ESRF	**Experiment title:** Application of XAFS techniques to the investigation of the redox properties in TWC's and related systems.	**Experiment number:** CH-299
Beamline: BM08	**Date of experiment:** from: 15-mai-97 to: 19-mai-97	**Date of report:** 1 S-august-98
Shifts:	**Local contact(s):** D'Acapito, Francesco	***Received at ESRF:*** 8 AOUT 1998

Names and affiliations of applicants (* indicates experimentalists):

Miguel A. Cauqui (*). Dept. Quimica Inorganica. Facultad de Ciencias. Univ. de Cadiz
D.C. Koningsherger. Dept. Inorganic Chemistry. Debye Institute. Utrecht University.
S. Bernal. Dept. Quimica Inorganica. Facultad de Ciencias. Universidad de Cadiz.
A. van der Eerden (*). Dept. Inorganic Chemistry. Debye Institute. Utrecht University

Report:

Ceria has been for years one of the components of catalytic automobile exhaust converters (TWC). The capacity and the rate of response to buffer the oscillations of the oxygen partial pressure in the waste gases are recognised among its key properties [l]. However, improvements in such features are currently demanded for designing better catalytic cartridges for cleaner cars. In particular, the so-called cold start operation conditions, closely related to the redox behaviour of the promoter phase at T< 500°C are considered as a factor to be improved in the next generation of three way catalysts. Some recent results [2] strongly suggest that cerium based mixed oxides can constitute an alternative to the bare ceria as promoter of the TWC.

Here we reports on the redox behaviour of a series of cerium-zirconium mixed oxides when submitted to different reduction treatments. CeZrOx samples with two different chemical compositions: (Ce/Zr molar ratios): 50/50 and 70/30 were prepared. For each of these compositions high (CeZrOx-50/50-HS) and low (CeZrOx-50/50-LS) surface area samples were investigated. Prior to any measurement, the samples were submitted to a cleaning treatment in flowing O_2/He at 500°C for 1 h, followed by cooling to 150°C in flowing O_2/He and then to room temperature in pure He.

The shape of the Ce L_{III} near-edge has been used as a fingerprint for the analysis of the cerium oxidation state.

The different contributions for Ce^{3+} and Ce^{4+} were calculated by using a computer program written and developed by G. Balducci at the University of Trieste. This program is based on a fitting procedure reported by Le Normand et al.[3]

The results are shown in Table 1. After cleaning, all the mixed oxides present a similar Ce^{3+} percentage in the range 5-8%. Reduction treatment at 500°C leads to a significant increase in the Ce^{3+} content, which is maximum for the CeZrOx-50/50-HS sample (46%). Reducibility for this sample was also investigated after treatments in flowing He at 500°C and H_2/He at 200°C. In both cases, as can be seen in Table I, the reduction processes, thought started, are not significant yet.

Some trends in the redox behaviour of the CZ samples could be pointed out. Thus, the higher the surface area and/or zirconium content, the deeper the reduction degree. The submission to consecutive redox cycles does not affect the original oxidation state of the sample.

Table I.- Ce^{3+} percentages estimated from near edge analysis.

Catalyst	Treatment	Ce^{3+}
CeZrOx-50/50- HS	----	7.4
	Cleaning	6.0
	He, 500°C	9.6
	H_2/He. 200°C	7.7
	H_2/He, 500°C	46.0
CeZrOx-50/50-LS	Cleaning	8.0
	H_2/He, 500°C	22.3
CeZrOx-70/30-HS	Cleaning	8.0
	H_2/He, 500°C	14.7
CeZrOx-70/30-LS	Cleaning	5.1
	H_2/He, 500°C	9.4

References:

[1] B.T. Kilbourn. "Cerium. A guide to its role in chemical technology". Molycorp Inc. (1992).

[2] P. Fornasiero, R. Di Monte, G. Ranga Rao, J. Kaspar, S. Meriani, A. Trovarelli and M.Graziani, J.Catal., **151, 168 (1995).**

[3] J. El Fallah, S. Boujana, H. Dexpert, A. Kiennemann, J. Majerus, 0. Touret, F. Villain and F. Le Normand, J.Phys.Chem., 98,5522 (1994).