ESRF	**Understanding the effect of reducing pre-treatment on Pt/CeO_2 and doped CeO_2 for the elimination of exhaust gas in diesel engines.**	**Experiment number**: 16-01-783
Beamline: BM 16	**Date of experiment**: from: 28/06/2017 to: 04/07/2017	**Date of report**:
Shifts:	**Local contact(s)**: Olivier PROUX	*Received at ESRF:*

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Report: The set up of the experiment is illustrated on Figure 1. Expriments were performed on FAME UHD (BM16) equiped with a crystal anlyzer spectrometer. Capillary reactors provided by KIT were used. The use of a capilllary reactors enables to record the spectra in a large collection angle. A helium bag was used to reduce as much as possible the absorption between reactor and the five crystal spectrometer. The mass spectrometer allowed to follow gas composition during the reaction. The µGC could not be used due to an interface problem. Installation and calibrations required two days (27-28). Scan settings at CeL3 egde were optimized for getting HERF-XANES within 14 minutes or preedge fast scan of 1.8 min. Samples were submitted to reduction/oxidation sequences, NOx storage and a light-off experiment .

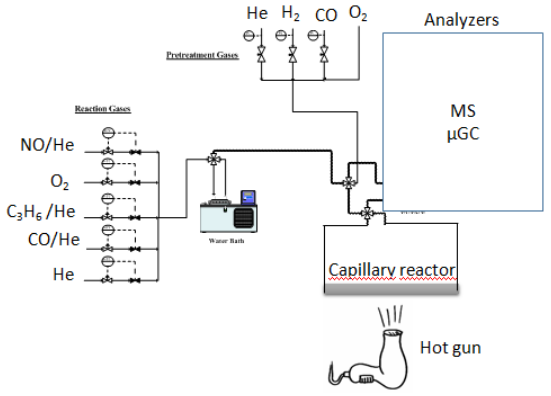

Figure 1 : Experimental set up for red/ox eperiments on Pt over ceria based catalysts

Figure 2 illustrates the HERF-XANES signal obtained after an *in situ* reduction of Pt/CeO_2 catalysts at 250°C. From TPR, the extent of reduction was estimated at 20%. We noticeed the shift in E_0, the variation of spectral features corresponding to the mixing of 4f levels and O 2p ($4f^1\underline{L}$ and $4f^0$configurations at 5730 and 5740 en respectively) and the appearance of a new contribution in the pre-edge. We attempted to follow the evolution of the pre edge and egde by fast analysis as illustrated in Figure 3. Thus, we recorded the variation of this egde during heating every 10K during the reduction under H_2 from RT up to 250°C (5K/min ramp).

We can notice on Figure 3 that a partial recution occurs at room temperature whereas a second stage of continous reduction (up to the final state) starts from 120°C.

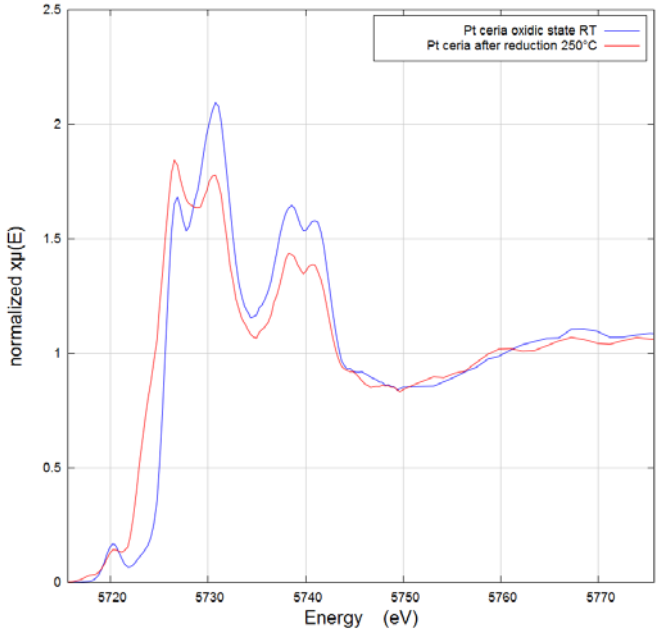

Figure 2 : HRXANES spectra at Ce L3 edge at RT of Pt/Ce in the oxidic state and after reduction at 250°C.

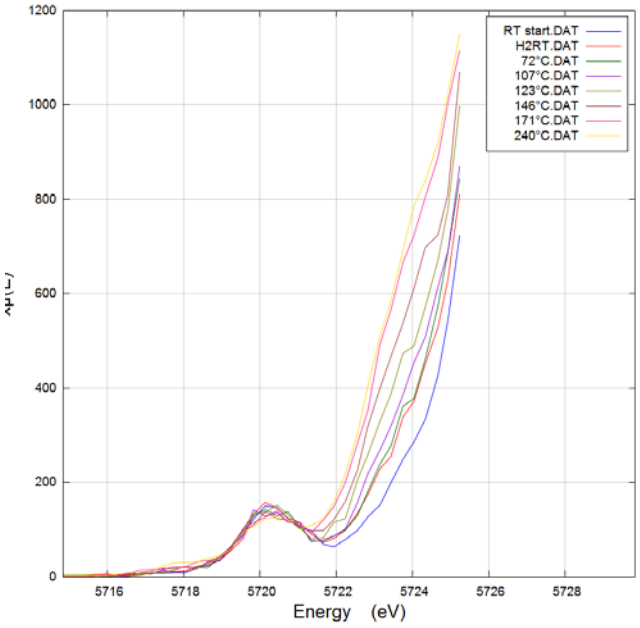

Figure 3 : Pre-edge evolution (1 spectrum every 1.8 min) during the reduction of Pt/CeO2 catalysts from RT up to 250°C.

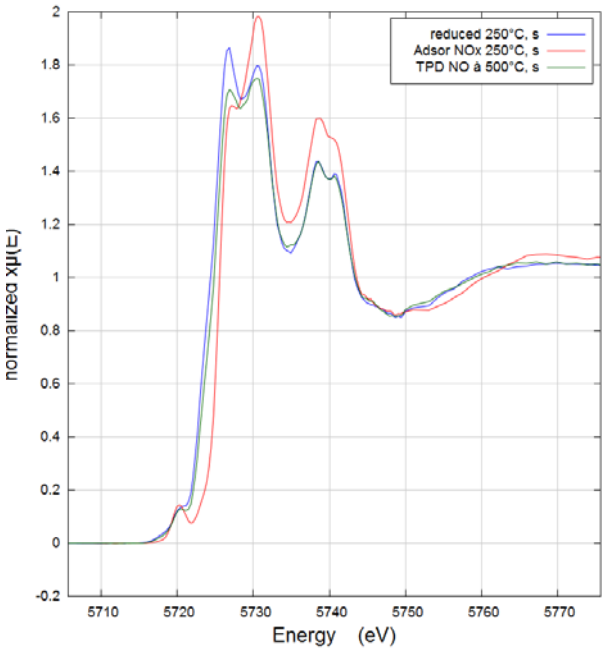

Figure 4 : HRXANES spectra of a Pt/Ce sample reduced at 250°C, after NOx adsoprtion at 250°C and TPD at 500°C.

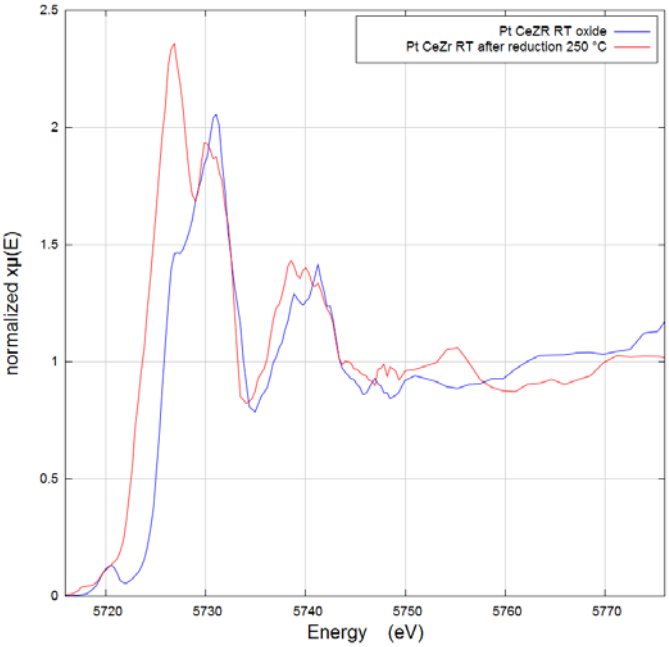

Figure 5 : HRXANES spectra at RT of Pt/CeZR in the oxidic state and after reduction at 250°C.

Several sequential reductions cycles demonstrate that reducibility was facilitated by the pretreatment procedure. Then, we proceeded to NOx absoption on the reduced catalyst. At 250 °C, adosprtion of NOx reoxidizes the ceria but desorption of the NOx at 500°C allowed to revover a partially reduced state. Similar types of experiments have been performed on a Pt/CeZr system (ceria zirconia). The reducibility of the system at 250 °C is illustrated by Figure 5. We can observe a drastic change in HRXANES suggesting an important degree of reduction of the Ce atoms in the solid solution. Reductions cycles were also performed on this sample. Data are under treatment.