

## BEHAVIOR OF CATALYTIC CERIUM-CONTAINING MIXED OXIDE NANOPARTICLES UPON HIGH TEMPERATURE TREATMENTS

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### Introduction

CeO<sub>2</sub> and mixed oxides based on it have marked catalytic capabilities for promoting the oxidation of various molecules, from pollutants (CO and unburnt fuel, as done in the three way catalysts (TWCs) widely used in automotive exhaust gas purifiers) to hydrocarbons in direct feed solid oxide fuel cells (SOFCs); they have other catalytic applications as the elimination of SO<sub>2</sub> in industrial gaseous streams or the conversion of CO (Water Gas Shift, WGS, and Preferential Oxidation, PROX reactions) in the generation of H<sub>2</sub> for low temperature fuel cells. Especially in the first two applications mentioned, these materials become exposed to high temperatures under oxidizing atmospheres (because of high power driving periods in the first case, and due to the high temperatures used in fuel cell manufacture and operation in the second case). This leads to an increase in particle/crystallite size from the very small values (a few nm) which maximize catalytic efficiency to significantly higher ones (several tens of nm) which appear due to Ostwald ripening and sintering upon high temperature exposure. It is interesting to understand at nano- and atomic levels the features of the thus generated larger particles.

In the work presented here two types of Ce-containing mixed oxides (Ce,M)O<sub>x</sub> (where M=Zr or Tb), of interest for TWCs and SOFCs, have been prepared via a colloidal method and subjected to calcination temperatures around 1000 °C, being then characterized with transmission electron microscopy (TEM) and other techniques.

### Experimental

(Ce,M) oxide materials were obtained from nitrate aqueous solutions through precipitation with aqueous (CH<sub>3</sub>)<sub>4</sub>NOH using a microemulsion technique [1]. Besides pure ceria, a (Ce,Zr) sample (Ce:Zr ratio ≈ 1.0) and two (Ce,Tb) samples (Ce:Tb ratios ≈ 4.0 and 1.0) were made; in the first case, a sample with the oxide dispersed on high surface area alumina (final load = 10% w/w of mixed oxide) was also prepared by adding γ-Al<sub>2</sub>O<sub>3</sub> (Condea, S<sub>BET</sub>=200 m<sup>2</sup>/g) to the metal-containing microemulsion before the precipitation step. These samples are labeled CT4, CT1, CZ and CZA. In all cases, the base samples have a final calcination temperature T<sub>c</sub>=773 K in air; from them, samples calcined in air at temperatures T<sub>c</sub> between 1173 and 1373 K were made, they will be designated with the temperature value appended to the main label.

TEM data of low T<sub>c</sub> samples were obtained with either a JEOL 2000 EX system with 0.21 nm p-p resolution or a JEOL 2000 FX system equipped with an EDS probe (spot size ≈ 100 nm) for chemical analysis; for high T<sub>c</sub> samples a Philips CM200 system with 0.24 nm p-p resolution, also equipped with EDS (spot size = 20 nm) was used also. X-ray diffraction data were taken with a Seifert XRD 300P diffractometer using Ni-filtered CuKα radiation.

### Results and discussion

The microemulsion method [1] yields for T<sub>c</sub>=773 K mixed oxide particles with sizes around 5 nm as shown by XRD broadening and TEM data; in CZA the sizes, obtained with dark field TEM images, are around 3 nm (Fig. 1A). Raman spectra and XRD show that the (Ce,M) oxide present has in all cases solid solution character within a fluorite-type structure, cubic for M=Tb and, for M=Zr, pseudo-cubic (the so-called t'' phase [2]) and with the cell parameter expected from the cation ratio. Particle shapes (see e.g. Fig. 2A) indicate that in all cases mainly (111) and (110) faces are exposed, in accordance with known differences in surface energies [3].

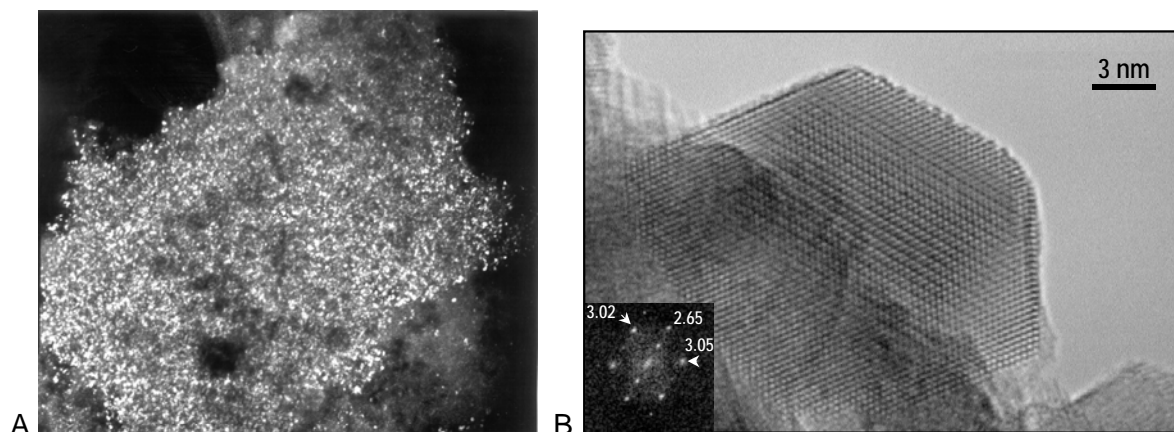


Fig. 1 TEM images of CZA sample calcined at A) 773 K, B) 1273 K

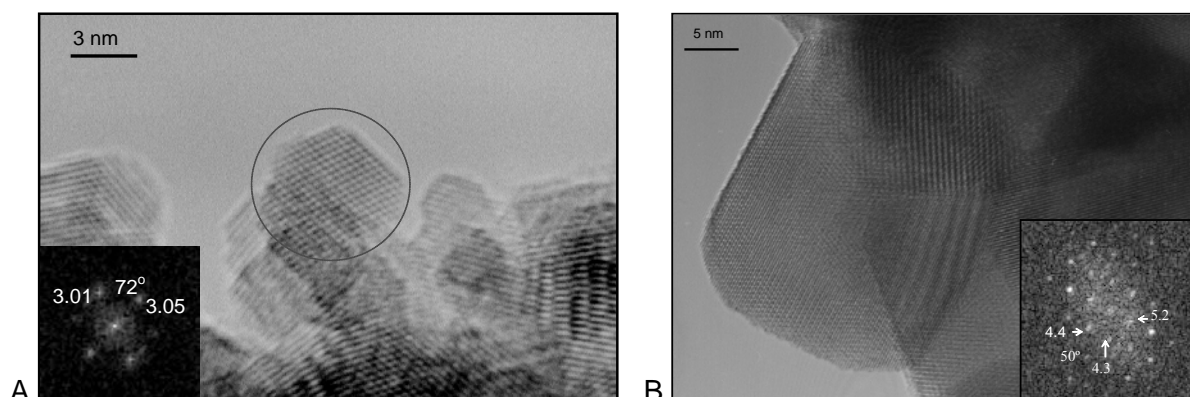


Fig. 2 TEM images and (fluorite-type) DDP of CT4 sample calcined at a) 773 K, b) 1273 K

Calcination at high temperature shows that CZ phases undergo, together with a crystallite size increase (while keeping a similar overall shape, Fig. 1B), a decomposition (known in the literature) in two fluorite-type solid solutions, rich in Zr and Ce respectively (and thus displaying different cell parameters). The CZA sample displays in this respect higher resistance to this decomposition, which appears for  $T_c=1373$  K but not yet for  $T_c=1273$  K, while unsupported CZ does show such effect at this latter  $T_c$ . This is ascribed to a stabilizing effect of alumina and/or to the smaller mixed oxide crystallite size; it is known that very small sizes may stabilize otherwise metastable phases in these fluorite type oxides. This phase decomposition has negative effects on the desired oxygen buffer capacity of this material; the capability, given by the microemulsion method, of achieving very small particle size in this dispersed state is thus an advantage.

Samples CT1 and CT4, on the other hand, display no phase decomposition (according to the diffraction data), showing thus promise as more stable materials for both TWC and SOFCs. The crystallite size increase is accompanied by a shape change: TEM images display a significant number of rectangular profiles (Fig 2B) indicating exposure of (100) planes (unfavoured in normal fluorite-type  $MO_2$  oxides [3]). Furthermore, digital diffraction patterns (DDPs) reveal additional spots suggesting the onset of cation and/or anion vacancy orderings within a crystal symmetry akin to that of the  $Tb_2O_3$  phase. The possible effect of these changes on the surface chemistry and performance of (Ce,Tb) oxides in SOFC anodes is currently under investigation.

### References

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