ESRF	**Experiment title:** Catalytic removal of nitrogen monoxide, carbon monoxide and hydrocarbons	**Experiment number**: MA-5119
Beamline: ID26	**Date of experiment**: from: 29/09/2021 to: 04/10/2021	**Date of report**: 01/04/2022
Shifts: 18	**Local contact(s)**: Jan Pieter GLATZEL	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Jan Pieter Glatzel*, ID26 Beamline, ESRF - The European Synchrotron - Grenoble, France

Alexander Suarez*, ID26 Beamline, ESRF - The European Synchrotron - Grenoble, France

Maria Casapu*, Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Sarina-Lena Heck*, Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Paolo Dolcet*, Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Jan-Dierk Grunwaldt, Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Report:

Because it is essential to promote the reduction of hydrocarbons (HCs), carbon monoxide (CO), and nitrogen oxides (NOx) emissions in the air, stricter regulations are progressively implemented (1). This has led to the development of several catalyst technologies for emission control in mobile and stationary applications. The three-way catalyst (TWC) technology, based on noble metals such as Pd, Rh, and Pt, is widely used to control emissions of gasoline engines. However, the limited amount of noble metals and regulations that are more stringent demand for more efficient use and further activity improvement for this class of catalysts.

A rational development of these materials implies the identification of active species and understanding the reaction mechanism as crucial steps. For this purpose, the study of the interplay between the noble metal, the support, and pollutant gases is highly important. During our beamtime MA5119 at the ID26 beamline of ESRF, high-energy-resolution fluorescence detection (HERFD) X-ray absorption near-edge structure spectroscopy (XANES) was used to study the Pd L_3 edge in a Pd/γAl_2O_3 TWC during exposure to realistic gas compositions (CO, NO and C_3H_6 presence). The new gas-dosing infrastructure available at ID26 allowed a successful completion of our study. An in-situ cell designed by ESRF was used to accommodate the catalyst sample in the tender X-ray emission spectrometer chamber [1]. Gas mixtures were dosed through mass flow controllers and H_2O via a saturator. The reaction products were monitored with a mass spectrometer and an FTIR spectrometer. The obtained results supplement the information obtain previously for the same catalyst during exposure to model gas mixtures (MA4916).

In general, the high sensitivity of Pd L_3 edge during catalyst interaction with various reagents was confirmed. Clear variations in the HERFD-XANES spectra profile were observed upon changes in the gas mixture. For instance, a pronounced decrease in the white-line intensity occurred already at room temperature when switching the gas mixture from O_2/He to CO+O_2/He (stoichiometric mixture - TWC) gas mixture, indicating the reduction of the noble metal (Figure 1). While Pd is partially reduced if CO is present in the gas mixture, NO maintains an oxidized state for the noble metal species. CO adsorption on catalyst surface is suggested by the shift towards higher energy, in comparison to the HERFD-XANES spectra collected for the H_2-reduced catalyst. Pronounced changes in the Pd L_3 edge intensity were observed also during light-off/light-out cycles in a more realistic gas mixture including CO, NO and C_3H_6, which reveal the formation of several intermediate species as well as competition for the active sites. The outcome of our study demonstrates the high potential of tender X-ray range for uncovering important details on the local electronic structure in Pd-based catalysts, which is relevant for numerous applications in catalysis and material science.

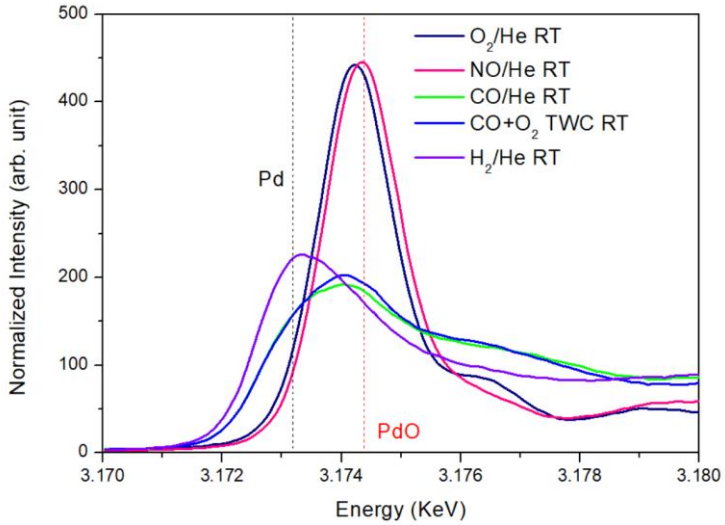

Figure 1. Normalized Pd L_3-edges HERFD-XANES spectra collected at room temperature for Pd/γAl_2O_3 under different gas compositions.

References

[1] Johnson, T. (2016). Vehicular emissions in review. SAE International Journal of Engines, 9(2), 1258-1275.

[2] Rovezzi, M., Harris, A., Detlefs, B., Bohdan, T., Svyazhin, A., Santambrogio, A., & Glatzel, P. (2020). Journal of synchrotron radiation, 27(3), 813-826.