ESRF	**Experiment title:** The role of coordination chemistry and structure of iron in zeolites for direct conversion of methane to methanol and NH_3-SCR and Co^{3+} in cobalt oxide for CO oxidation	**Experiment number**: CH4232
Beamline: ID24	**Date of experiment**: from: 2015-02-25 to: 2015-03-03	**Date of report**: 2015-04-29
Shifts: 15	**Local contact(s)**: Giovanni Agostini	*Received at ESRF:* *xxxxxx*

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Report:

We start this report with a short clarification of the title of the experiment. The CH4232 experiment was an invitation by G. Agostini with the aim to use the new ID24 beamline for catalytic experiments using XAS/DRIFTS/MS. It turned out early (before we arrived) that iron and cobalt was not possible to study with the present the design of the reaction cell since these elements would require more transparent windows. Instead we were asked to study elements using higher energies. We chose to study palladium in palladium-based catalysts.

During the beamtime we studied three different series of catalysts:

- Pd/alumina calcined accordincg to two different protocols
- Pd and alloyed Pd-Pt on alumina
- Pd/alumina and Pd/ceria/alumina

The main reactions investigated were total oxidation of methane by oxygen and ammonia formation from nitrogen oxide and hydrogen. All reactions were systematically studied at different temperatures during pulsed reaction conditions. Since we employed modulation excitation spectroscopy experiments we will analyse the transient results within the framework of phase sensitive detection (PSD). We have started the analysis and will publish XANES for all experiments and EXAFS for some of the experiments, as the ceria containing samples will most likely be quite challenging. In all cases structural changes will be correlated to activity as measured by mass spectrometry (MS). During the beamtime we needed to focus on the XAS/MS, thus proper DRIFTS measurements were not prioritized.

Figure 1 shows one example on methane oxidation over Pd/alumina during oxygen pulsing. In panel (a) some selected XAFS spectra are shown. The time of recording of the spectra is indicated and corresponds to the end/beginning of the oxygen pulses, which can be seen in the MS signal in the bottom of panel (b). The top of panel (b) shows a color map of the time-

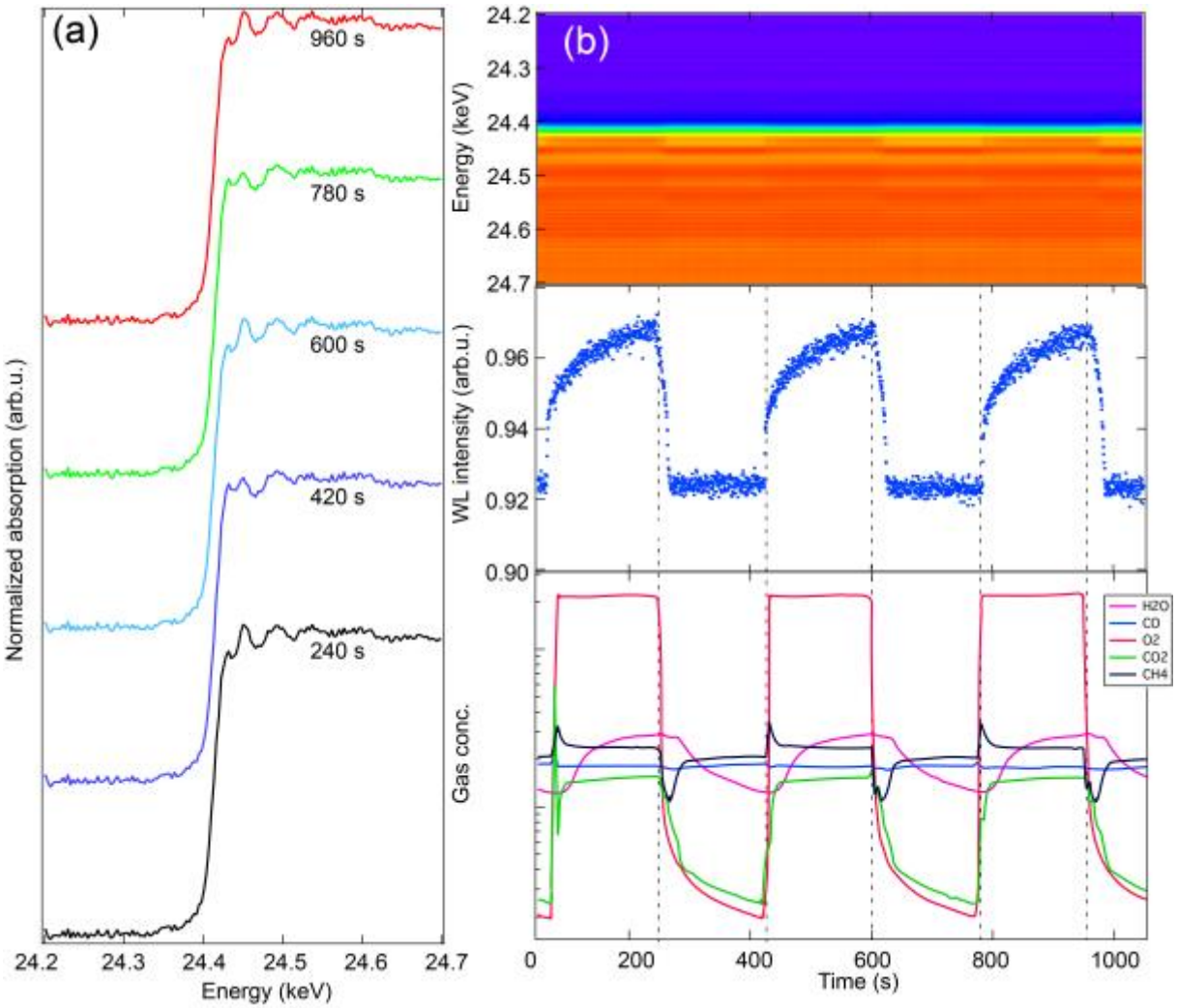

Figure 1: XAFS spectra recorded during consecutive 200 s lean (1.5% O_2 and 0.1% CH_4) and rich (0.1% CH_4) periods over Pd/Al_2O_3 at 400 °C. (a) XAFS spectra recorded at the end of the rich and lean periods. (b, top) Color-coded intensities of XAFS spectra (blue, low intensity; yellow, high intensity) (b, middle) white-line intensity of the Pd K edge and (b, bottom) outlet concentrations of oxygen, methane, carbon monoxide, carbon dioxide and water as a function of time recorded during the lean–rich cycling experiment.

resolved XAFS spectra (energy *vs* time with blue and yellow indicating low and high absorption, respectively). The middle panel of (b) shows the changes in the white-line regio

It is clear that the oxidation state of the Pd phase changes during the transient experiments. This in turn has an impact on the methane oxidation activity (*cf.* MS response for CH_4). We will study this in more detail using PSD analysis. Of special interest is the comparison with the corresponding experiment with alloyed Pd-Pt on alumina, which show much smaller changes of the white-line during oxygen pulsing (not shown).

UPDATE: A more detailed analysis has been performed and a manuscript has been written and is to be submitted to ACS Catalysis during September 2017.

Manuscript: Methane oxidation over Pd/Al_2O_3 under rich/lean cycling followed by in situ XAFS and modulation excitation spectroscopy by Johan Nilsson, Per-Anders Carlsson, Natalia Martin, Emma Adams, Giovanni Agostini, Henrik Grönbeck and Magnus Skoglundh.