| ESRF | **Experiment title:**<br>***In situ* WAXS experiments on Ce/La mixed oxides catalysts** | **Experiment number**: |
|---|---|---|
| **Beamline**:<br>BM08 | **Date of experiment**:<br>from: 4 February 2001 to: 9 February 2001 | **Date of report**:<br>25 February 2002 |
| **Shifts:**<br>12 | **Local contact(s)**:<br>Carlo Meneghini | *Received at ESRF:* |

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**Report:**

**Samples**. Three-Way Catalysts (TWC) are complex systems constituted of a metal nanophase supported on mixed oxides; they are designed to remove simultaneously CO, NOx and hydrocarbons (HC) from automotive exhaust gases. All the investigated samples are ceria-based, due to the property of Ce(IV) in the $CeO_2$ network to be easily reduced to Ce(III) in reductive environment, and to the corresponding straightforward oxidation Ce(III)→Ce(IV) in oxidative atmosphere. The oxygen, released or uptaken from the reaction environment during the Ce(IV)↔Ce(III) transitions, has the fundamental role of bringing the reaction mixture within the so-called stoichiometric window, i.e. the optimal composition for the simultaneous redox processes taking place on the TWC system. Ceria is modified with trivalent (La) and tetravalent (Zr) dopants to improve its ability of oxygen exchanging. Some of the samples are supported on alumina, other ones are unsupported.

***In situ* XRD experiments**. The oxygen exchange of TWC systems with the reaction environment can be monitored by *in situ* XRD experiments, because the presence of reticular Ce(III), due to its larger ionic radius (1.14 Å vs. 0.97 Å of Ce(IV)), determines an increase of the lattice constant of ceria. Time-resolved XRD patterns were achieved using the Translating Image Plate detector and the heating gun available on BM08. Samples were enclosed in a quartz capillary tube, constituting a proper catalitic microreactor. The reactant gas mixture was flowed at one end of the capillary and the output gases were transported to a quadrupole mass spectrometer from the other capillary side. In the first part of the experiment (5-9 July 2000) the overall experimental setup and the experimental procedures

were tested. The investigated TWC samples were submitted to isothermal treatment at 500 and 700 °C and temperature ramps from RT to 700 °C. O2/He 10% and CO/He 0.1% mixtures were alternately flowed in order to monitor the structural changes related to the oxygen storage and release by the catalyst.

**Results.** Temperature ramps. In Figs.1-2 the results relative to the temperature ramps in He and CO/He for a Zr-doped and a La-doped ceria representative samples are shown. It is evident that both type of samples show a remarkable expansion of the (cubic) cell in CO/He flux, with respect to the mere thermal expansion in pure He. This effect is due to the reduction of part of the reticular Ce(IV) to Ce(III). The Zr-doped sample, Fig. 1, seems to have better properties of oxygen exchange, as can be seen from the onset of the difference with the He treatment, beginning at lower temperature (<200 °C) with respect to the La-doped sample (>300 °C).

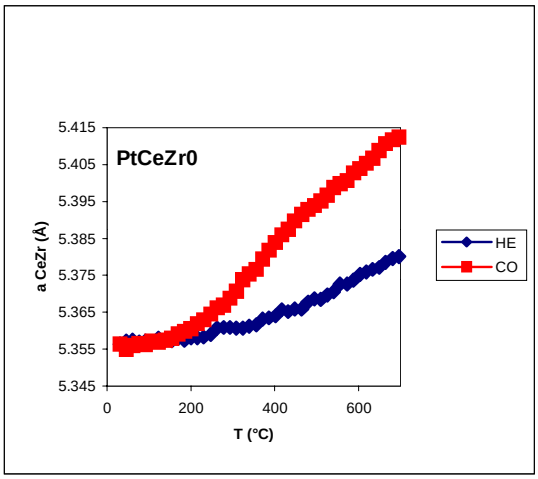


Fig.1

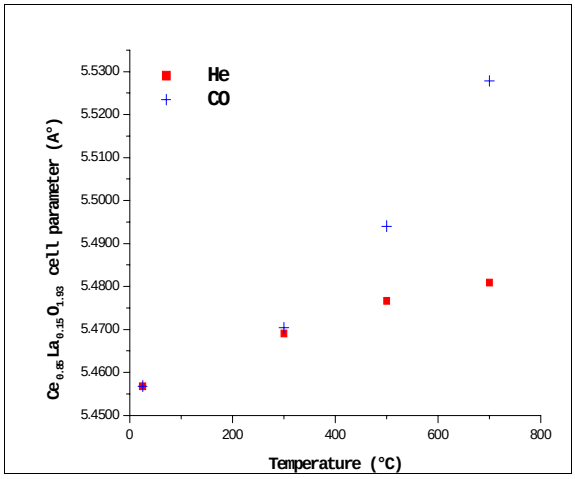


Fig.2

**Isothermal Treatments**. In Fig. 3 the $CO_2$ yield, as monitored by quadrupole mass spectrometry, on a Zr-doped sample supported on alumina is shown. The time derivative of the ceria cell constant is also plotted, demonstrating that the sudden (taking place, in fact, in about 5') structural rearrangement of the Zr-doped ceria corresponds to the release of oxygen for the CO oxidation.

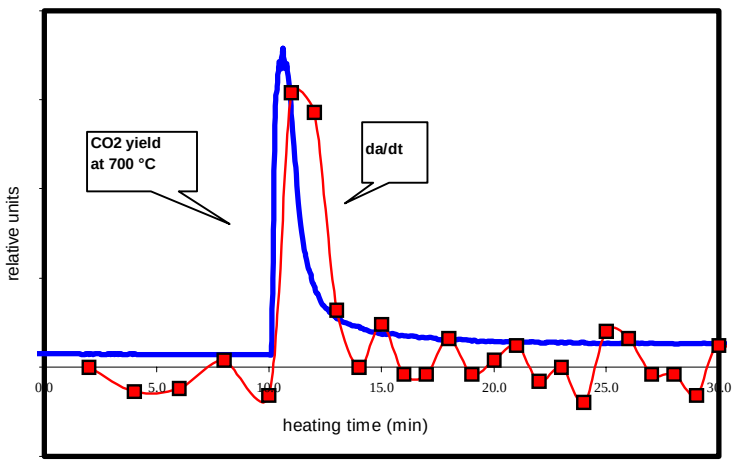


Fig.3

Publications. 1) A. Martorana, G. Deganello, A. Longo, F. Deganello, L. Liotta, A. Macaluso, P.G. Prieto Martinez, A. Balerna, C. Meneghini, S. Mobilio. "In situ X-ray diffraction: a study of Ceria based catalytic systems for automotive pollution control". IX Meeting SILS, Firenze, 5-7 July 2001.

2) A. Martorana, G. Deganello, A. Longo, F. Deganello, L. Liotta, A. Macaluso, G. Pantaleo, A. Balerna, C. Meneghini, S. Mobilio (2002). " Time-Resolved X-ray Powder Diffraction on TWC catalysts at the GILDA beamline". Submitted to J. Synchrotron Rad.