm{NO}_{2}$ gas. The reported data call for systematic studies with atom-probe, so as to directly quantify the evolution of the local surface compositions with time.

To assess the morphological shape of the Pt tip after reaction, controlled characterisation, at atomic resolution using helium as imaging gas at low temperatures, are presented in Fig. 6 and lead to conclusions different from those drawn for Rh. Fig. 6 shows a series of snapshots of a Pt tip sample exposed to pure oxygen. Fig. 6a is a classical high-resolution FIM micrograph of the field evaporation end form of a pure and clean Pt , together with Miller indices of the main facets, as well as the [ $\overline{110]}$ and [100] zone lines. This figure represents an example of initial state for the experiments presented (Fig. 4). Fig. 6b shows a typical field emission pattern of the sample. After having exposed the tip to $5 \times 10^{-3} \mathrm{~Pa}$ of pure oxygen gas at 300 K in the absence of field, the surface can be imaged at 300 K with pure hydrogen as imaging gas. At such temperature, the resolution of the micrograph - not shown - is limited and the brightness is low. No surface reaction is observed. Care is taken to avoid the occurrence of field evaporation. Fig. 6c shows the sample imaged with hydrogen at 170 K . The $\{111\}$ facets appear dark and a careful analysis reveals their well-defined triangle shapes. The (001) centre evolves towards a square form as compared to a circle in Fig. 6a. This structural changes are rather minimal, but indicate the occurrence of a surface mobility of Pt atoms in the presence of

O(ads) species. By decreasing the temperature to 145 K still with hydrogen as imaging species (Fig. 6d), the square ( 001 ) centre is preserved. The facets lying along the $\langle\overline{1} 10\rangle$ direction ( $\{113\}$, $\{115\}$, \{1 12 \}) appear darker. The structural change observed in Fig. 6c and d seems responsible for the drastic increase of the catalytic activity at the top-most $(001)$ facet during $\mathrm{NO}_{2}$ hydrogenation presented (Fig. 5). The FEM patterns of the latter are easily reproduced on different tip samples. Like for the rhodium case study, this image indicates the presence of a strong morphological reconstruction. However, this interpretation is likely to be wrong in the present case.

A further decrease of the temperature down to 29 K is presented in Fig. 6e. Helium gas is used here instead of hydrogen. Under these conditions, crystal planes lying along the $\langle 100\rangle$ lines are atomically resolved. Facets along the [ $\overline{1} 10$ ] line appear dark although they were visible at higher temperatures (see Fig. 6c). The tip morphology may be modified by preferential field evaporation [23,24]. The experiment was conducted here to avoid field evaporation as much as possible. Less than one single atomic layer has been evaporated between Fig. 6d and e. In Fig. 6f, the dark regions centred by the $\{113\}$ facets are now resolved by field ionisation of helium atoms in the presence of a higher imaging field. Note that a careful analysis of the sample excludes the occurrence of field evaporation between the two micrographs. The conclusions of that observation differ from the rhodium case where field evaporation of several tens of atomic layers - counted on the bright regions - is necessary to restore the original field evaporation end form. In the case of Pt , the difference between Fig. 6e and f has its origin in the imaging process. The presence of an O (ads) layer over the $\mathrm{Pt}\{113\}$ and vicinal facets surface is proposed. Its presence can drastically decrease the ionisation probability over the sample. This is in good agreement with previous experimental data obtained by field ion appearance energy spectroscopy [42] and might be associated with the lack of a resonance mechanism according to the theoretical concepts developed by Kreuzer and Wang [43].

## 4. Conclusions

Field emission techniques were used to study the morphological and structural changes occurring over rhodium and platinum nanosized model catalysts.

When a clean sample of rhodium is exposed to pure oxygen at 390 K and subsequently field evaporated, dissolved oxygen assists in the morphological reconstruction after heating the sample at 500 K for 30 s . The $\mathrm{O}_{2}-\mathrm{H}_{2}$ reaction on Rh in reducing conditions can be imaged by FIM at 500 K . Quite remarkably, the patterns are similar and show the extension of $\{137\}$ twin faces. At higher temperatures - up to 600 K - the extension of $\{113\}$ and $\{011\}$ facets is achieved to the detriment of their vicinal orientations. The origin of imaging contrast of these dark extended areas is due to the extension and the flattening of the facets leading to a polyhedral morphology. The $\mathrm{O}_{2}-\mathrm{H}_{2}$ reaction shows a structure sensitivity towards surface oxidation at temperatures of 505 K and lower, and occur first along the $\langle 001\rangle$ zone lines. This effect is less and less observed at increasing temperatures. A cross comparison of the influence of the temperature and the tip morphologies indicates that reconstructions have only a limited influence on the reactivity at temperatures above $\sim 500 \mathrm{~K}$.

The case of platinum is rather different. Catalytic $\mathrm{NO}_{2}$ hydrogenation is investigated via FEM mode at 390 K . The brightness signal resulting from the water production is followed in real-time and the level of brightness is used as a qualitative indicator of the local catalytic activity. The most active facets for the reaction appear to be the $\{011\}$ and $\{012\}$. Inversely, the $\{113\}$ and $\{111\}$ remain dark and inactive during the whole process. The ( 001 )-centre is
inactive when the catalytic grain is fresh, but its activity becomes significant after approximately 15 min of reaction. The brightness in FEM is due to the emission of electrons from the sample, which depends on the local work function. The presence of oxygen species at the surface increases the work function. The inactivity of the $\{113\}$ and $\{111\}$ facets may thus be due to the presence of oxygen adsorbates at their surface. Control experiments by FIM at different temperatures show that the FEM pattern during the reaction at 390 K is very similar to the FIM pattern at 145 K . Cooling the sample down to 29 K and imaging it in helium allows the observation of $\{113\}$ and $\{111\}$ facets with atomic resolution, without further field evaporation on the total visible surface area. The presence of oxygen species on the $\{113\}$ and $\{111\}$ facets decreases the ionisation probability of helium and is considered to explain the extension of dark patterns. From these control experiments, we conclude that Pt undergoes only limited structural changes during the ongoing $\mathrm{NO}_{2}-\mathrm{H}_{2}$ reaction at 390 K . These have however important consequences over the activity of the ( 001 ) plane which turns to be active as the reconstruction proceeds. The comparison of the two case studies shows that even if the systems are similar, the results on one metal cannot be transferred to another without reserves.

The approach proposed in the present paper shows how one reaction proceeds at the molecular level and how the catalyst behaves during in situ conditions, and the synergistic effects between the catalyst structure and the adsorption of reactants. The study of the reconstruction of catalytic nanoparticles under different reactive conditions by field emission techniques is relevant to obtain information to successfully design nanoparticles with higher catalytic activity/selectivity for a given system.

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