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- 1st September for experiments carried out up until January of the same year.

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- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Structure of the Pt (997) step surface "in operando" during the oxidation of CO.	**Experiment number:** SI-2432
Beamline:	**Date of experiment:** from: 13.06.2012 to: 19.06.2012	**Date of report:** 28.02.2014
Shifts:	**Local contact(s):** Olivier Balmes	*Received at ESRF:*

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Report:

The experiment was consisting on investigating the structure of Pt(977) under reaction conditions ($CO+O_2 \rightarrow CO_2$) at 200 mbar total gas pressure and revealed that the reaction induces the formation of surface steps and that the optimal step generation occurs when the mixture of the gas has the reaction stoichiometry ([CO] / [O2] = 2).
We report here new results on in situ CO oxidation experiments near atmospheric pressure on a vicinal Pt(977) surface, which consists of a periodic array of equally separated monatomic steps, where we have identified the role of the steps on the reaction rate not by measuring the evolution of the width of the diffracted peaks from the surface lattice as previously, but by monitoring the evolution of the intensities of the diffracted peaks arising from the step array itself. In our experiments, the partial pressures of CO and O2 during the reaction were always kept outside of the self-sustained oscillatory regime described in Ref. [1].

Introduction and results

At T=0 K, a simple cubic model of a crystal with first and second nearest neighbour interactions predicts an equilibrium crystal shape consisting in (100), (110) and (111) faces with sharp edges between them. A vicinal surface close to a low index face would be stable, on the basis of simple thermodynamic arguments, if the interaction between steps is repulsive which is often the case even considering entropic terms at non zero T [2] . However, experiments show that the above prediction is too simplistic and fails in many cases. Vicinal surfaces are often unstable and undergo faceting, step bunching and/or surface reconstructions. In addition, gas adsorption or metal deposition on vicinal surfaces may also cause destabilization of the ideal, bulk terminated, surface morphology. Relevant examples are the oxygen induced step doubling in Pt and Ni (997) [3,4] and the oxygen induced step bunching and faceting on Rh(553) [5]. Faceting and step bunching diminish the step density and originate larger flat areas (terraces) than the original surface.

We investigated the oxidation of CO on Pt(977). The crystal was mounted in the flow reactor of ID3 that was installed in the diffractometer in EH1. The surface was initially prepared with standard UHV methods. At room temperature the reaction rate was below our detection limit. At T=90-100C, CO_2 production was clearly detected with a gas analyser. The central result is that whereas the mixture of CO and O_2 did not cause any change in the surface morphology when the reaction did not proceed (between room temperature and ~100 C) , it originated an increase of the surface density of monoatomic steps and a decrease of the (111) facets when CO_2 was produced. More important, the step generation and (111) facet reduction occurred optimally only when the proportion of the reactants was close to the stoichiometric 2:1 CO/O_2 ratio. The correct reactant proportion stabilize the (977) surface , an excess of O_2 or CO rapidly causes the increase of the (111) facets at the expenses of the (977) areas.
The figure below illustrates the first of above claims.

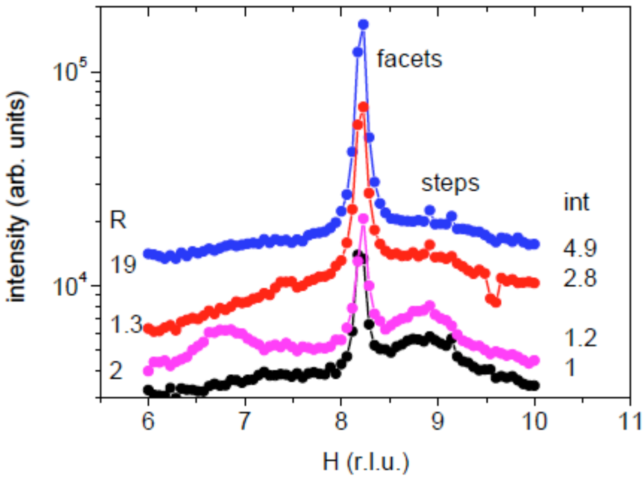

Fig 1. Reciprocal space H scans (K=1, L = 4) under reaction conditions at T ~190 C and different values R of the relative concentration of CO and O_2. The bottom curve (black) corresponds to the initial state of the surface under reaction conditions at R= 2. It exhibits a sharp central peak due to (111) faceting and also a broad peak at H ≅ 9 due to the step periodicity. The intensity of the central peak is defined as 1 and displayed at the right side of the figure. If the ratio R is diminished to 1.3 (oxygen rich mixture), the facet peak intensity increases to 2.8 and the step peak diminishes strongly (red curve) . If R= 19 (very rich CO mixture) the facet intensity reaches 4.9 and the step peak completely vanishes (blue curve) . Setting again R= 2 causes the facet peak to decrease to 1.2 and the reappearance of the step peak (magenta) . The vicinal surface becomes more ordered that at the beginning since an additional step peak shows up at H ≅ 7. The stability range for regular steps is very small, $\Delta R = 0.15 \pm 0.05$, as seen in the figure below.

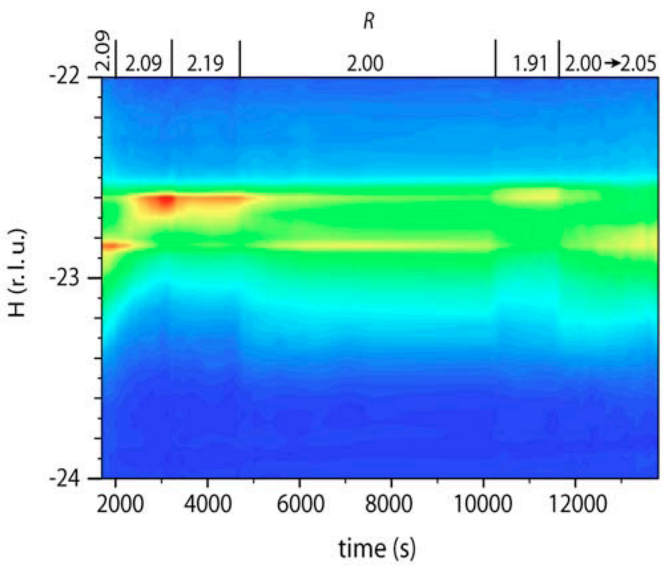

Fig. 2 represents the variation with time of the diffracted intensities during a reaction at different R values ranging from 2.19 to 1.91. The intensity at H = -22.8 that arises from regular surface steps is only visible at the part of the time interval where R= 2.0.
(The step array has a periodicity slightly different from the original interstep distance which would originate a peak at exactly H=-23.) . Alternatively, the intensity at H= -22.6 which originates from the facets, is most pronounced at R= 2.19 and 1.91 i.e. it is maximum when the step intensity is minimum. Interestingly the behaviour is reversible.

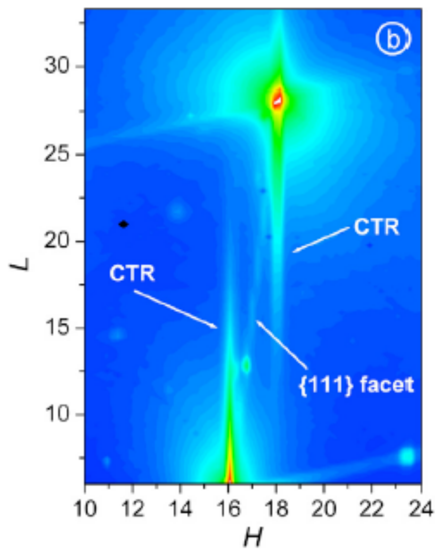

Fig. 3 shows a portion of the H–L plane (at K = 0) of reciprocal space and the corresponding diffracted intensities. In addition to the Bragg reflections from the bulk of the crystal which have the largest intensities, the diffuse streaks (CTRs) of intensity emanating from the Bragg reflections and parallel to the L axis are evident. They are fingerprints of the 977 plane at the surface. The inclined streak of intensity in the figure arises from 111 surface facets [6].

Conclusions

1. Under reaction conditions near atmospheric pressure, the Pt surface is faceted and consist of (977) and (111) regions.
2. The density of monoatomic steps, monitored by the intensity of the diffracted peaks arising from the periodic step array, is máximum when the reactants have the stoichiometric proportions. Under these conditions, the reactivity of the surface is máximum.
3. Departure of stoichiometry reduces the density of monoatomic steps that can be recovered by setting back the stoichiometric proportions.

References

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