



## 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 using the **Electronic Report Submission Application**:

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

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

Reports can now 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.



**Experiment title: Time-resolved in-situ EXAFS/XANES study of low temperature catalytic oxidation of CO and Hydrocarbons on Pt and CoO catalysts**

**Experiment number:**  
CH-865

<b>Beamline:</b> ID24	<b>Date of experiment:</b> from: February 2, 2000 to: February 5, 2000	<b>Date of report:</b> February 24, 2004
<b>Shifts:</b> 18	<b>Local contact(s):</b> Dr. Sakura Pascarelli	<i>Received at ESRF:</i>

**Names and affiliations of applicants (\* indicates experimentalists):**

Lic. Eng. Jonas Jansson \*

Dr. Erik Fridell \*

Dr. Anders Palmqvist \*

Dr. Magnus Skoglundh \*

Lic. Eng. Peter Thormählen \*

Dr. Lars Österlund \*

Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96  
Göteborg, Sweden

**Report:**

**On the Catalytic Activity of  $\text{Co}_3\text{O}_4$  in Low-Temperature CO Oxidation**

Jonas Jansson, Anders E. C. Palmqvist, Erik Fridell, Magnus Skoglundh, Lars Österlund, Peter Thormählen and Vratislav Langer

Journal of Catalysis, 211 (2002) 387-397

**Abstract**

Oxidation of CO over  $\text{Co}_3\text{O}_4$  at ambient temperature was studied with flow reactor experiments, and in-situ spectroscopic and structural methods. The catalyst deactivates during the reaction. The rate of deactivation increased with increasing CO or  $\text{CO}_2$  gas phase concentration but decreased with increased  $\text{O}_2$  concentration or increased temperature. Regeneration of the catalyst in 10%  $\text{O}_2/\text{Ar}$  was more efficient than regeneration in Ar alone. The presence of carbonates and surface carbon on the deactivated catalyst was concluded from TPO experiments. None of these species could, however, be correlated with the deactivation of the catalyst. In-situ FTIR showed the presence of surface carbonates, carbonyl, and oxygen species. The change in structure and oxidation state of the catalyst was studied by in-situ XRD, in-situ XANES, XPS, and flow reactor experiments. One possible

explanation for the deactivation of the catalyst is a surface reconstruction hindering the redox cycle of the reaction.

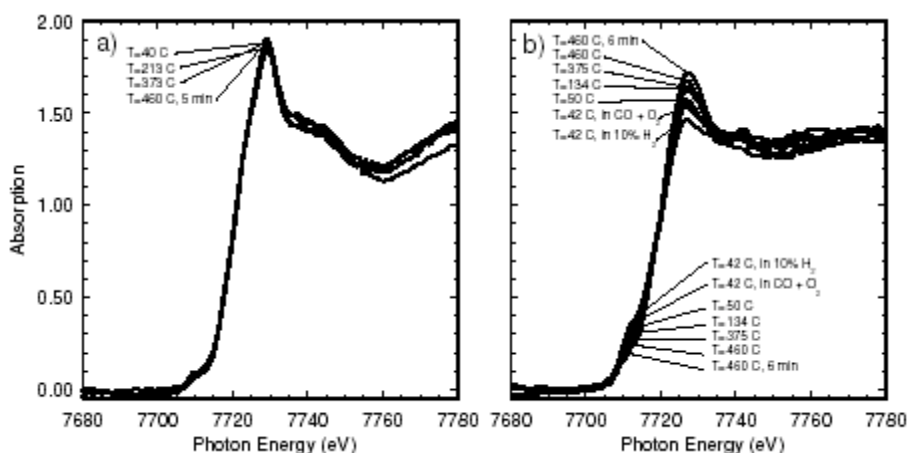


Figure 1. Co K-edge XANES analysis during CO oxidation in 1% CO+1% O<sub>2</sub> over (a) preoxidised Co<sub>3</sub>O<sub>4</sub> and (b) prerduced Co<sub>3</sub>O<sub>4</sub>.

## A Transient in-situ FTIR and XANES Study of CO Oxidation over Pt/Al<sub>2</sub>O<sub>3</sub> Catalysts

Per-Anders Carlsson, Lars Österlund, Peter Thormählen, Anders E. C. Palmqvist, Erik Fridell, Jonas Jansson and Magnus Skoglundh

Submitted to Journal of Catalysis

### Abstract

We report experimental results for the oxidation of CO over supported Pt/Al<sub>2</sub>O<sub>3</sub> catalysts operating in oxygen excess at atmospheric pressure. To study the reaction kinetics under transient conditions we have employed step changes of the O<sub>2</sub> concentration by intermittently switching off the O<sub>2</sub> supply at various temperatures ranging 523-623 K. Detailed *in situ* FTIR and XANES data for CO coverage and chemical state of Pt are presented, while in both cases monitoring the CO conversion by mass spectrometry. A red-shift of the frequency of linearly bonded CO which correlates with an up-shift of the Pt L<sub>III</sub> binding energy indicates that the Pt catalyst initially is partially oxidised and gradually is reduced when the O<sub>2</sub> supply is switched off. Control experiments with a NO<sub>2</sub> oxidised Pt/Al<sub>2</sub>O<sub>3</sub> catalyst support these findings. A hysteresis in the catalytic activity due to the different rates whereby Pt is oxidised and reduced as a function of gas phase composition is observed. The activation energy for the Pt oxide reduction (decomposition) process is estimated to be about 50 kJ/mol. The results further emphasise that the conventional three-step Langmuir-Hinshelwood (LH) scheme used to interpret CO oxidation on Pt surfaces must be complemented by a Pt oxidation and reduction mechanism during transient conditions. Moreover, FTIR data suggest that during the extinction, the (partially) oxidised platinum is reduced by chemisorbed CO which should be explicitly accounted for in the reaction mechanism.

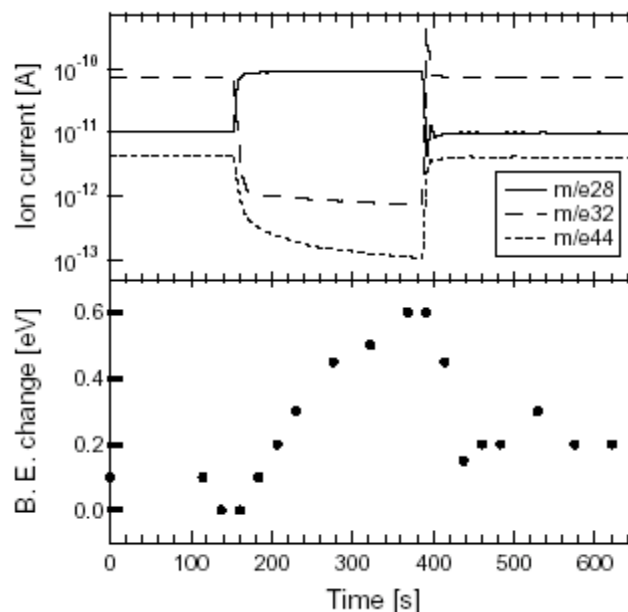


Figure 2. Measured MS ion currents ( $m/e$  28, 32, 44) for the product stream (top panel) and Pt  $L_{III}$  binding energy change ( $\Delta$ BE) from 11572.2 eV (bottom panel) for a 2.0%Pt/ $Al_2O_3$  catalyst exposed to 1.0 vol.-% CO in Ar while switching the  $O_2$  concentration stepwise from 5.0 to 0.0 vol.-% at  $t=120$  s (reduction phase) and then back to 5.0 vol.-% at  $t=400$  s at 523 K.

### Acknowledgements

This work has been performed within the Competence Centre for Catalysis, which is hosted by Chalmers University of Technology and financially supported by the Swedish Energy Agency and the member companies: AB Volvo, Johnson Matthey-CSD, Saab Automobile Powertrain AB, Perstorp AB, AVLMTTC AB, Akzo Nobel Catalysts BV and the Swedish Space Agency.

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