

## Surface effects in formation and application nanoparticles based on zirconia

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### Abstract

Oxide nanopowders based on zirconia have attracted in the last time researchers and manufacturers due to high progress in technology of nanopowder production. Zirconia nanopowders are used in catalysis, thermal barrier coating, SOFC components, drug delivery and markers in medicine, microelectronics and wide variety of applications in composite nanoparticles and ceramic nanocomposites.

In present report we will discuss effect of nanoparticles surface in two variants of nanopowder composition: 1)  $ZrO_2$ -3mol% $Y_2O_3$  (ZYC<sub>00</sub>); 2)  $ZrO_2$ -3mol% $Y_2O_3$  + 0.3...3%  $Cr_2O_3$  (ZYC<sub>xy</sub>).

At first we describe surface effects in the process of hydroxide-oxide transformation and nanoparticles growth during calcination in yttrium stabilized zirconia (ZYC<sub>00</sub>). In the second variant of nanopowders the role of chromium oxide in change of surface state of nanoparticle is analyzed.

Nanopowders of zirconia hydroxide were prepared by co-precipitation technique. Mixed together water solutions of high purity  $ZrO(NO_3)_2$  and  $Y(NO_3)_3$  salts taken at stoichiometric composition (3 mol%  $Y_2O_3$ ) were used as starting materials.

The hydroxide precipitates were dried with using pulse magnetic and microwave fields. Nanopowders were calcined in the temperature range of 350-1000°C.

Nanoparticles obtained by our technology are single crystals with soft and easily destroyed agglomerates. They have low degree of dispersion (<20%) and homogeneous dopants distribution and are 100% tetragonal. The morphology of these nanopowders and the structure of initial xerogel are shown in Figure 1.

On the base of analysis of nanopowder structure by TEM and HRTEM it was found that the growth process of nanoparticles synthesized by co-precipitation has three stages (Figure 2): cooperative oriented crystallization of ordered areas in xerogel polymer matrix and disintegration of crystallized areas (350–400°C); oriented attachment of particles into single crystal caused by electrostatic interaction (400–600°C); attachment of particles to single and poly-crystals by oxygen diffusion through vacancies in surface layers of joining crystals (600–1,000°C).

These phenomena should be treated from the mesoscopic point of view as they attributed to the interaction of groups of particles between each other. Proposed conception on mesoscopic processes of nanoparticles formation makes the understanding and theoretical description of significant amount of experimental data possible and open the way for purposeful governing by oxide powder system on the stages of obtaining, compaction, and sintering.

The investigations of zirconia nanopowders doped yttrium and chromium ( $ZrYC_{xy}$ ) [2] found unexpected result: the introduction of chromium oxide increases crystalline size comparing to reference sample (ZYC<sub>0.0</sub>) and with increasing chromium content particles begin to grow slower, reaching minimum value at maximum concentration of chromium (Figure 3).

The Y/Zr, Cr/Zr and O/(Zr + Y + Cr) ratios were calculated from Zr 3d, Y 3d, Cr 2p and O 1s measured XPS spectra by dividing corresponding areas under the curve. The comparison with stoichiometric ratios clearly shows dramatic surface enrichment with yttrium for the ZYC<sub>0.1</sub> sample. Other samples exhibit considerable yttrium depletion, which increase with the rise of chromium molar fracture. Four samples doped with chromium demonstrate significant enrichment with Cr atoms of the nanoparticles surface.

Deconvolution of Cr 2p<sub>3/2</sub> spectra shows Cr present in three states Cr(II) (575.5 eV), Cr(III) (576.5 eV) and Cr(III) (577.5 eV) Table 1. These states correspond to CrO,  $Cr_2O_3$  and  $Cr(OH)_3$  respectively [4-6]. Ratio between oxide states of chromium is changing with chromium concentration increase. ZYC<sub>0.1</sub> sample include almost equal amounts of  $Cr^{2+}$  and  $Cr^{3+}$  states with 18% of chromium hydroxide states. Cr(II) amount is maximum for ZYC0.25 sample with reverse for Cr(III) and  $Cr^{3+}(OH)_3$  states correlating with m-phase maximum.

It is found the increase of m-phase value could be connected with lattice distortion due to presence of chromium atoms on the surface of nanopowders in  $Cr^{2+}$  states.

Results obtained for chromium doped zirconia nanopowders are important for using these material catalytic processes for formation nanoparticles of tipe "core-shell", nanocomposites, etc.

Table 1

Components intensities for deconvolution of Cr 2p<sub>3/2</sub> XPS spectra.

Sample	Cr <sup>2+</sup> , %, E <sub>b</sub> =575.5 eV [4]	Cr <sup>3+</sup> , %, E <sub>b</sub> =576.5 eV [7]	Cr <sup>3+</sup> (OH) <sub>3</sub> , %, E <sub>b</sub> =577.5 eV [5]
ZYC <sub>0.1</sub>	41.3	41.1	17.6
ZYC <sub>0.25</sub>	58.8	31.0	10.3
ZYC <sub>0.5</sub>	33.8	43.0	23.1
ZYC <sub>1.0</sub>	28.5	47.6	24.0

### Acknowledgment

This work is supported by the European Commission's Seventh *Framework Programme* (FP7), through the Marie Curie International Research Staff Exchange Scheme NANO\_GUARD (PIRSES-GA-2010-269138).

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### Figures

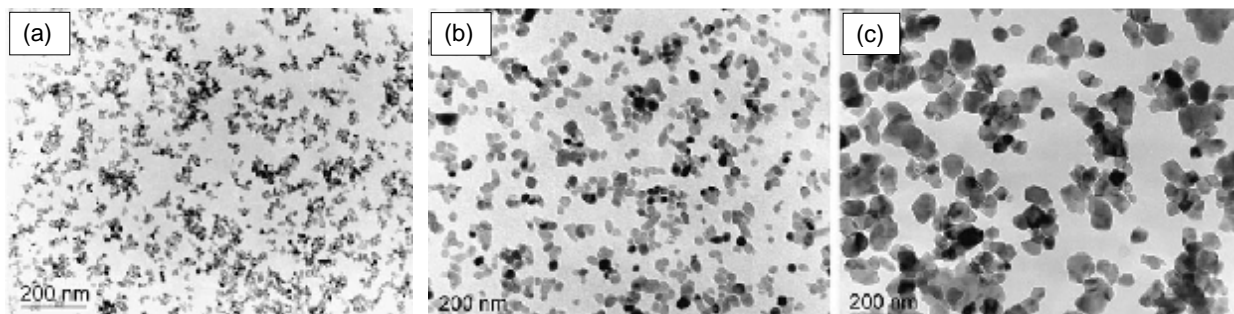


Figure 1. Morphology of nanopowders ZrO<sub>2</sub>+3 mol% Y<sub>2</sub>O<sub>3</sub> calcined at different temperatures (a) -500°C; (b) -700°C; (c) -1,000°C

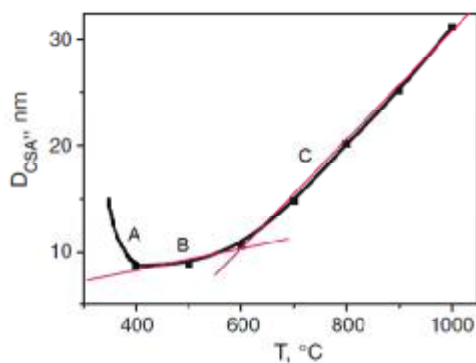


Figure 2. Dependence of nanoparticle size (coherent scattering area (CSA)) via calcination temperature, calcination time 2 h

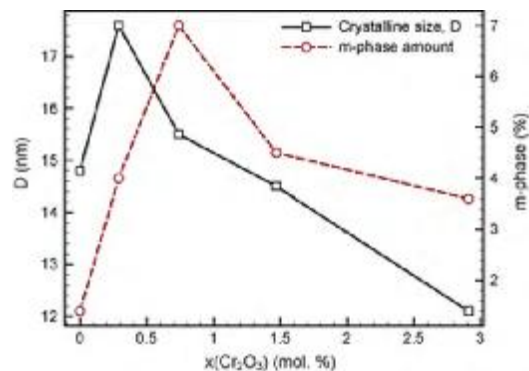


Figure 3. Crystalline size and phase composition vs. Cr<sub>2</sub>O<sub>3</sub> concentration as determined by XRD analysis (line is drawn only to guide the eye).