

**Experiment title:**

X-ray absorption studies of a serie of Pt/CeZrOx catalysts

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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 [1]. However, improvements in these features are currently demanding for designing of better catalytic cartridges for cleaner cars. 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 report 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 O₂/He at 500°C for 1 h, followed by cooling to 150°C in flowing O₂/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 Ce³⁺ and Ce⁴⁺ 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%). Reducability 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, though 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. The investigation of the influence of Pt on the reduction degree is currently underway.

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

Also the Zr edge was investigated in order to get structural information about the mixed oxides. The main problem in analysing Zr exafs is the fact that for a stoichiometric oxide $Zr_xCe_{(1-x)}O_2$ which posses a tetragonal structure 8 (4+4) oxygen atoms are expected. However in literature models are reported in which 2 oxygen atoms are missing although in that case the support experienced a servere temperature treatment [4]. We found that at high k values the phases of the two different oxygen atoms are opposite and therefore when a high k weighting is used a too low coordination number was found. Thus a low k-weighting (k0 or k1) should be used in order to obtain reliable data. The further analysis of the Zr EXAFS is in progress.

References:

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