esrf ESRF	**Experiment title:** Modulation Excitation High Energy XRD Study of the Effect of CeO_2/ZrO_2 Ratio in Ceria-Zirconia based Pt catalysts	**Experiment number:** MA-3145
Beamline: ID11	**Date of experiment:** from: 28.09.2016 to: 04.10.2016	**Date of report:** 23.11.2016 *Received at ESRF:*
Shifts: 15	**Local contact(s):** Dr. Andrea Bernasconi	

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Report:

Set up of the home equipment (gas manifold, cell, mass spectrometer, gas lines, switch valves; Figure 1) and alignment of the beamline lasted 1 day.

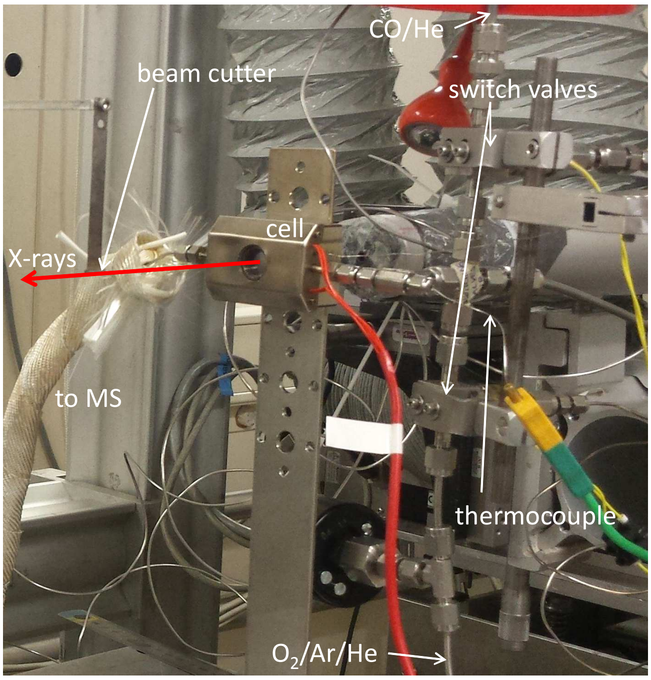

Figure 1. Setup of the modulation experiments.

The aim of the experiment was to explore the effect of the Ce/Zr ratio (C/Z) in undoped and Pt-doped CZ compositions on the dynamic structural changes that can be mirrored by high energy X-ray diffraction (HEXRD). The modulated exitation approach was used in order to be able to follow the kinetics of reduction (in CO) and re-oxidation (in O_2) of the various CZ samples as a function of the C/Z ratio (CZ100, CZ75, CZ50 and CZ25, where the number indicates the percentage of Ce), the presence of Pt (1 wt%) and the calcination temperature (500 or 900 °C, air, 3 h simulating thermal ageing). Beside allowing for improved statistics, the approach also allows to monitor subtle structural changes that would not be accessible under steady state conditions. HEXRD data where collected continuously (0.5 s/pattern; Q= 0-12 $Å^{-1}$; Pt K-edge, 78.4 keV; FReLoN camera) during concentration modulation experiments consisting in the periodic switch between two gas feeds, 5vol% O_2/He (120 s) and 4.9vol% CO/1 vol% Ar/He (120 s) at 400, 375, 350, 325, 300, 250 and 200 °C. The samples were re-oxidized in 5 vol% O_2/He at 400 °C for 15 min after the pulse experiment at each temperature for the sake of comparison. Static diffraction data was recorded at the given temperatures before and after each pulse experiment in either oxidizing or reducing conditions. A full modulation period is defined as the time required to conclude a full CO vs O_2 sequence (240 s). A homemade flow cell equipped with two graphite windows and allowing fast switching was used throughout. The exhaust of the cell was monitored online using a mass spectrometer (MS).

High quality XRD data was obtained at the given time-resolution (Figure 2). Depending on the C/Z ratio and temperature, the repeated CO vs O_2 pulsing caused more or less evident changes around the reflections of the cubic fluorite structure of ceria. Figure 2 shows that in the cvase of CeZr75 the changes were not really visible because not all the material participates in the process at the given temperature [1]. Such changes were fully reversible and characterize the expansion of the lattice due to loss of lattice oxygen in the CO pulse and contraction due to oxygen uptake. The kinetics of structural change were observed to be dependent on the C/Z ratio and on the experimental temperature. Figure 2 shows that in the Pt-free samples, ther sample with the least Ce exchanged lattice O_2 readily in presence of CO, while ther samples exchanged less within the same time. Re-oxidation was equally fast in all materials. Apparent activation energies of reduction (E_{aR}^{app}) can be obtained from this data for each sample. The online MS data allowed to quantify the Oxygen Storage Capacity (OSC) that characerizes the ease of oxygen release of the materials from the signal of evolved CO_2 in the CO pulse. The values (Figure 2) are in perfect agreement with available data and demonstrate that OSC increases with increasing amount of ZrO_2 in the Pt-free samples.

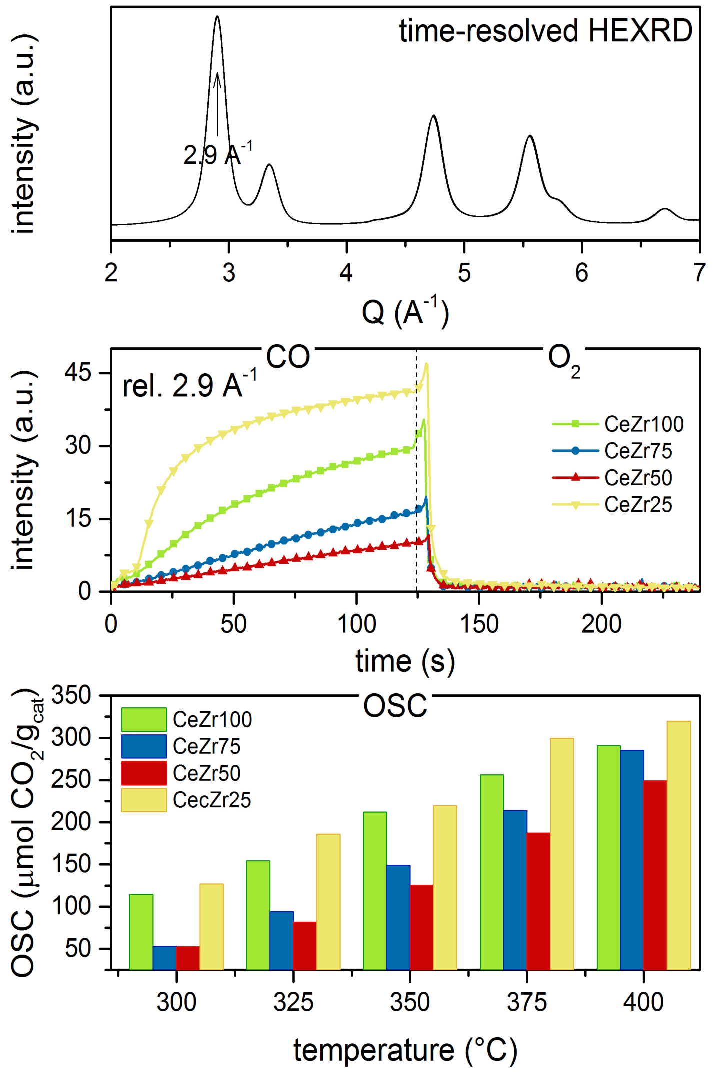

Figure 2. Set of averaged time-resolved HEXRD patterns obtained in a modulation experiment (CO vs O_2) on $Ce_{0.75}Zr_{0.25}O_2$ (CeZr75, calcined 500 °C) at 400 °C; relative change of intensity of the reflection at ca. 2.9 Å^{-1} for the series of CeZr samples at 400 °C; Oxygen Storage Capacity (OSC) of the various CeZr samples calcined at 500 °C at various temperatures determined from the CO_2 signal in online mass spectrometry.

Hence, we are able to correlate the kinetics of the structural changes with a macroscopic property of the material thus going considerably beyond what has been previously attained in understanding the structure-function relationships and kinetics of the OSC process. The applied approach provides novel and quantitative structural information on phenomena occurring on time scales that are otherwise inaccessible to conventional diffraction and spectroscopic investigations.

Extensive data evaluation of both HEXRD and MS datasets is on-going. The data obtained in this campaign will be complemented by infrared spectroscopy and X-ray emission spectroscopy data obtained in identical experiments with the same experimental setup to obtain a full picture of the OSC process.

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References

[1] D. Ferri, M.A. Newton, M. Di Michiel, G.L. Chiarello, S. Yoon, Y. Lu, J. Andrieux, Angew. Chemie Int. Ed. 53 (2014) 8890.