



	Experiment title: Study of Pt clusters segregation from CeO ₂ nanopowders: XAS investigation at the Pt L ₃ -edge and Ce K-edge	Experiment number: MA-2357
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Report:

Background

The nanopowders which were investigated by means of X-ray Absorption Spectroscopy (XAS) were differently post-treated samples of 1 wt% Pt/CeO₂, which is employed as a catalytic system for CO oxidation. In conventional preparation methods, the catalytically active noble metal species is deposited on the non-innocent oxidic support. In contrast to that, the powders prepared in our lab were obtained via a wet chemical route, which allowed a novel approach to obtain control over the Pt particle size by ionic dispersion in the supporting lattice, followed by segregation of sub-2 nm metallic entities upon thermal treatment. Hence, by changing the parameters of the thermal treatment such as duration and temperature of the respective treatment, as well as atmosphere, the catalytic activity is readily tuneable by the higher surface area and the unique bonding situations between Pt species and CeO₂. In previous HR-XRD studies at the Swiss Light Source (SLS, Material Science Beamline) and XPS/TEM experiments we were able to follow the *in-situ* segregation kinetics via the evolution of previously absent Pt peaks in oxidative conditions (Arrhenius plot, kinetic constant *k*), as well as in *ex-situ* experiments carried out for samples treated in reductive atmosphere. To gain further insight about the interplay of the Ce³⁺/Ce⁴⁺ redox couple with the ionic and metallic Pt species, one has to investigate the change of bonding conditions as well as the oxidation states during the thermal treatment and the corresponding segregation process.

Experiment

By the planned XAS experiments at the BM08 of the European Synchrotron Radiation facility (ESRF, Grenoble) we wanted to monitor the change of oxidation states for both Ce- and Pt-species (from the XANES region) and the respective change of coordination (from the EXAFS region). According to the previous HR-XRD experiments, the window of interest for the segregation could be defined for the Pt/CeO₂ powders in oxidative and reducing atmosphere. This led to a set of powders, treated at different temperatures for a

certain duration, to investigate the segregation and formation of metallic Pt entities in an *ex-situ* manner. The sets of powders were mixed with cellulose binder and pressed into pellets ($d=13$ mm) to measure the Ce L₃-edge (5723 eV, RT) in transmission and the Pt L₃-edge (11564 eV, 80 K) in fluorescence mode, respectively. Pellets of cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O), ammonium cerium(IV) nitrate ((NH₄)₂Ce(NO₃)₆) and anhydrous cerium(IV) oxide (CeO₂) were used as references for the different Ce oxidation states. For Pt, references of tetrammine platinum(II) nitrate (Pt(NH₃)₄(NO₃)₂), Pt(IV) oxide (PtO₂) and metallic Pt foil (Pt(0), $d=50$ μm) were measured.

Four sets of samples were measured:

Set I: Pt/CeO₂ treated in air for 3 h, from 500 to 900 °C (10 samples)

Set II: Pt/CeO₂ treated at 900 °C in air, for treatment durations ranging from 0.5 to 6 h (5 samples)

Set III: Pt/CeO₂ treated in 2% H₂ (balance Ar), from 500 to 900 °C (6 samples)

Set IV: Pt/CeO₂ treated in 2% H₂ (balance Ar) at 650 °C and 850 °C, respectively, for treatment durations ranging from 0.5 to 6 h (9 samples)

Total: 30 samples + 6 references

Each sample was measured at the Ce- and at the Pt- L₃ edges, which sums up to a total number 66 scans of around 2 h duration each during the allocated beamtime

Preliminary results

From the previous HR-XRD results, the increase of Ce³⁺ species upon thermal treatment could not be directly followed unless considering the respective lattice parameters and taking the formation of electronically and lattice space compensating oxygen vacancies (and the corresponding effect on the Pt species) into account.

From a preliminary analysis of the collected XAS data sets, there are no clear changes of the Ce³⁺/Ce⁴⁺ redox ratio upon thermal treatment. The samples treated under different atmospheres show features of the undoped CeO₂ material, although a reduction of the amplitude of the two peaks in the white line is observed on the sample treated under reducing conditions. Further evaluation of the EXAFS part might allow some more detailed insight into the bonding distances upon reduction.

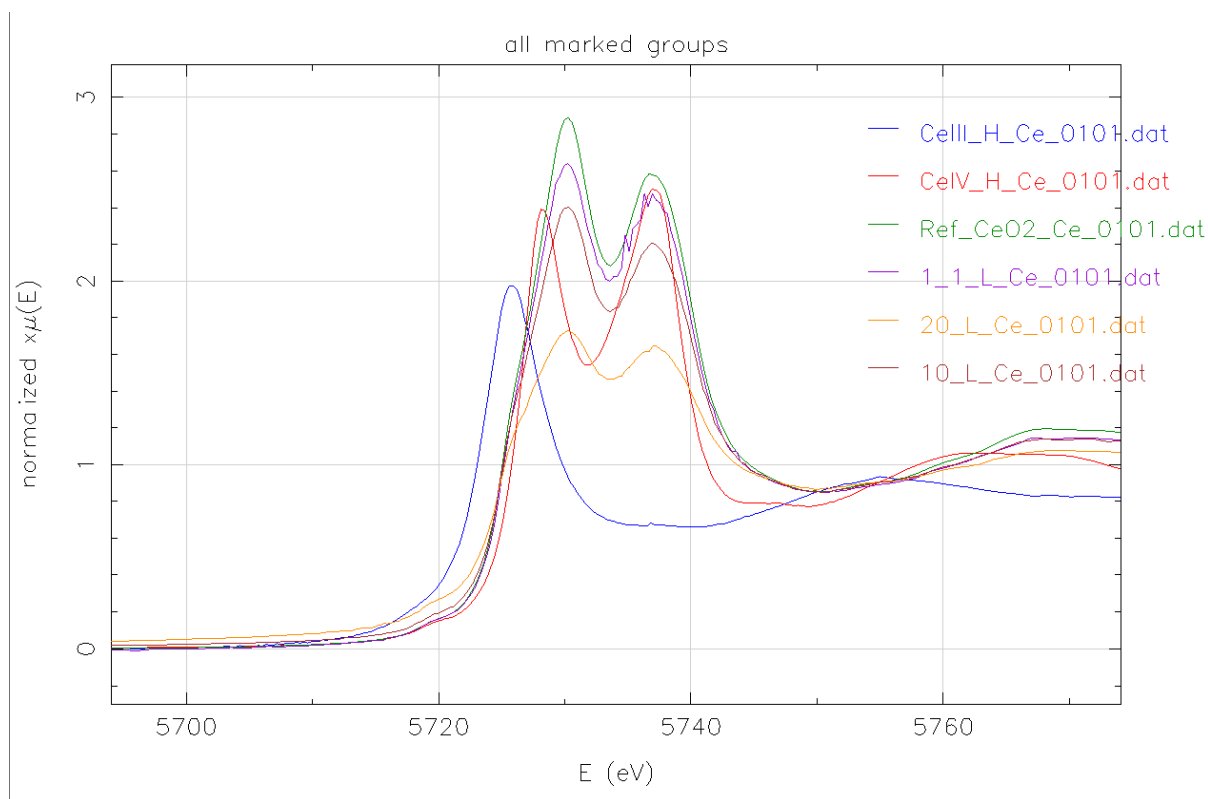


Figure 1: Collected XANES for the measured reference Ce(III), Ce(IV)-precursor salt and Ce(IV)-pure oxide compounds (blue, red and green, respectively). Sample 1_1 (violet) and 20 (yellow) were both treated in air for 3 h at 500 and 900 °C, respectively. Sample 20 (brown) was treated under reducing conditions for 3 h at 900 °C. They all show features of the undoped CeO₂ material.

The measurements at the Pt L₃ edge allowed clear insight into the average Pt oxidation states by comparing the XANES spectra. According to the previous HR-XRD results, the evolution of Pt peaks – and therefore segregation of ionically dispersed Pt as Pt⁰ entities on the surface of the CeO₂ matrix – is expected in the window of 875 – 900 °C under oxidizing conditions (Fig. 2 a)), whereas the reducing atmosphere 2% H₂/Ar promotes the occurrence of XRD-detectable Pt species already at 500 °C (Fig. 2 b)). From the XANES spectra, the increase of the Pt(0) signal upon thermal treatment can be clearly followed (amplitude reduction and shift of the white line) and was found to occur at different temperatures depending on the annealing atmosphere in full agreement with the HR-XRD results. Corresponding changes of the EXAFS signals were also detected.

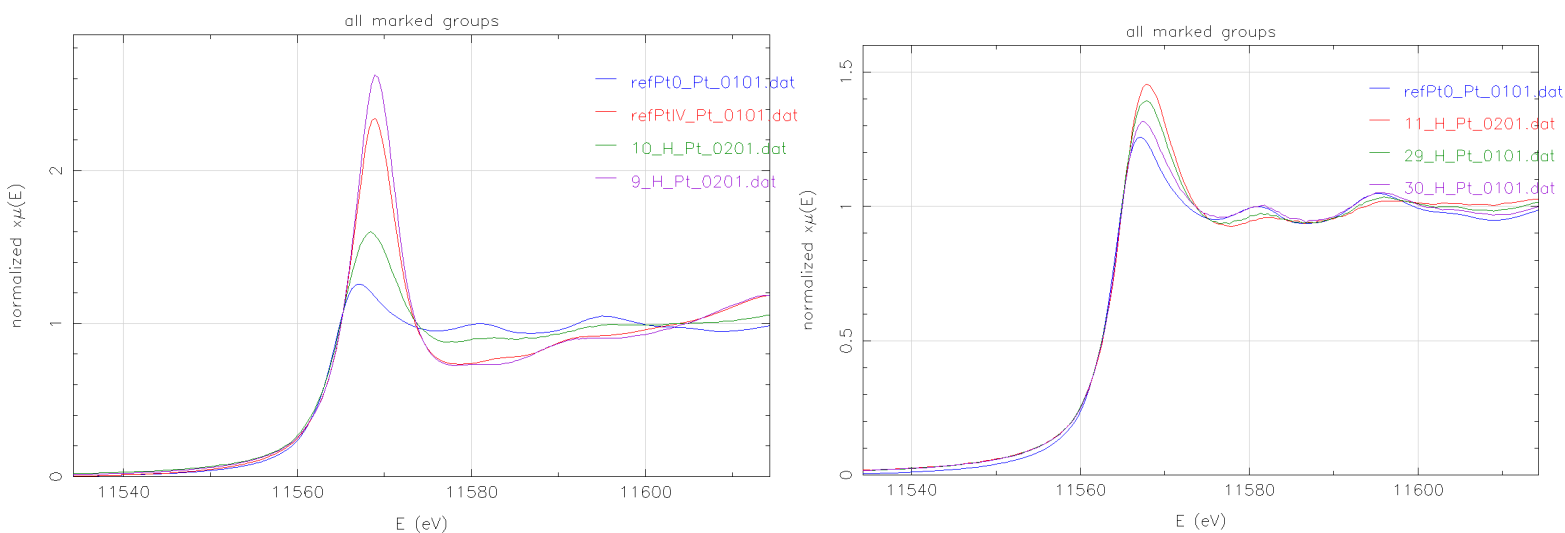


Figure 2: a) Collected XANES for the measured reference Pt(0), and Pt(IV)-oxide compounds (blue and red, respectively). Sample 10 (green) and 9 (violet) were both treated in air for 3 h at 875 and 900 °C, respectively. b) Collected XANES for the measured reference Pt(0) (blue). Sample 11 (red), 29 (green) and 30 (violet) were all treated in 2% H₂/Ar for 3 h at 500, 550 and 600 °C, respectively. With increasing temperature, the overall amount of Pt⁰ increases, as it can be determined by the shift and amplitude reduction of the white line.

Further investigation

To link the previously obtained HR-XRD results with the corresponding XAS, further data evaluation is in progress. The evolution of Pt peaks in the XRD can be linked to the coordination shells of Pt species while segregating on the surface. The diffractograms furthermore point at two different populations of Pt(0), which might correspond to Pt(0) species with slightly distorted lattice in vicinity of the supporting CeO₂ matrix and the particles visible in TEM images. To complete the picture of segregation under oxidizing and reducing atmosphere, we plan to record *in-situ* XAS during the segregation process in reducing conditions, since ex-situ measurements of differently treated samples do not provide enough insight about the intermediate migration of Pt species to the surface. Since the data is insufficient in respect of obtaining a full Arrhenius plot / kinetic constant *k*, further planned experiments are required.