

**Experiment title:**Tender X-ray HERFD-XANES studies to elucidate the deactivation of Pd/Al<sub>2</sub>O<sub>3</sub> methane oxidation catalysts**Experiment number:**

MA-5566

<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 02 Nov 2022 to: 07 Nov 2022	<b>Date of report:</b> 05/04/2023
<b>Shifts:</b> 15	<b>Local contact(s):</b> Pieter Glatzel	<i>Received at ESRF:</i>

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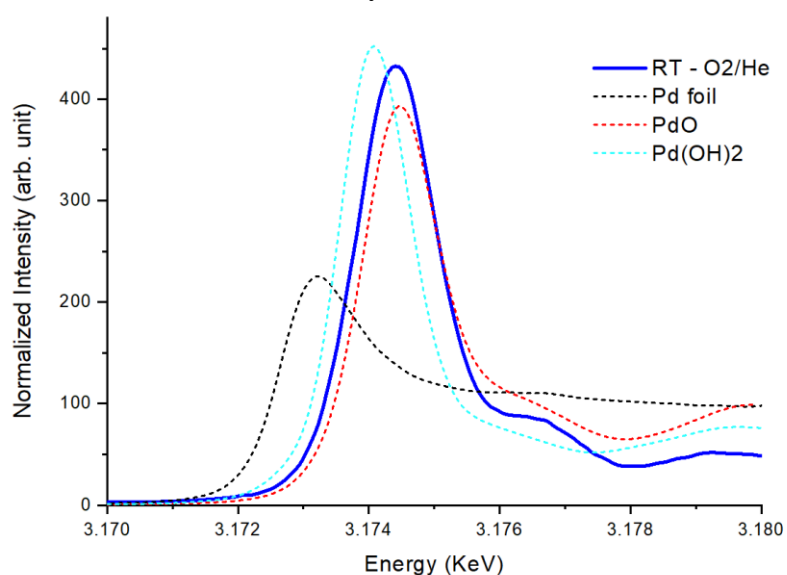
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**Report:**

To meet tightening environmental legislation and to achieve efficient environmental protection, alternatives to conventional diesel or gasoline engines must be found. Engines powered by natural gas/biomethane (or by power-to-X-processes) seem to be a promising solution, as their high fuel efficiency and low pollutant emissions stand out. However, the small amounts of the strong greenhouse gas CH<sub>4</sub> that are emitted must be catalytically removed. Pd-based catalysts are presently considered the most efficient systems for total oxidation of methane [1, 2]. Numerous studies have been conducted to better understand their functionality and especially for coping with their high sensitivity towards water deactivation and sulfur poisoning. Two stages have been identified during water deactivation at low temperatures (450°C) for Pd/Al<sub>2</sub>O<sub>3</sub> catalysts: a fast inhibition with significant increase of the light-off temperature (temperature of 50% conversion) followed by additional decrease in activity with time on stream (long-term deactivation). Both processes strongly depend on reaction conditions and gas atmosphere [3-5].

Our study aimed at conducting tender X-ray HERFD-XANES measurements to uncover the interactions of CH<sub>4</sub> and H<sub>2</sub>O with Pd species that lead to the fast



**Figure 1.** Comparison of the HERFD-XANES spectra collected at Pd L3-edge for Pd foil, PdO, Pd(OH)<sub>2</sub> references and the as prepared Pd/Al<sub>2</sub>O<sub>3</sub> catalyst (middle catalytic bed position) at RT in 10% O<sub>2</sub>/He

inhibition and long-term H<sub>2</sub>O-deactivation behaviour of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> methane oxidation catalysts. Firstly, a series of Pd reference samples with different oxidation states and coordination geometries were investigated as pellets. For the *operando* measurements a newly developed cell of ESRF with plug-flow geometry was used. The catalyst samples were used as sieved powders (125-250  $\mu$ m), and were exposed to different gas mixtures containing low concentrations of CH<sub>4</sub>, NO, O<sub>2</sub> and H<sub>2</sub>O vapours. The reaction products were monitored with MS and FTIR spectroscopy instruments. Preliminary evaluation of the data collected for Pd referenecs indicate a high sensitivity of the L3 edge to the noble metal oxidation state and ligand type. In the as prepared Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, Pd was found in oxidized (Figure 1). Unfortunately, due to numerous technical issues at the beamline and with the *operando* equipment, the experiment could not be conducted as initially planned. For completing this study, further measurements during exposure of the catalyst at various gas mixtures are necessary.

## References

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- [5] N. Sadokhina, G. Smedler, U. Nysten, M. Olofsson, L. Olsson, *Appl. Catal. B* 2017, 200, 351-360.