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Redox behavior of nanocrystalline $Ce_{1-x}Lu_xO_{2-x/2}$ mixed oxide obtained by microemulsion method

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ABSTRACT

Nanocrystalline $Ce_{1-x}Lu_xO_{2-x/2}$ ($x = 0.17, 0.25, 0.5$) mixed oxides with narrow size distribution (4–5 nm) were prepared by a water-in-oil (W/O) microemulsion method. Microstructure and reduction–reoxidation properties of the oxides were analyzed by HRTEM, STEM-EDX, XRD, H_2-TPR and TPO. The presence of Lu^{3+} ion in the cation sublattice generates strain in the ceria lattice through the creation of crystal imperfections and oxygen vacancies and drastically affects redox properties of the system. All synthesized samples had fluorite structure of CeO_2 from XRD and all exhibited significant, low temperature reducibility (max. at 368 °C), persisting after repeated reduction and low temperature oxidation cycles at 500 °C. Oxidation treatment at higher temperature (950 °C) destroyed completely the low temperature reducibility of the mixed oxides, that could not be accounted for to particle growth. TPO data indicated that Ce^{3+} species formed after reduction at 930 °C in the $Ce_{0.83}Lu_{0.17}O_{1.915}$ and $Ce_{0.75}Lu_{0.25}O_{1.875}$ samples were very sensitive to oxygen atmosphere even at room temperature. However, some Ce^{3+} species formed in the $Ce_{0.5}Lu_{0.5}O_{1.75}$ sample were very stable in air. Additionally, the existence of biphasic region (F + C) was also unequivocally detected by HRTEM and TPO method in nanocrystalline $Ce_{0.5}Lu_{0.5}O_{1.75}$ after oxidation treatment at 950 °C.

1. Introduction

CeO_2-based oxides have proved to be materials of exceptional technological importance due to their unique properties, including high oxygen storage capacity (OSC) [1,2], and oxygen ion conductivity [3–5]. As catalytically active materials [6], nanocrystalline ceria-based oxides are used to reduce the emissions of CO, HC, NO_x from automotive exhaust [7,8], and to oxidize harmful diesel soot particles [9–11]. Most important for these applications is that fluorite-type (F-type) ceria-based oxides, containing various doping elements, exhibit high oxygen mobility and OSC under operating conditions at either lower or higher temperatures.

Due to their higher ionic conductivity at lower temperatures than conventional yttria-stabilized zirconia (YSZ), ceria-based oxides have recently attracted a lot of interest as potential solid oxide ion-conducting electrolytes or composite anodes in intermediate temperature solid oxide fuel cells (IT-SOFC) [12–14], and as gas sensors [15]. The control of the morphology of doped ceria starting powders through grain size, grain boundaries, dopant content, sintering temperature are key factors for tailored processing of SOFC components [16,17]. The performance of ceria in SOFC applications can be enhanced mainly by its doping with small concentrations of lower valent cations like Gd, Sm, Y, La, Nd, Lu, Ca, etc. [18–26], while maintaining the fluorite structure of ceria.

Doping of nanocrystalline CeO_2 with various cations (Zr, Tb) is applied to enhance the OSC property, especially to improve reducibility at low temperatures [27–30], and to stabilize the structure against sintering [30], enabling practical use in catalytic applications. Up till now, many attempts have been made to lower the oxygen release temperature of CeO_2-based oxides including nanomaterials synthesis by soft chemistry [31], and doping ceria with tri- or divalent cations, and surface modifications by chemical filing process [32]. We have also shown recently that various dopants (Zr, Pr, Tb, Lu) hinder crystallite growth of ceria in oxidizing atmosphere and improve the redox properties [11,33,34].

Recently, much attention is devoted to nanocrystalline binary Ce–Ln–O oxides, which show improved performance in comparison with their microcrystalline counterparts [35–37]. It is now commonly understood that the behavior of nanophase materials strongly depends also on the shapes and sizes of the particles [38]. Characterization of the nanosized material brings serious challenges because many of the classical characterization methodologies are unable to provide a detailed picture of the material at nanoscale [39]. Ce–Ln–O nanomaterials of similar composition

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may have very different properties due to different nanodomain structure and texture. Therefore, there is an urgent need to use multi-technique characterization of these materials to find their possible nanoscale heterogeneities [40–42].

There are various methods of preparation of nanocrystalline ceria based mixed oxides [43–45]. In this work we used reversed micelle microemulsion method, which enables production of small (4–5 nm) particles, with narrow size distribution and homogeneous composition of the powder [46–48]. In the present study, we investigated, for the first time, the reduction–oxidation cycle behavior of Lu^{3+} substituted nanocrystalline ceria $Ce_{1-x}Lu_xO_{2-x/2}$ ($x = 0, 0.17, 0.25, 0.5$) to see the effect of structural modification on the redox behavior of Ce^{4+} ions. Though the redox properties of ceria and ceria zirconia mixed oxides are well characterized [37], the properties of lutetium doped nanocrystalline ceria have not been reported yet.

2. Experimental

Nanoparticles of $Ce_{1-x}Lu_xO_{2-x/2}$ ($x = 0.17, 0.25$, and 0.5), shortly CeLu17, CeLu25, and CeLu50), were prepared by precipitation in water-in-oil (W/O) microemulsion method described in our previous paper [11]. In brief Triton X-100 was used as a non-ionic surfactant and cyclohexane and 1-penthanol as an organic phase. Aqueous solutions of lanthanides (as nitrates) and ammonia were used as a water phase. Powder samples obtained by centrifugation were dried and standardized by heating in oxygen at 550 °C for 3 h. This pre-treatment procedure was carried out to leave the surface in a clean reproducible state. Composition of the samples was confirmed with EDS spectroscopy (EDAX PV 9800 spectrometer). Further thermal treatment was performed in tubular oven in H_2 or O_2 flow.

Phase composition and lattice parameter of the samples were determined by XRD (STOE, Cu Kα_1 radiation) with WinPLOTR program [49] used for display and analysis of XRD patterns. Morphology and microstructure were investigated by TEM (Philips CM-20 SuperTwin operating at 200 kV and providing 0.25 nm resolution). Analysis of HRTEM images was made with ImageJ program [50]. Specimens for TEM were prepared by dispersing some powder sample in methanol and putting a droplet of the suspension on a copper microscope grid covered with perforated carbon. Local composition of the CeLu50 sample at the nanometer scale was studied by STEM-EDX technique using Jeol JEM 2010F (FEG, 200 kV, 0.19 nm resolution) equipped with Oxford Instruments INCA X-sight EDX nanoanalizator.

Temperature-programmed reduction and oxidation (TPR/TPO) experiments were performed in a flow apparatus using U-shaped quartz micro-reactor. 50 mg of catalyst was reduced in a H_2 (5 vol.%)/Ar mixture at temperature ramped from room temperature to 930 °C, with heating rate of 10°/min. Before the TPR experiment the samples were activated in a flow of O_2 (N55) at 550 °C for 0.5 h. The hydrogen consumption was measured by a thermal conductivity detector (TCD) with a PC for data storage and processing. The water produced during the TPR experiments was removed in a cold trap filled with a mixture of liquid N_2 and 2-propanol. The TCD response was quantitatively calibrated by the reduction of a known amount of CuO. After the reduction experiment the sample was cooled to RT and then oxidized in the flow of O_2 at 550 °C for 0.5 h (mild oxidation – MO). The TPR experiment was then repeated. After the second run the sample was cooled to RT in 5% H_2/Ar mixture. Then the gas was changed to He (6N) to clean the sample and finally 1% O_2/He mixture was used as an oxidant (flow rate 50 ml/min) in the TPO experiment. The oxidation of the materials was performed from 30 to 930 °C at a rate of 10°/min to reveal the stability of the reduced Ce^{3+} ions. After the TPO experiment, the sample was calcined in the flow of O_2 at 950 °C for 1 h (severe oxidation – SO). The TPR experiment was then repeated (3rd run). The analysis of O_2 concentration in the effluent gas during TPO was performed with a mass spectrometer (OmniStar QMS 200, Pfeiffer Vacuum). The mass spectrometer has an electron impact (EI) source, a quadrupole mass analyzer and a Channeltron SEM detector (a discrete dynode secondary electron multiplier). It should be pointed out that the reduction–reoxidation cycles were performed without the exposure to air and without the replacement of the catalyst on repeated runs. The purpose of the reoxidation treatment was to reveal the oxidation properties of the reduced samples.

3. Results and discussion

3.1. Structural properties of $Ce_{1-x}Lu_xO_{2-x/2}$ mixed oxides

The XRD profiles of CeLu50 sample as prepared (550 °C, O_2) and heat-treated at 950 °C in O_2 or in H_2 are shown in Fig. 1. According to XRD, CeLu50 and other as prepared oxides had the fluorite type structure of CeO_2 (*Fm*-3*m*) and contained crystallites with size 4–5 nm. Lattice parameter of the as prepared mixed oxides (Table 1) was smaller than that of CeO_2 and decreased with increasing Lu content indicating the formation of a homogeneous solid solution [25,51]. Simultaneously, the maximum average stress in the crystal lattice is increased. This observation is consistent with the simple model assuming that Lu^{3+} (ion radius 0.86 Å) substitute for Ce^{4+} (0.97 Å) in $Ce_{1-x}Lu_xO_{2-x/2}$ mixed oxides with simultaneous formation of oxygen vacancies. The larger the content of lutetium in $Ce_{1-x}Lu_xO_{2-x/2}$, the higher the number of oxygen vacancies. For every two Lu^{3+} ions that replace Ce^{4+} ions, one double-charged oxygen vacancy is needed to balance the charge. It may be concluded therefore that the magnitude of the strain increases with the number of oxygen vacancies. As the result of thermal treatment of $Ce_{1-x}Lu_xO_{2-x/2}$ oxides at 950 °C in various atmospheres (hydrogen

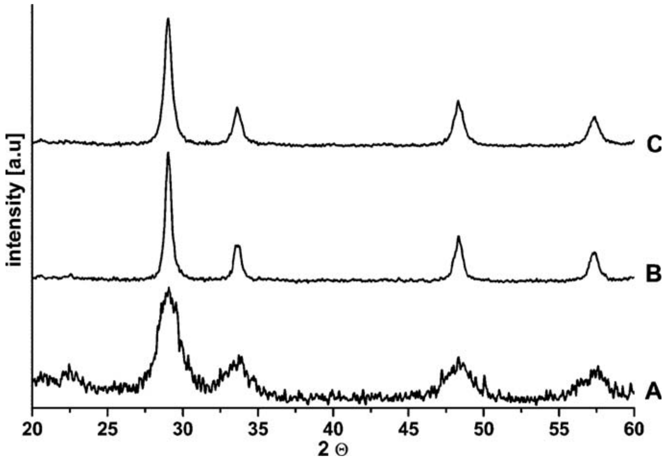

Fig. 1. XRD patterns CeLu50 samples heated at (A) 550 °C for 3 h in O_2, (B) 950 °C for 3 h in O_2, (C) 950 °C for 3 h in H_2.

Table 1
Microstructure data for $Ce_{1-x}Lu_xO_{2-x/2}$ mixed oxides.

	Lattice parameter (nm)		Average size (nm)		Maximum average strain (10^{-3})	
Sample	Fresh	Cycled	Fresh	Cycled	Fresh	Cycled
CeLu0	0.5411	0.5406	9.7 ± 0.5	19.6 ± 0.5	12 ± 3	6.0 ± 1
CeLu17	0.5391	0.5388	5.7 ± 0.4	14.1 ± 2	20 ± 5	8 ± 2
CeLu25	0.5385	0.5385	5.2 ± 0.3	12.8 ± 1	22 ± 5	9.0 ± 2
CeLu50	0.5323	0.5328	3.7 ± 0.6	8.3 ± 0.4	31 ± 6	14 ± 3