



	<b>Experiment title:</b> The role of Pd and Rh in three-way catalysts (TWC) under realistic reaction conditions	<b>Experiment number:</b> MA-5358
<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 28/06/2022 to: 04/07/2022	<b>Date of report:</b> 16/12/2022
<b>Shifts:</b> 18	<b>Local contact(s):</b> Jan Pieter GLATZEL	<i>Received at ESRF:</i>
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## Report:

For the development of more stable and efficient catalysts, it is crucial to understand the interactions between the active sites of a catalyst and the support. Elucidating how the catalyst activation, deactivation, and regeneration processes occur under various gas atmospheres is as well essential. Particularly for catalysts containing a low concentration of active species, X-ray absorption spectroscopy (XAS) has become a powerful tool for element specific studies under reaction conditions. Within XAS, High-Energy Resolution Fluorescence Detected (HERFD) - X-ray absorption near edge structure (XANES) spectroscopy in the tender x-ray range (1.5 – 5 keV) stands out because it allows studying the electronic structure and the local geometry variation based on the L<sub>3</sub>-edges of 4d transition metals in the catalyst. HERFD -XANES provides background-free data with spectral broadening below the width given by the core-hole lifetime. For all spectroscopic methods, high time and spatial resolution are essential to reveal the evolution of the active catalyst state [1].

During our MA-5358 beamtime at ID26 beamline, HERFD-XANES was used to study the Rh-L<sub>3</sub> edge in a catalyst based on Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under simplified reaction conditions. Using the new cell designed by the ESRF (Sample environment) allowed us to perform spatially resolved *in situ/operando* HERFD-XANES measurements. The information collected is relevant because it links the catalyst structure at different locations in the catalytic bed with surface reactivity. The *in situ/operando* cell was placed inside the X-ray emission spectrometer chamber. The gas mixtures were dosed through mass flow controllers, while the reaction products were monitored with a mass spectrometer and an FTIR spectrometer.

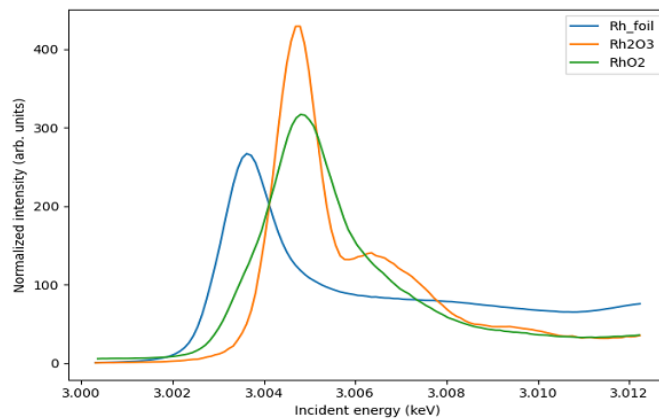


Figure 1 Normalized Rh L<sub>3</sub>-edges HERFD-XANES spectra collected for different Rh references samples

The collected HERFD-XANES spectra showed pronounced variations of the Rh-L<sub>3</sub> edge profile for the different reference materials (Figure 1). Additionally, the *in situ/operando* measurements showed a high response of the spectral features during the applied changes in the gas mixture and reaction temperature on Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. We can conclude that Rh exhibits different binding states when CO, NO and/or C<sub>3</sub>H<sub>6</sub> are dosed over the catalytic bed. It is important to emphasize that these results will serve as basis for further investigations involving more complex gas mixtures, i.e. water presence.

## References

[1] Rovezzi, M., Harris, A., Detlefs, B., Bohdan, T., Svyazhin, A., Santambrogio, A., & Glatzel, P. " *J Synchrotron Radiat.* 27.3 (2020): 813-826.