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## State Peculiarities of Hydrate Shell on the Surface of Nanoparticles of $ZrO_2$ - $Y_2O_3$ under Cr Doping

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Nanopowders of  $ZrO_2 + 3 \text{ mol. \% } Y_2O_3 + x \text{ Cr}_2O_3$  composition with x taking values of 0, 0.29, 0.74, 1.47, and 2.91 mol. % were synthesized by coprecipitation technique and investigated by means of XRD, BET, NMR and FTIR spectroscopy. Crystalline size, specific surface area and m-phase amount demonstrate non uniform dependence on concentration of chromium. NMR spectra of chromium free sample consists of three components assigned to water molecules, terminal and bridging OH groups. Two new lines emerge for all chromium containing samples and have been assigned by their shape and position to chromium hydroxide and water molecules affected by the presence of surface chromium cations.

**Key words:** nanopowders, yttrium stabilized zirconia, Cr-doping, NMR, FTIR, hydrate shell.

*Стаття поступила до редакції 22.09.2009; прийнята до друку 15.12.2009.*

### Introduction

For many years, zirconia has been extensively studied by a large number of techniques, for its application as functional and structural ceramics, SOFC electrolytes, catalyst, sorbents, medicine etc. Stabilization of high temperature phases of zirconia is carried out by adding oversized cations such as  $Y^{3+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ . The influence of other doping additives is not studied well. Chromium oxide is used as third additive for SOFC electrolytes conductivity improvement [1], as catalyst [2] and as suitable tool for investigation of microstructure of doped zirconia crystals by means of ESR [3]. Several works available on the influence of chromium on structure of zirconia nanopowders [4,5]. However, there is a lack of literature data on the influence of chromium doping on hydrate shell state of yttrium stabilized zirconia.

Our previous works [6,7] on chromium doping of yttrium stabilized zirconia have shown that introduction of chromium leads to inhibition of particles size growth and increase of crystallization temperature. Results of computer simulation [8,9] has shown that presence of chromium atom in the cation's position of zirconia plate increase the energy of thermal deposition of hydrogen and thus inhibits grain growth and crystallization temperature.

It is well known fact that surface of oxide nanopowders is covered with OH-groups and adsorbed water

molecules. A great amount of literature data is available on spectroscopic studies of zirconia powders hydrate shell. Investigations are carried out in several directions, for example: the investigation of hydrate shell state and influence of hydroxyls on stability of zirconia [10-13], interaction of zirconia surface with different molecules [14,15] influence of hydrate shell on catalytic performance in different reactions [16,17], etc. According to Tsyganenko and Filimonov [11] OH groups on the surface of oxides are present in several states depending on coordination of lattice oxygen. On the surface of  $ZrO_2$  nanoparticles three types of hydroxyl groups are usually observed, these groups are commonly assigned to terminal, bi-bridged and tri-bridged. Most of the above mentioned investigations are carried out using mid-range FTIR spectroscopy but  $^1H$  NMR technique is also used [18]. In present work we present results of  $^1H$  NMR and FTIR spectroscopy investigation of chromium doping influence on hydrate shell of yttrium stabilized zirconia nanopowders.

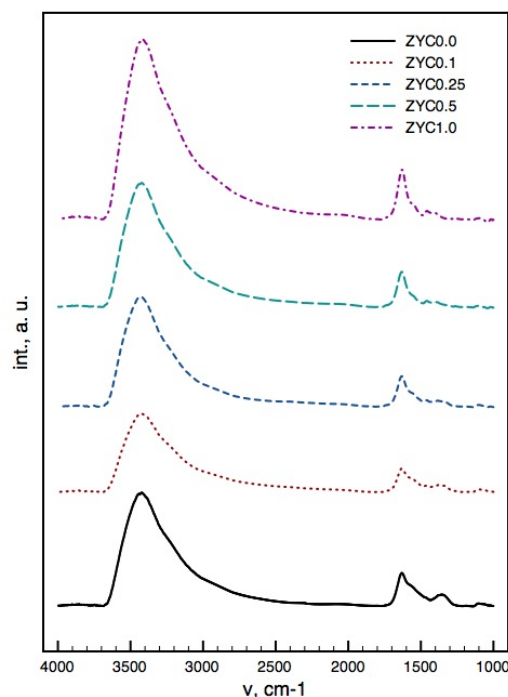
### I. Experimental details

Nanopowders of  $ZrO_2$ - $Y_2O_3$ - $Cr_2O_3$  system were synthesized by co-precipitation technique. Chemical composition of samples were:  $ZrO_2 + 3 \text{ mol. \% } Y_2O_3 + x \text{ Cr}_2O_3$  with x taking values of 0, 0.29, 0.74, 1.47 and 2.91 mol%. Samples labeled as  $ZYC_x$  with x taking values of

0, 0.1, 0.25, 0.5, 1 and indicating ratio of molar fractions of Cr to Y oxides (see Table 1. for details). Sediments were dried in air at 120 °C and calcined at 600 °C for 2 h and naturally cooled with furnace. X-ray diffractometer (XRD) with nickel-filtered Cu K $\alpha$  radiation was used to determine phase and crystalline size of calcined powder. Crystalline size was estimated using Scherrer formula [19]. Phase composition was calculated from the intensities of the diffraction lines 111 and  $\bar{1}\bar{1}\bar{1}$  of m-ZrO<sub>2</sub> and 111 line of t-ZrO<sub>2</sub> [20]. NMR spectra were acquired on Bruker Avance 400 instrument at room temperature with the following parameters:  $f = 100.61$  MHz, sweep - 602 ppm, MAS frequency - 12 kHz, pulse duration - 2.9  $\mu$ s, pulse period - 4.0 s. Deconvolution of spectral lines was done using Gauss-Newton method. Self supported thin KBr wafers were prepared and investigated by means of transmission FTIR spectroscopy in the mid-infrared region (4000-400 cm<sup>-1</sup>) on Bruker Tensor 27 instrument, 100 scans were taken. BET specific surface of nanopowders was measured using 4-point BET method and nitrogen adsorbate gas.

## II. Discussion

Crystalline size, monoclinic phase and specific surface area values are shown in Table 1. Maximum crystalline size is reached for ZYC<sub>0.1</sub> sample and is higher than for Cr-free sample, ongoing chromium fracture increase gradually decrease crystalline size value. Concentration dependence of specific surface area shows contrary behavior with minimum value of 48.34 m<sup>2</sup>/g for ZYC<sub>0.1</sub> sample. Maximum amount of monoclinic phase corresponds to ZYC<sub>0.25</sub> sample and is equal to 7%. IR spectra of prepared powders demonstrate a significant amount of residual water on the surface of the nanoparticles Fig. 1. Broad line at 3400 cm<sup>-1</sup> corresponds to the stretching vibrations of H<sub>2</sub>O molecules and line at 1640 cm<sup>-1</sup> represents bending vibrations. Spectral lines corresponding to OH groups are shaded by significant amount of residual water and though are not observed. Besides water absorption bands all of the samples exhibit several spectral lines with small intensities corresponding to carbonates formed on the



**Fig. 1.** FTIR spectra of chromium doped yttrium stabilized zirconia nanopowders.

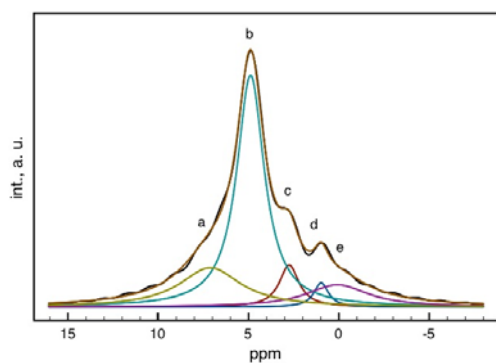
surface of the nanoparticles due to interaction with air contained CO<sub>2</sub> [9]. According to intensity of IR band at 3400 cm<sup>-1</sup> the amount of water on the surface of the nanoparticles reach it's minimum for ZYC<sub>0.1</sub> sample with ongoing increase in intensity for Cr fracture rise.

NMR spectra of chromium free samples consist of three components: broad line corresponding to residual water, sharp line corresponding to terminal groups and line corresponding to bridging hydroxyl groups. However, two new lines emerge when adding chromium oxide to zirconia and thus deconvolution of NMR spectra was based on five spectral lines Fig 2. These lines have been assigned to water molecules and hydroxyl groups in the following way: broad line at 4.91 ppm assigned to physically absorbed water, lines at 0.96 and 0.06 ppm assigned to terminal and bridging hydroxyl

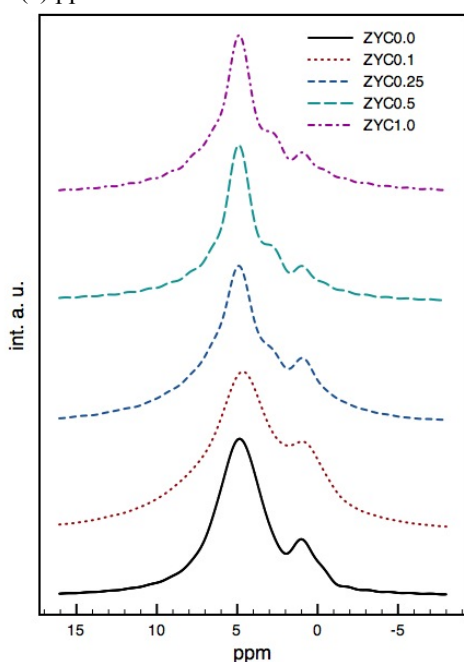
**Table 1**

Label, chemical composition, crystalline size, monoclinic phase amount and specific surface of investigated samples

Label	Chemical composition	Crystalline size, nm	Specific area, m <sup>2</sup> /g	m-phase amount, %
ZYC <sub>0.0</sub>	ZrO <sub>2</sub> + 3 mol. % Y <sub>2</sub> O <sub>3</sub>	14.8	61.51	1.4
ZYC <sub>0.1</sub>	ZrO <sub>2</sub> + 2.99 mol. % Y <sub>2</sub> O <sub>3</sub> + 0.29 Cr <sub>2</sub> O <sub>3</sub>	17.6	48.34	4.0
ZYC <sub>0.25</sub>	ZrO <sub>2</sub> + 2.98 mol. % Y <sub>2</sub> O <sub>3</sub> + 0.74 Cr <sub>2</sub> O <sub>3</sub>	15.5	60.64	7.0
ZYC <sub>0.5</sub>	ZrO <sub>2</sub> + 2.95 mol. % Y <sub>2</sub> O <sub>3</sub> + 1.47 Cr <sub>2</sub> O <sub>3</sub>	14.5	68.98	4.5
ZYC <sub>1.0</sub>	ZrO <sub>2</sub> + 2.91 mol. % Y <sub>2</sub> O <sub>3</sub> + 2.91 Cr <sub>2</sub> O <sub>3</sub>	12.1	85.36	3.6



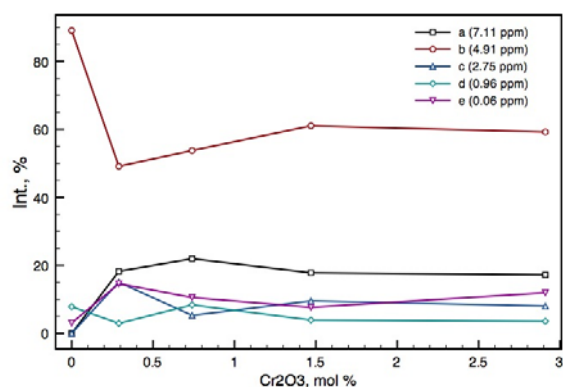
**Fig. 2.** Deconvolution of  $ZYC_{1.0}$  NMR spectra, values of chemical shift are 7.11 (a), 4.91 (b), 2.75 (c), 0.96 (d), 0.06 (e) ppm.



**Fig. 3.** NMR spectra of chromium doped yttrium stabilized zirconia nanopowders.

groups respectively, sharp line at 2.75 ppm and broad one at 7.11 ppm have been assigned to chromium hydroxide and to the water molecules influenced by the presence of surface chromium cations. The presence of two new lines shows that chromium is more active than zirconium and yttrium since no such states are seen in Cr-free sample.

NMR spectra of all five samples are shown at Fig 3. and intensities of components vs concentration at Fig 4. Addition of chromium oxide leads to increase in line intensity at 2.75 ppm for the smallest chromium concentration and decrease of terminal groups amount (0.96 ppm). Such behavior shows the change in surface structure of zirconia nanopowders which becomes more



**Fig. 4.** Concentration dependence of NMR spectra components (line is drawn only to guide the eye).

favorable for bridging groups rather than terminal. Though intensities of spectral components unevenly distributed through concentration of chromium, general trend is the hydroxyl groups fracture increase when adding chromium oxide. The most significant change is the water fracture for  $ZYC_{0.1}$  sample that correlates well with the biggest value of crystalline size (Table 1.). FTIR measurements support NMR spectroscopy results for residual water very well. Obtained results support computer simulations made in [9] showing that presence of Cr at cations site of zirconia plate dramatically increase the energy of thermal deposition of hydrogen, while yttrium has the smallest impact from 26 d-elements chosen for simulation. Since the crystallization of zirconia is controlled by OH groups and water and chromium influence these species, experimental results demonstrate the inhibition of particles growth. Thus, the sample with highest crystalline size value could indicate yttrium segregation because if yttrium is on the surface then particles will grow faster as opposed to chromium oxide presence.

## Conclusions

In summary of all above mentioned following conclusions can be made: 1) addition of 0.29 mol. % of chromium leads to particle size increase though crystalline size growth is inhibited for all other concentrations of chromium, 2) two new lines emerge in NMR spectra of chromium doped samples which have been assigned to chromium hydroxide and water molecules affected by the presence of chromium surface cations contrary to NMR spectra of chromium free sample which exhibits only three components, 3) obtained results shows that peculiarities of hydrate shell state under chromium doping are devoted to the fact that chromium is more active than zirconium or yttrium.

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## Особливості стану гідратної оболонки на поверхні наночастинок ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> при легуванні Cr

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Нанопорошки складу ZrO<sub>2</sub> + 3 мол. % Y<sub>2</sub>O<sub>3</sub> + x Cr<sub>2</sub>O<sub>3</sub>, де x дорівнює 0, 0,29, 0,74, 1,47 та 2,91 мол. %, було синтезовано методом сумісного осадження та вивчено методами рентгенівської дифракції, ЯМР та ІЧ спектроскопії. Питома поверхня наночастинок визначалась чотирьох точковим методом BET. Розмір наночастинок, питома поверхня та вміст моноклінної фази немонотонно залежать від концентрації хрому. Спектр ЯМР зразка без хрому містить три компоненти, які були віднесені до адсорбованої води, термінальних та місткових OH груп. Дві нові компоненти, які з'являються у спектрі для всіх зразків що містять хром, були відповідно до їх форми та положення віднесені до гідроксиду хрому та молекул води, які знаходяться під впливом поверхневих катіонів хрому.