ESRF	**Experiment title:** Systematic *operando* XAS studies of Pd/Al_2O_3 and Pd/CeO_2-ZrO_2 three-way catalysts	**Experiment number**: MA-5467
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Report:

Noble metals play a crucial role in numerous catalytic reactions including emission control. To eliminate harmful pollutants such as carbon monoxide (CO), hydrocarbons (HC), and nitrogen oxides (NO_x) from gasoline-powered vehicles the so-called three-way catalysts (TWC) containing Pd, Rh and Pt have been used since decades [1,2]. However, given the challenges involved in making catalysts more efficient, the stricter pollution standards in the automotive industry, and the limited availability of noble metals in nature, it is essential to enhance the performance of TWCs. To achieve this goal, there is a need for a more comprehensive understanding of how noble metals behave and function under various catalyst *operando* conditions.

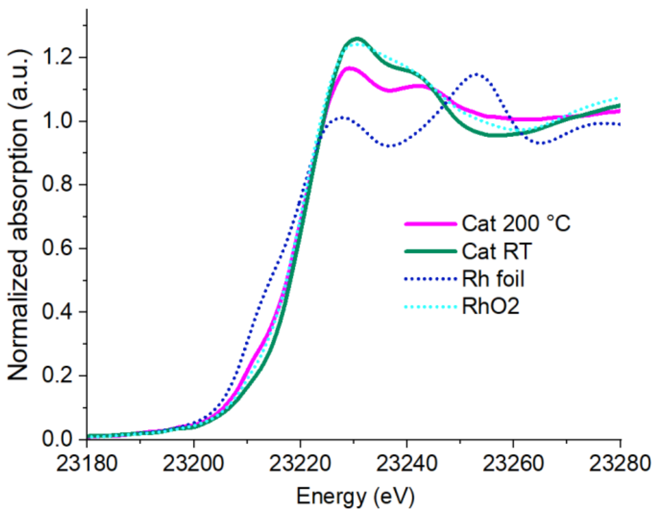

Figure 1. Comparison of the XANES spectra collected at Rh K-edge for Rh foil, RhO_2, and Rh/Al_2O_3 catalyst (middle catalytic bed position) during CO oxidation under stoichiometric reaction conditions

In this context, our study focuses on elucidating changes in the electronic structure of Pd and Rh during the simultaneous NO reduction and CO/C_3H_6 oxidation on Pd/Al_2O_3 and Rh/Al_2O_3 catalysts. The sieved catalyst powders (125-250 µm) were placed in quartz capillary reactors (OD = 1.5 mm), which were heated by a commercial gas blower (Oxford). The gas mixture containing low concentrations of CO, C_3H_6 and NO was dosed via mass flow controllers. The reaction products were monitored with MS and FTIR spectroscopy instruments. Initially, a series of Pd and Rh reference samples with different oxidation states and coordination geometries were investigated. Then, the focus was on observing the behaviour of the two catalysts under simplified to more complex reaction conditions in *operando* mode. Preliminary analysis of the XAS data collected at the middle position of Rh/Al_2O_3 catalyst bed during exposure to a stoichiometric $CO/O_2/He$ mixture indicates a slight reduction of Rh species with increasing the temperature and progress of CO conversion. The Rh K edge XANES spectra measured under reaction conditions at RT and 200°C are shown in Fig. 1 together with those of RhO_2 and Rh foil references. For most reaction conditions a gradient in the structure of Rh and Pd was observed at inlet, mid and outlet positions of the reactor.

Adding to the complementary data collected at Rh and Pd L_3 edges (ID26), the obtained information is valuable for understanding the impact of individual reagents and their combinations on the catalyst structure, such as $CO+O_2$, $CO+NO+O_2$, $CO+NO+C_3H_6+O_2$, and $CO+NO+C_3H_6+H_2O+O_2$. Altogether, these findings will serve as a rational basis for developing more efficient catalysts and advanced microkinetic models that account for the structural changes of the active noble metal under reaction conditions. The collected data will be analyzed in a systematic way to publish detailed information about reagents interactions with three-way catalysts.

References

[1] Deutschmann, O., & Grunwaldt, J. D. (2013). Exhaust gas aftertreatment in mobile systems: Status, challenges, and perspectives. *Chem. Ing. Tech*., 85(5), 595-617.
[2] Votsmeier, M., Kreuzer, T., Gieshoff, J., & Lepperhoff, G. (2009). Automobile exhaust control. *Ullmann's encycl. ind. chem*, 4, 407-424.