

## 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.**

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

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

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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> <b>De- and reactivation of Pd-Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for total oxidation of methane</b>	<b>Experiment number:</b> CH-3919
<b>Beamline:</b> BM01B	<b>Date of experiment:</b> from: 06.11.2013	

## Report:

### Introduction

The catalytic total oxidation of methane is a process of general interest. Especially in the field of exhaust gas aftertreatment methane oxidation becomes more important, since gas engines enjoy growing popularity [1]. Pd based catalysts are reported to have a very high activity at low temperatures and the most active form is discussed to be PdO. Optimization of the support material as well as addition of small amounts of Pt can even increase the low temperature activity and resistance towards sintering [2-3]. However, under lean burn reaction conditions methane conversion decreases and the catalyst deactivates. Different treatments are able to reactivate the catalyst such as rich pulses [4] or the addition of NO and NO<sub>2</sub> [5]. However, the cause of this deactivation and reactivation of Pd catalysts is still under debate, and processes such as inhibition by water have been proposed [6]. In order to determine structural changes of Pd during deactivation and reactivation, we performed XAS-experiments on Pd-Pt/Al<sub>2</sub>O<sub>3</sub> catalysts under different conditions to get a better insight.

### Experimental

The catalyst used in this study with a surface area of 140m<sup>2</sup>/g consisted of 2wt.% Pd and 0.4wt.% Pt on Al<sub>2</sub>O<sub>3</sub>. The catalyst was pressed, crushed and sieved to obtain the fraction 0.13 – 0.25 mm.

The synchrotron study was performed at the Swiss-Norwegian Beamline (BM01B) of the ESRF. The catalyst powder was placed inside a quartz capillary with a diameter of 3mm (approx. 1 cm long catalyst bed, 30 mg of catalyst) serving as micro-reactor. It was mounted on top of a hot air gas blower (Oxford GSB-1300), connected to gas lines and placed across the X-ray beam [7-8](beamsize 3x0.5mm). Gases were provided from gas bottles and dosed by mass flow controllers (Bronkhorst). Water vapor (~ 2% H<sub>2</sub>O) was dosed via a saturator. The catalyst was heated from room temperature to 450°C in He with a flow of 100 mL/min. The temperature and gas flow was kept constant for the whole experiment, but gas concentrations were changed over time as described in the following list (reaction mixture, addition of NO<sub>x</sub>, switching off

CH<sub>4</sub>, reduction, reoxidation): **1.** 8000 ppm CH<sub>4</sub>, 2% H<sub>2</sub>O, 10% O<sub>2</sub> in He for 19h; **2.** 200ppm NO, 200ppm NO<sub>2</sub> 8000 ppm CH<sub>4</sub>, 2% H<sub>2</sub>O, 10% O<sub>2</sub> in He for 1h; **3.** 8000 ppm CH<sub>4</sub>, 2% H<sub>2</sub>O, 10% O<sub>2</sub> in He for 1h; **4.** 2% H<sub>2</sub>O, 10% O<sub>2</sub> in He for 1h; **5.** 8000 ppm CH<sub>4</sub>, 2% H<sub>2</sub>O, 10% O<sub>2</sub> in He for 1h; **6.** 5% H<sub>2</sub> in He for 1h, **7.** 8000 ppm CH<sub>4</sub>, 2% H<sub>2</sub>O, 10% O<sub>2</sub> in He for 1h. X-ray absorption spectra were recorded in transmission geometry at Pd K-edge with Pd foil used as a standard. Background removal, energy calibration, normalization and extraction of the EXAFS functions as well as linear combination analysis were conducted using ATHENA and ARTEMIS of the IFEFFIT package [9].

## Results

To study the deactivation process of a Pd-Pt/Al<sub>2</sub>O<sub>3</sub> catalyst during CH<sub>4</sub> oxidation, XAS spectra were recorded for several hours during reaction. Although the catalysts activity decreases under similar conditions as applied in our experiment in ref. [5], the XAS spectra (XANES+EXAFS) do not present any difference after 19 hours of reaction. Pd is present as PdO and doesn't change over time. This supports the idea that the deactivation is not related to any bulk transformation. The addition of small amounts of NO and NO<sub>2</sub> didn't change the signal either. A reactivating effect of NO<sub>x</sub> therefore cannot be ascribed to changes in the Pd oxidation state. Surface related changes like adsorption of reactants and "cleaning" of the surface have to be considered to explain the phenomenon of de- and reactivation at the applied conditions.

However, when stopping the CH<sub>4</sub> dosage (thus only O<sub>2</sub>, H<sub>2</sub>O and He present) the EXAFS region slightly changed (and completely went back when CH<sub>4</sub> was added again). As seen in Fig.2 the amplitude is slightly increased and a broadening of the peaks can be observed in the Fourier transformed EXAFS spectrum. The removal of CH<sub>4</sub> seems to influence the noble metal particles structure. Changes in morphology e.g. restructuring could explain the changes in the spectra. However, a change in temperature due to the stop of the exothermic reaction on the catalyst might also contribute to the observed phenomenon. Further experiments have to be performed to have a closer look on this issue and to validate one of the mentioned explanations. This also requires catalysts with higher noble metal dispersion, which are presently prepared and tested in our laboratories.

Since reduction steps are reported to reactivate Pd based catalysts for methane oxidation [4] 5% H<sub>2</sub> in He were dosed to the catalyst at 450°C. PdO immediately was reduced and metallic Pd was formed. Analysis of the EXAFS data demonstrated the presence of Pd-Pt alloy in the reduced state. An explanation of the beneficial effect of short reduction pulses could be a stronger interaction between Pd and Pt and maybe an advantageous distribution of the noble metals after restructuring. However, going back to the reaction

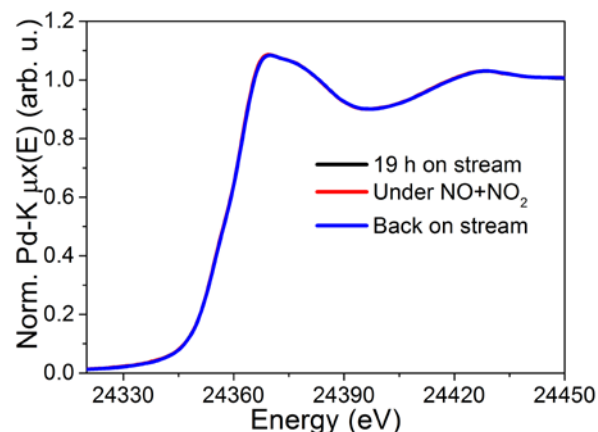


Fig. 1. XAS spectra measured at different stages during long-term de- and reactivation experiment at Pd K-edge at 450°C.

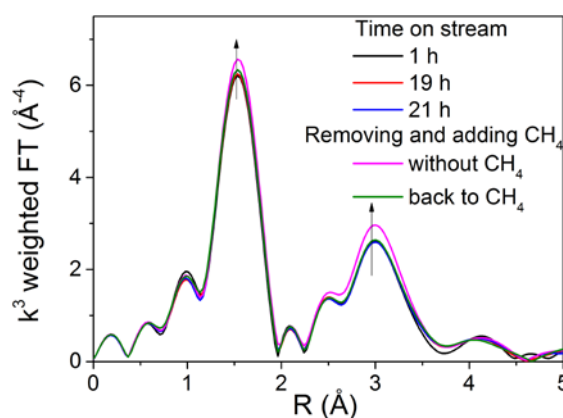


Fig. 2. Fourier Transformation of  $\chi(k)$  at different stages during long-term experiment ( $k^3$  weighted, not corrected for the phase shift).

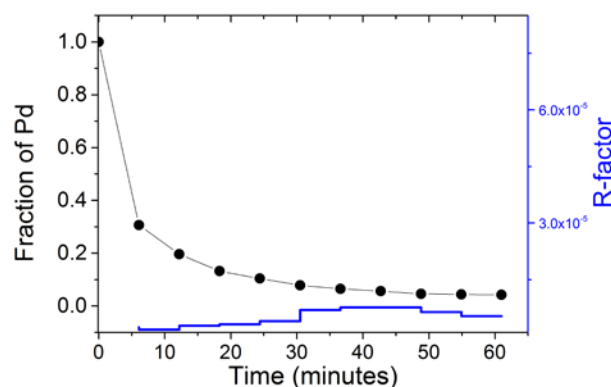


Fig. 3 Linear combination fitting of the XANES spectra recorded during reoxidation after complete reduction with H<sub>2</sub>.

mixture (CH<sub>4</sub>, O<sub>2</sub>, H<sub>2</sub>O, He) leads to a rapid reoxidation of Pd. Figure 3 shows, that within a 5 min XAS-scan the fraction of PdO increased to ~ 70 %. It seems like the process of reoxidation is an exponential process with respect to time. After 1h the catalyst is almost completely reoxidized and > 95% PdO are detected.

## Conclusions

In this study a Pd-Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was investigated with regard to de- and reactivation during complete oxidation of methane. The results showed that a bulk transformation is not responsible for deactivation or reactivation by NO<sub>x</sub>. Furthermore alloy formation after reduction in H<sub>2</sub> and a fast reoxidation under reaction conditions were observed. All the obtained information help to better understand the ongoing processes. Based on this, strategies can be developed to synthesize more stable catalysts in future or to optimize reactivation procedures.

## Acknowledgements

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