

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

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

### **Instructions for preparing your Report**

- 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.



	<b>Experiment title:</b> Reaction induced step generation on vicinal Pt surfaces	<b>Experiment number:</b> CH-3712
<b>Beamline:</b>	<b>Date of experiment:</b> from: 12.06.2013 to: 18.06.2013	<b>Date of report:</b> 28.02.2014
<b>Shifts:</b>	<b>Local contact(s):</b> Olivier Balmes	<i>Received at ESRF:</i>

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**Report:**

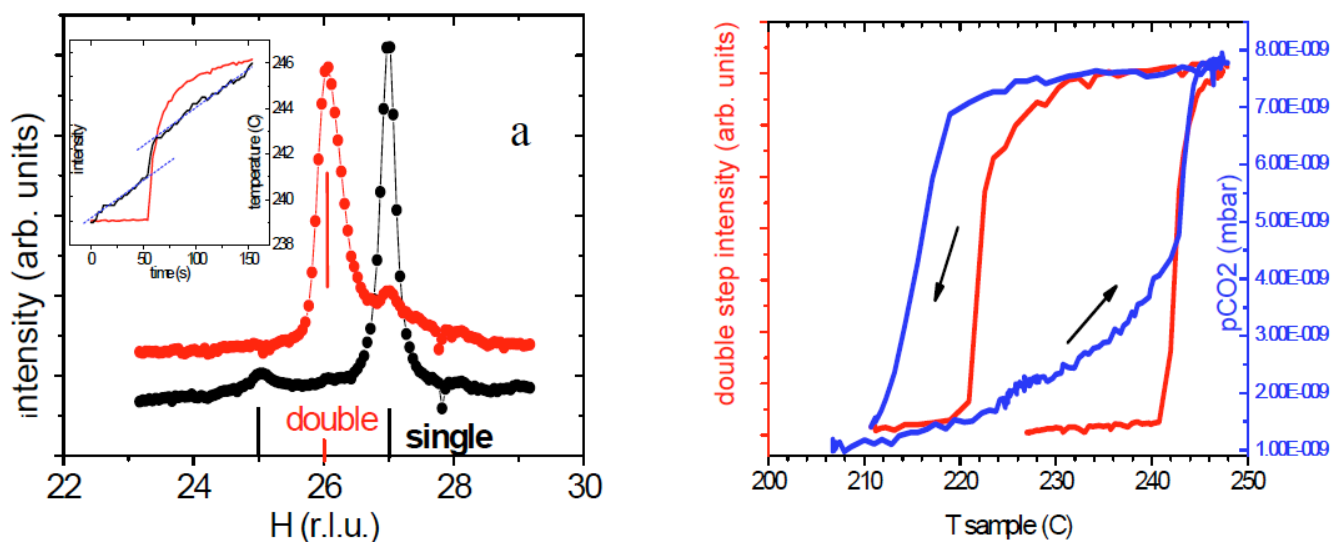
The main aim of the experiments on the oxidation of CO to CO<sub>2</sub> on Pt<sub>997</sub> near atmospheric pressure was to compare the results with those obtained from Pt<sub>977</sub> (SI-2432). Both surfaces are very similar and differ only in the structure of the steps (100 vs 111 for 977 and 997 respectively). Our previous results in the 977 surface [1] indicated that under reaction conditions the actual surface consisted in 977 and 111 coexisting areas the proportion of which was dependent on the stoichiometry of the gas mixture. The nominal CO/O<sub>2</sub> = 2/1 gas proportion was associated to maximum reaction rate and maximum density of monoatomic steps. Departure of these conditions diminished the rate of production of CO<sub>2</sub> and the density of monoatomic steps at the expenses of an increase of 111 facet areas.

The 997 surface behaves completely differently. We observed that in a stoichiometric gas mixture, upon increasing the sample temperature the reaction rate increased steadily until *ca.* 220 °C where a clear sudden jump on the reactivity occurred that was associated to a transition from single to double steps. Lowering the temperature caused single steps to appear again at the expenses of the double steps. The jump in reactivity was also accompanied by the formation of 111 surface facets (as in the 977 surface) which degraded the reversibility of the single/double step transition. However, it was found out that by diluting the CO and O<sub>2</sub> reactants in Ar while keeping the total pressure invariant, the 111 faceting was completely eliminated and a good reversibility single/double steps occurred. Under these conditions the reaction rate exhibited a clear and marked jump directly correlated to the transformation from single to double stepped surface. Lowering the temperature reverted to low reactivity and single steps. We consider this as an outstanding result since it clearly demonstrates that higher reactivity is associated to double steps and lower reactivity to single steps.

## Results

We investigated the oxidation of CO on Pt(997). 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  $T=90-100\text{C}$ ,  $\text{CO}_2$  production was clearly detected with a gas analyser. The central result is that whereas the mixture of CO and  $\text{O}_2$  did not cause any change in the surface morphology when the reaction did not proceed (between room temperature and  $\sim 100\text{C}$ ), it originated an increase of the surface density of monoatomic steps and a decrease of the (111) facets when  $\text{CO}_2$  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/ $\text{O}_2$  ratio.

Figure 1 (left side) illustrates the single step/double step transition observed in Pt997 under reaction conditions in aAr rich gas mixture (total gas pressure 200 mbar). The black curve is a H scan (perpendicular to the direction of the steps) which exhibits peaks at  $H=25$  and  $27$  characteristic of equally spaced single steps separated by terraces of 8 atoms in width. The red curve has the main peak at  $H=26$  which arises from the doubling of the dimensions of the terraces that results from the formation of double steps although a small peak at  $H=27$  from monoatomic steps still remains. The inset of the figure shows in red the temporal evolution of the intensity of the double height step peak while the sample temperature was being increased with the ceramic heater and the transformation single to double atomic height steps was occurring (the black H scan evolved to the red one). The sudden and rapid increase of the intensity is a consequence of an exponential dependence of the rate of formation of double steps with a time constant of few seconds. The sample temperature depicted in black exhibits two approximately linear regimes (marked with blue dashed lines) which correspond to the linear temporal increase of the current of the sample heater. However, between  $t=50$  and  $60$  seconds the sample temperature has a jump which coincides with the formation of the double steps. The rate of increase of the sample temperature is about 6 times larger during the transition than before or after and it is in fact a fingerprint of the reaction rate as depicted in the right side of figure 1. Again, in red the intensity of the double steps are displayed and in blue the signal of  $\text{CO}_2$  measured with the mass spectrometer while the temperature is first increased (bottom branch of the loop), then lowered (top branch of the loop). The transformation double/single steps is reversible with hysteresis and it was observed many times.



## References

- [1] O. Balmes a, G. Prevot b, X. Torrelles c, E. Lundgren d, S. Ferrer, Journal of Catalysis 309 (2014) 33–37