Low-temperature hydrothermal synthesis of nanostructured solid solutions in the system $CeO_2 – ZrO_2$

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Thanks to the unique physicochemical properties of cerium dioxide, the materials based on it are used as protective coatings, three-way catalysts, sensing devices, in biomedical preparations, etc. The small difference in the energy levels of Ce^{4+} and Ce^{3+} cations along with the high mobility of oxygen anions and dimensional factor provide nanostructured CeO_2-ZrO_2 complex-oxide compositions with high specific surface area and oxygen capacity, contribute to higher catalytic activity. The concentration of oxygen vacancies in the anion sublattice of the synthesized $Zr_xCe_{1-x}O_2$ solid solutions can be increased by the isomorphic implantation of zirconium cations. The nanoparticles of CeO_2-ZrO_2 solid solutions show an increased stability against change in their size at high temperatures through the ability of zirconium dioxide to hinder aggregation and retain in this case all properties of nanoscale cerium dioxide.

This paper presents results of a hydrothermal synthesis of nanostructured solid solutions based on cerium and zirconium dioxide using decomposition products of Ukrainian zirconium-bearing raw materials as starting zirconium-containing compounds.

The hydrothermal breakdown of zircon concentrate was carried out with alkaline solutions (400–800 g/dm^3 NaOH) in the presence of calcium fluoride:

$$ZrSiO_4 + 2NaOH + 3CaF_2 + H_2O \rightarrow Na_2ZrF_6 + CaSiO_3 + 2Ca(OH)_2$$

To synthesize solid solutions, zirconium compounds which are formed on the dissolution of zircon decomposition products obtained were used:

$$Na_2ZrF_6 + 4HCl + H_2O = ZrOCl_2 + 2NaCl + 6HF;$$
$$CaSiO_3 + 2HCl = CaCl_2 + H_2SiO_3$$

Zirconium hydroxide was precipitated from acid solutions obtained. Since the stock solutions contain up to 25 wt % CaO, doping of zirconium dioxide by calcium dioxide takes place, which facilitates the formation of its tetragonal modification and raises the rate of the synthesis of $Zr_xCe_{1-x}O_2$ solid solutions.

Solid solutions were synthesized from reactive cerium nitrate ($Ce(NO_3)_3$•$6H_2O$ 0.06 M) and a specially prepared hydrochloric acid solution of decomposition products of zircon concentrate, zirconium oxychloride ($ZrOCl_2$ 0.05 M). The homogeneous precipitation of cerium and zirconium hydroxo-compounds was carried out in a 0.5 M hexamethylene tetramine solution with thermostatting at 70–80^{0}C during 5–6 h and continuous stirring. The resulting washed precipitates as a suspension were placed in autoclaves, and a hydrothermal synthesis of $Zr_xCe_{1-x}O_2$ solid solutions was carried out in a temperature range of 150–180^{0}C during 2-4 h.

$Zr_xCe_{1-x}O_2$ solid solutions with different zirconium dioxide concentration (x = 10–60 mol % ZrO_2) have been obtained.

According to the data of an X-ray phase analysis, all synthesized samples were single-phase ones and had a fluorite crystal structure. There were no diffraction maxima corresponding to oxo- and hydroxo-compounds in the diffractograms. As the zirconium dioxide concentration in the solid solution was increased from 0 to 60 mol % the position of diffraction maxima shifted towards larger angles, which indicated that zirconium ions entered the cerium dioxide lattice.

The plots of unit cell parameters against zirconium dioxide content for nanocrystalline $Zr_xCe_{1-x}O_2$ solid solutions are satisfactorily approximated by the Vegard law. It was noted that the lattice parameters of $Zr_xCe_{1-x}O_2$ solid solutions synthesized using hydrothermal decomposition products of Ukrainian zirconium-bearing raw materials as starting zirconium-containing compounds have larger values than the analogous phases synthesized from reagents. This indicates that calcium ions, whose radius is larger than that of zirconium and cerium ions, enter the solid solution lattice. Chemical analysis of such solid solutions confirms the presence of calcium in them.