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Sonochemical synthesis of mesoporous $Gd_xZr_yTi_zCe_{1-x-y-z}O_2$ solid solution

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Abstract

$Gd_xZr_yTi_zCe_{1-x-y-z}O_2$ ($x+y+z \leq 0.3$) solid solutions with a crystallite size of 5–10 nm have been prepared by the sonochemical method from inorganic salts without any additives. In all cases, ceria based materials exhibited a mesoporous structure with polymodal pore size distribution with diameter of 2–10 nm. It was shown that crystallite size and specific surface area remained practically unchanged while changing the dopant concentration.

Keywords: Ceria; Solid solution; Mesopores; Nanoparticle

1. Introduction

Nanoscale ceria is very attractive for TWC, SOFC, biological applications, solar cells, UV radiation filters, electrochromic devices, polishing mixtures and abrasives etc. Doped ceria based materials are considered as more promising solid solutions for use in these goals. The special attention paid to ceria is due to its unique redox properties. The reason is oxygen donation of ceria caused by partial Ce^{4+}/Ce^{3+} reduction on the particle surface. In pure ceria, there are two kinds of oxygen species available for its oxygen storage capacity (OSC): one is surface oxygen and the other is bulk. The introduction of smaller isovalent non-reducible cations like Zr^{4+} and Ti^{4+} into the ceria lattice enhances the OSC by creating intrinsic oxygen vacancies thereby increasing the oxygen mobility by facilitating the Ce^{3+}/Ce^{4+} redox process. Whereas the doping of aliovalent non-reducible cations (Gd^{3+}) into the ceria lattice enhances the OSC mainly through the extrinsic oxygen vacancies [1–3]. Recently, the use of variable valence dopants into ceria lattice has attracted much attention.

It is known that the properties of ceria materials are dependent on the initial powder properties such as homogeneity, particle size, porous structure, and phase purity. It is clear that the quality of the synthesized powder changes with the preparation method [4,5]. However, the simplest method for production of nanoscale ceria, especially for catalytic applications, is necessary to be used for obtaining a large quantity of intermediates. Among them, the most suitable and simplest method is co-precipitation with ultrasonic treatment (sonochemical method). Ultrasound irradiation can induce the formation of particles with much smaller size and higher surface area than those reported by other methods, and this technique has good reproducibility [6].

In this work, we describe the synthesis of $Gd_xZr_yTi_zCe_{1-x-y-z}O_2$ ($x+y+z \leq 0.3$) solid solution by sonochemical method from inorganic salts without any additives [7–9]. Unfortunately, such solid solutions previously were not obtained, but there is the perspective of the using of similar composition systems [10–12].

2. Material and methods

2.1. Synthesis

Cerium(III) nitrate, zyrconyl nitrate, gadolinium nitrate, and titanium(IV) chloride were used as metal precursors. Appropriate amounts of salts were dissolved into 500 mL distilled water containing of nitric acid (pH=2) to give final concentrations of 0.04 M. Then, the deposition was carried out by addition of aqueous ammonia at 30 °C under stirring to reach

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pH 10. Sonication (frequency 35 kHz, power 150 W, Sapphire UZV-4.0) was used during dissolution of salts in distilled water (10 min), and after receiving the sediment (10 min). The resulting precipitate was filtered, washed with distilled water (H_2O/C_2H_5OH=9 vol.), dried at 150 °C for 12 h, and calcined in static air by heating at a rate of 4 °C/min from room temperature to 500 °C and kept at 500 °C for 1 h in a muffle furnace.

2.2. Characterization

Powder XRD data were collected at room temperature (DRON-3M, Russia) with Cu*K*α radiation. Particle size (d_{XRD}) measurements were made by applying the Scherrer equation to the full-width at half maximum after accounting for instrumental broadening using germanium as reference; d_{XRD} was calculated not on a separate peak, but was on all planes during the fitting of the spectrum. Quantitative phase analysis was calculated by the Rietveld method.

Specific surface area (S_{BET}) of the powders was measured by a conventional (BET method) nitrogen sorption method at 77 K (TriStar 3000 Micromeritics). Pore-size distributions were calculated from desorption isotherm data using BJH method. Samples were degassed at 120 °C for 5 h prior to measurement.

TEM analyses were conducted on Omega Leo-912AB transmission electron microscope with accelerating voltage of 100 kV.

SEM was obtained with TescanVEGAII LEO 1420 scanning electron microscope with accelerating voltage of 20 kV, equipped energy-dispersive X-ray spectrometer (EDS) INCA Energy 300.

FT-IR spectra were recorded using Thermo Nicolet AVATAR330 FT-IR spectrometer.

Thermal analysis (TG/DSC) was carried out under air flow with Netzsch STA449F3. The samples were heated to 900 °C at the rate of 5 °C/min.

3. Results and discussion

XRD patterns of ceria based nanopowders are shown in Fig. 1. All planes were perfectly indexed as the pure cubic phase (Fm3m, JCPDS-34-0394) of CeO_2, indicating the formation of solid solutions by the incorporation of respective dopant ions into the ceria lattice. The introduction of dopants into ceria caused a slight shift in the diffraction peaks of various samples when compared to that of pure ceria. This shift indicates of the change in the lattice parameter (Table 1). This corresponds to a decrease of cell parameter (a) with the increase of dopant content in the mixed oxides directly related to the ionic radii. SAED method (Fig. 2, inset) also confirmed the formation of fluorite structure solid solution.

One can see that, while the dopant concentration (Gd or Ti or Zr) was changed, the crystallite size (d_{XRD}) remained practically unchanged (Table 1) according to XRD data calculation by Scherer equation, and this was confirmed by TEM data (Fig. 2). Upon increasing calcination temperature a gradual sharpening of the peaks is observed in the XRD patterns revealing the increase in the crystallite size (sample 5-150–5-900). Slight increase in size at temperatures up to 500 °C and a sharp increase at higher

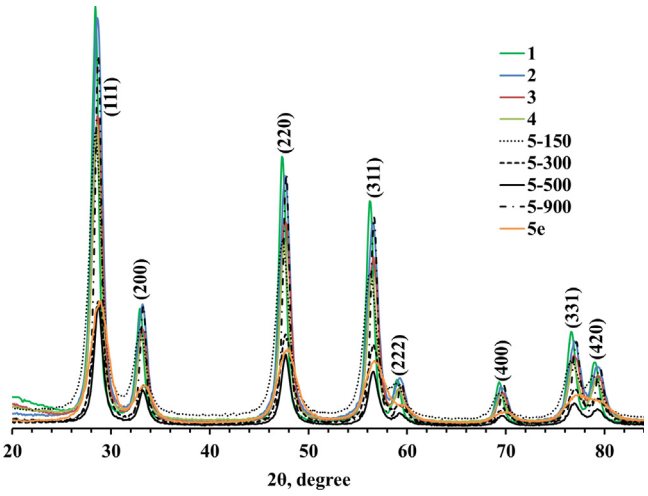

Fig. 1. XRD patterns of powders with Cu*K*α radiation.

Table 1
Main characteristics of ceria-based powders (150–900—calcination temperature, e—ethanol as solvent).

No	Sample	d_{XRD} (nm)	Lattice parameter (Å)	S_{BET} (m^2/g)
1	CeO_2	14.0	5.4094	53
2	$Gd_{0.05}Ti_{0.05}Zr_{0.1}Ce_{0.8}O_2$	9.8	5.4005	87
3	$Gd_{0.05}Ti_{0.1}Zr_{0.05}Ce_{0.8}O_2$	9.3	5.3988	83
4	$Gd_{0.1}Ti_{0.05}Zr_{0.05}Ce_{0.8}O_2$	10.2	5.4046	85
5-150	$Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$	6.8	5.4123	62
5-300	$Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$	7.4	5.4050	112
5-500	$Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$	9.2	5.4045	83
5-900	$Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$	18.8	5.3895	7
5e-500	$Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$	4.9	5.3971	110

temperatures can be explained on the basis of a growth model based on the mechanism of oriented attachment [13,14]. It can be seen that the lattice parameter decreased at an increase in the sintering temperature. Such a variation in the lattice parameter can be explained by the fact that dopant introduction resulted in the formation of the substitutional solid solution and the degree of dopant intercalation into the lattice grew at the increase in the temperature. When replacing the solvent with aqueous upon ethanol (sample 5e) crystallite size was decreased from 9 to 5 nm.

The calcination temperature was chosen after TG-DSC measurements (Fig. 3). Endo-effect was observed at 100–120 °C and associated with the removal of the adsorbed water, and exo-effect at 235–245 °C—crystallization of the solid solution, thus, according to XRD, the formation of the solid solution has already occurred during the deposition and drying, so the temperature of 300 °C was the end of the formation of a crystalline powder.

IR spectra (Fig. 4) exhibit a broad band around 3200–3700 cm^{-1} and around 1630 cm^{-1} corresponding to stretching mode and deformation vibration of OH group, accordingly, which is contributed by adsorbed water contents. The Me–O band till 500 cm^{-1} attributed to the vibration of ceria-based solid solution.

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