



**Experiment title:**  
The role of Pd in three-way catalysts

**Experiment number:**  
MA-4916

**Beamline:** ID26  
**Date of experiment:** from: 01/06/2021 to: 07/06/2021

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**Local contact(s):** Jan Pieter GLATZEL

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**Report:**

Noble metals play an important role in catalysis, with more than 50% going into emission control applications. Among different catalysts, the three way catalyst (TWC) is one of the most important emission control system to reduce the emissions of CO, hydrocarbons (HCs) and NO<sub>x</sub> of gasoline engine vehicles, when operated at conditions close to stoichiometric air-to-fuel ratios (14.7:1,  $\lambda = 1$ ). Stricter regulations and the limited resources of the noble metals require an improvement of the efficiency of such systems, which can only be done by detailed understanding of the noble metal functionality and behaviour during catalyst lifetime.

In this context, our study aimed at conducting *operando* HERFD-XANES studies at Pd L<sub>3</sub> edges for Pd/CeO<sub>2</sub>-ZrO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> three-way catalysts (TWC) for elucidating detailed mechanistic aspects of the concurrent CO and C<sub>3</sub>H<sub>6</sub> oxidation and NO reduction reactions. For this purpose, a series of reference samples containing

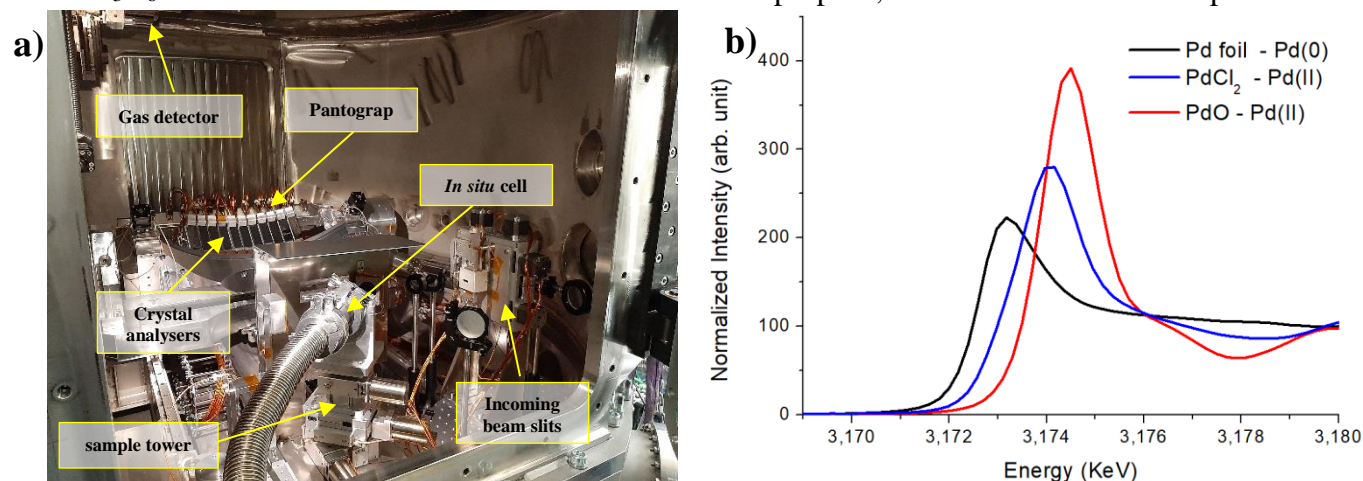


Figure 1 (a) Experimental setup of the *in situ* cell located in TEXS of line ID26 (b) Normalized Pd L<sub>3</sub>-edges HERFD-XANES spectra collected for different Pd references samples Pd in different oxidation states and coordination geometries were investigated alongside with Pd TWCs under

simplified reaction conditions. As shown in Figure 1 a, for the *in situ* experiments the catalysts samples were located in a specially designed cell, inside in-vacuum tender X-ray emission spectrometer of ESRF [1]. The gas mixtures were dosed via mass flow controllers and H<sub>2</sub>O via a saturator. The reaction products were monitored with a mass spectrometer and FTIR spectrometer.

Preliminary analysis of the obtained data confirmed the high sensitivity of such measurements and revealed pronounced variations in the HERFD-XANES spectra collected at Pd L<sub>3</sub> edges for the different reference materials (Figure 1b). Moreover, the *in situ* measurements on the Pd-catalysts showed a high response of the spectral features during the applied changes in gas mixture and reaction temperature. For concluding on the different bonding states of Pd species with CO and C<sub>3</sub>H<sub>6</sub> as a function of temperature and catalyst bed position the results are presently analysed in detail. **Unfortunately, the installation of a gas distribution infrastructure was not finalized at the time our beamtime and, following the guidelines of the ESRF safety group, the maximum concentrations of toxic gases was significantly reduced. The planned *operando* investigations including the NO presence in the gas mixture could therefore not be conducted. These experiments need to be rescheduled for a future beamtime at ID26.**

## References

[1] Rovezzi, M., Harris, A., Detlefs, B., Bohdan, T., Svyazhin, A., Santambrogio, A., & Glatzel, P. " Journal of synchrotron radiation 27.3 (2020): 813-826.