



	Experiment title: In situ XRD experiments on Ceria-Zirconia TWC catalysts	Experiment number: CH-1112
Beamline: BM08	Date of experiment: from: 6 December 2001 to: 11 December 2001	Date of report: 26 February 2002 <i>Received at ESRF:</i>
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Report:

Introduction. Three-Way Catalysts (TWC) are complex systems constituted of a metal nanophase supported on mixed oxides; they are designed to remove simultaneously the major environment pollutants CO, NO_x and hydrocarbons (HC) from automotive exhaust gases.

Nowadays, most of the TWC systems are based on modified CeO₂, due to the peculiarity of ceria of acting as an oxygen buffer. This property allows to control the reaction environment that should be kept within a narrow composition range in order to ensure the effective catalytic abatement of all the pollutants.

Most of the recent research work on TWC's is devoted to the development of new systems that should be able to comply with the UE zero emission demand for the year 2005. To this aim, it is particularly important to improve the catalytic yield at relatively low temperatures (200-300 °C), in the cold-engine regime, where the maximum environmental pollution is observed. During the experiment 08-02-218 "*In situ* WAXS experiments on Ce/La mixed oxides catalysts", it was proved that the Zr-doped ceria has better properties, as concerns the oxygen buffer capacity at low temperatures, with respect to La-doped CeO₂. The present CH-1112 experiment, therefore, was entirely devoted to the study of ceria-zirconia systems, with particular attention to the behaviour at low temperatures.

Samples, treatments and *in situ* XRD. A Ce_{0.6}Zr_{0.4}O₂ mixed oxide, prepared by a sol-gel procedure, was impregnated with Platinum acetylacetonate, successively calcined at 800 °C and finally reduced at 1000 °C. Two catalysts were obtained with this procedure, characterized by a homogeneous ceria-zirconia solid solution and by two different Pt loadings, respectively 0.5 and 1 wt%. Contrary to the previous 08-02-218 experiment, these

samples were not supported on transitional θ -alumina. This choice was dictated by the will of dealing with systems as simple as possible, deserving to further experiments the possibility of a more detailed study of alumina-supported materials.

As well known, the possibility of monitoring by *in situ* XRD the oxygen buffering capacity of the ceria-based TWC systems depends on the straightforward Ce(IV)→Ce(III) transition in reductive environment and on the opposite Ce(III)→Ce(IV) conversion in oxidative atmosphere. These redox processes, involving reticular cerium, are accompanied by a corresponding lattice constant variation (Ce(III) ionic radius is larger, 1.14 Å, than Ce(IV), 0.97 Å) and, to ensure charge neutrality, by bulk oxygen release.

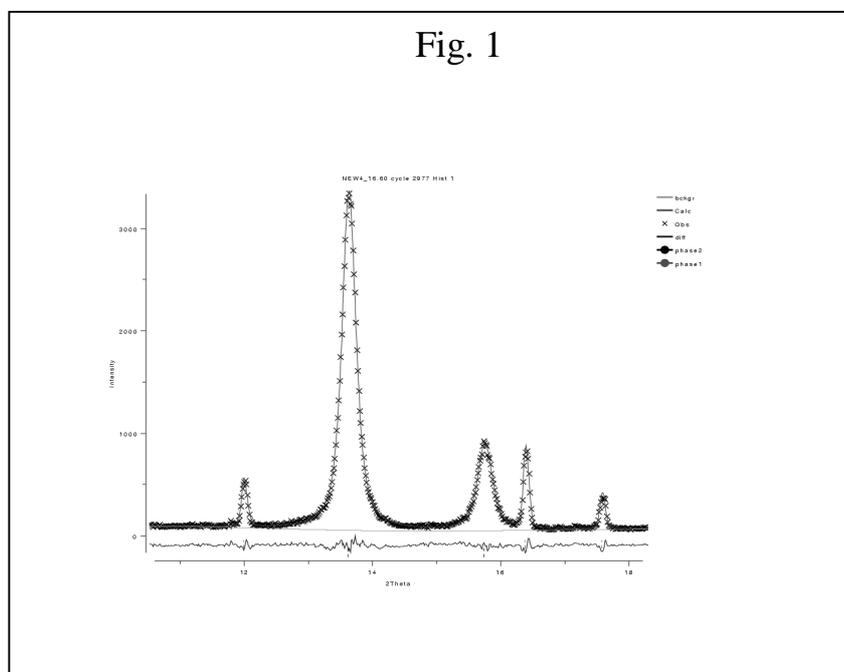
The samples under investigation were flowed with gas mixtures CO/He 0.1% and CO-NO/He 0.1%; the relative amount between CO and NO was 1:1 2:1 and 3:1, respectively. The XRD data were taken with the Translating Imaging Plate detector implemented at BM08, allowing to record the time-resolved scattering intensities in successive vertical strips on the Imaging Plate. The time-resolved XRD patterns were recorded in the flow of the above quoted mixtures and at the temperatures of 200, 280, 320 and 500 °C, while the reaction products were monitored by a mass quadrupole spectrometer. The samples were contained in quartz capillaries, 1mm internal diameter. Actually, the capillary diameter was not optimal for high resolution XRD measurements, but the choice was required by the necessity of ensuring a stable gas flow throughout the capillary. With respect to the previous 08-02-218 experiment, a better confidence in the ceria-zirconia lattice constant determination was achieved by mixing the catalyst with a chemically inert α -alumina diffraction standard.

Results. A typical fit quality obtained by GSAS can be seen in Fig. 1, showing in a limited angular range two peaks of the ceria-zirconia phase and three reflections (the narrower ones) of the standard α -alumina.

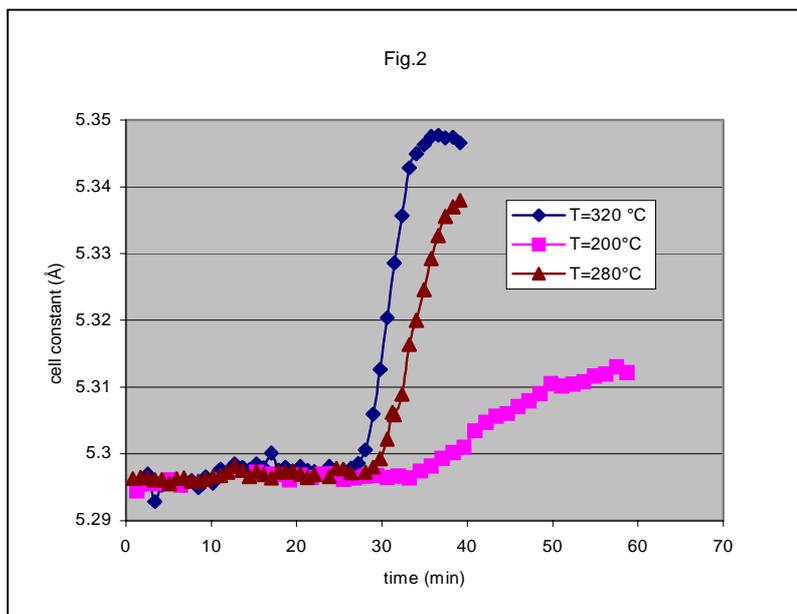
The refined value of the ceria - zirconia cell constant at RT (5.296 Å) is in agreement with a Ce_{0.6}Zr_{0.4}O₂ composition of the fully oxidized sample, so ensuring that its composition is very close to the nominal one.

In Fig.2 the values of cell constant at different temperatures are shown, after correction for thermal expansion. All the samples are fluxed for the first ten minutes in He and for the remaining treatment time in CO/He. After the accomplishment

of the XRD experiment, the temperature is raised to the next one, the sample is fluxed in 10% O₂/He for 30' to restore the lost oxygen and for further 10' in He. The most striking result of the experiment is that the release of reticular oxygen begins with a delay of about 20' with respect to the switch of the flowing mixture to CO/He, while, as demonstrated by the mass spectrometer, the CO oxidation to CO₂ takes place with no delay. It is probable that, during the delay time, oxygen for the reaction is recovered from the surface of ceria-zirconia, where its chemisorption is catalyzed by the supported Pt, and that only after consumption of



this more accessible oxygen the lattice provides further oxygen by the above described Ce(IV) reduction. It is also worth to note that the latter process takes place, except for $T=200^{\circ}\text{C}$, in a few minutes and that the delay is shorter in the successive cycles. Repeated treatments in CO/He flux at 500°C , followed by 30' of O_2/He 10% and by 20' of pure He,



gave the time dependence of the cell constant showed in Fig.3, where the first ten minutes are relative to He and the last 50' to CO/He. It is evident that the step of cell constant variation is well reproducible in the subsequent cycles, but that the onset of reticular oxygen release, like the cycles at different T, is anticipated. The reason why this phenomenon occurs is not entirely clear: a possible explanation could be that the release of oxygen produces the progressive disruption of the Ce-Zr aggregates of crystallites, so improving the availability of

surface oxygen. On the basis of the cell constant value, the composition after the step at 500°C is $\text{Ce(IV)}_{.32}\text{Ce(III)}_{.28}\text{Zr}_{.4}\text{O}_{1.86}$.

Finally, Fig. 4 accounts for some preliminary results concerning the experiments in CO/NO flux. These experiments were proposed with the aim of investigating the behaviour of the catalysts in a reaction environment similar to that effective in operative conditions, where pollutants to be oxidized (CO) and reduced (NO) are simultaneously present. From Fig. 4, it results that in the CO:NO 3:1 treatment at 500°C the release of reticular oxygen is slower and the increase of cell constant, at least after 60', is smaller. It looks like therefore that oxygen coming from NO reduction is put into play, limiting the consumption of bulk oxygen for the CO oxidation. The other CO:NO mixtures confirm this interpretation, showing larger delays and even slower increase of the cell constant.

