Ceria-based solid solutions for environmental application

I V Zagaynov1*, I V Shelepin1,2, S V Fedorov1, A A Klimashin1 and I V Kulbakin1

1 Baikov Institute of Metallurgy and Materials Science
2 Mendeleev University of Chemical Technology of Russia

*igorscience@gmail.com

Abstract. The work is focused on the investigation of the influence of metal oxide promoted ceria based materials with various dopants on the physicochemical, electrical and catalytic properties for CO oxidation in model reaction. The formation of stable solid solutions by doping gadolinium, bismuth, and third metal enhances the redox properties, oxygen vacancies, stability, and, of course, catalytic activity and electroconductivity.

1. Introduction

In the context of significant interest in energy efficient technologies and environmental protection, materials based on nanostructured ceria are promising for solving existing problems. The advantage of such materials is due to that CeO2 has a large oxygen storage capacity (OSC) and high oxygen mobility, which can ensure its high catalytic activity and electrical conductivity. Solid solutions based on ceria with the dopant of Bi have recently attracted attention to the production of both electrolytes and catalysts due to the special electron orbital structure to improve conversion efficiency [1-3]. The development of more stable systems based on GDC and bismuth oxide, using as a sintering additive without preservation of bismuth oxide or a second dopant with the preservation of the initial composition of the solid solution based on ceria, is proposed. Moreover, triple-doping or multi-doping in ceria has been studied and succeeded to improve the properties of ceria [4-6]. However, further investigations are still required on tri- or multi-doped ceria in order to develop new materials for future catalytic and SOFC applications. Thus, it is necessary to investigate systems, based on ceria solid solution with three dopants Gd0.05Bi0.15M0.05Ce0.75O2 (M = Cu, Zr, Ni, Co, Mn) as a promising.

2. Materials and Method

Ce(NO3)3·6H2O, Bi(NO3)3·5H2O, Gd(NO3)3·6H2O and Cu(NO3)2·3H2O or ZrO(NO3)2·7H2O or Ni(NO3)2·6H2O or Co(NO3)2·6H2O or Mn(NO3)2·4H2O (Acros Organics) were used as initial salts. Appropriate amounts of salts were dissolved in concentrated nitric acid (68%) with the concentration of salts of 0.667 M. After the dissolution of salts, this mixture was added to distilled water, giving the concentration of 0.1 M and after stirring acetylacetone (Hacac) was added (Hacac/Σ(Me)=1). Then, the co-precipitation was carried out by the addition of 2.5 M KOH solution up to pH 11. Ultrasonic processing (35 kHz, 150 W) was used during all process at 30°C under stirring. The resulting precipitates were filtered, washed with distilled water-ethanol solution (H2O/C2H5OH=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 the muffle furnace.

The as-obtained powders were pressed into pellets (with 5 wt.% binder made of 5% aqueous solution of polyvinyl alcohol) with 10 mm in diameter and 1 mm in thickness at 180 MPa. Then they were...
sintered at 750°C (T_{sir}) for 4 h in air with heating of 4°C/min. To fabricate symmetric cells for the impedance studies (Elins Z-350M impedance meter, the frequency range from 0.1 Hz to 1 MHz at the amplitude of AC signal of 30 mV), platinum paste was brushed onto both sides of the electrolyte pellets, and were dried at 150°C for 1 h and annealed at 750°C for 4 h in air. A platinum wire was used as current conductors.

The catalytic activity of the synthesized samples in the oxidation of CO was determined by the flow method at atmospheric pressure. The process was conducted in a U-shaped quartz reactor at the total flow rate of 60 ml/min within a temperature range of 20-500°C. The temperature was measured with a thermocouple placed in the center of the catalytic bed. The catalyst sample mass was 0.3 g. The model gas mixture has the following composition, vol.%: CO – 1; O₂ – 2; N₂ – balance. The concentrations of gases were determined by a gas chromatograph (Varian 450GC).

All powders and ceramics were characterized by XRD (Rigaku MiniFlex 600, CuKα radiation), SEM (TESCAN VEGA II SBU with INCA Energy 300 energy dispersive spectrometers), TG-DSC-MS (Netzsch STA449F3, the samples were heated to 1350°C at the rate of 10°C/min in air), TEM (Omega Leo-912AB), nitrogen adsorption-desorption method (TriStar 3000 Micromeritics).

3. Results and discussion

The stability and availability of solid solutions Gd₀.₅Bi₀.₅₂M₀.₅⁻Ce₀.₇₅O₂ (M = Cu, Zr, Ni, Co, Mn) were evaluated. The endothermic peaks at 750-800°C can be attributed to the formation of other phases and at >1000°C with the evaporating process of Bi compounds.

### Table 1. Some characteristics of initial powders and ceramics.

| No | Sample | d_{XRD} (nm) | S_{BET} (m²/g⁻¹) | T(100% conversion of CO, °C) | σ_{600°C} (*10⁻³, S/cm⁻¹) |
|----|--------|-------------|------------------|-----------------------------|---------------------------|
| 0  | Gd₀.₅Bi₀.₅₂Ce₀.₇₅O₂ | 8           | 23               | 404                         | 5.0                       |
| 1  | Gd₀.₅Bi₀.₅₂Cu₀.₅₅Ce₀.₇₅O₂ | 11          | 60               | 424                         | 1.0                       |
| 2  | Gd₀.₅Bi₀.₅₂Zr₀.₅₅Ce₀.₇₅O₂ | 11          | 69               | 485                         | 0.1                       |
| 3  | Gd₀.₅Bi₀.₅₂Ni₀.₅₅Ce₀.₇₅O₂ | 10          | 72               | 464                         | 0.9                       |
| 4  | Gd₀.₅Bi₀.₅₂Co₀.₅₅Ce₀.₇₅O₂ | 12          | 62               | 441                         | 2.4                       |
| 5  | Gd₀.₅Bi₀.₅₂Mn₀.₅₅Ce₀.₇₅O₂ | 8           | 95               | 395                         | 8.3                       |

According to XRD (Figure 1a), samples have single-phase with fluorite structure (Fm3m, JCPDS-34-0394). The XRD pattern of calcined powders at 500 and 1000°C (Fig. 1a) shows that the only single phase of the solid solution was formed, and no peaks of other phases were detected. When the spectrum is completely approximated, it is determined that it is also possible to form an amorphous copper oxide and cobalt oxide in the corresponding samples (rather in the form of very small particles). XRD pattern of calcined powders at 1000°C (Fig. 1a) shows that both phase of ceria solid solution and other phases were formed. In all samples, there is a phase of Bi₂O₃ (γ-Bi₂O₃, sillenite, cl66), which was not found in the system without a third dopant [7].

The shape of the adsorption-desorption curves for all samples (Figure 1b) corresponds to the IV type, which is typical for the formation of the mesoporous structure. For all samples, the shape of the hysteresis loop corresponds to the H2 type: apparently, individual or connected cylindrical and bottle-shaped pores may be present, which is also confirmed by the pore size distribution (Figure 1c).

The average crystallite size calculated using Scherrer formula was about 5-10 nm for all samples, which corresponds to the individual particles according to TEM (Figure 1d).

It is known that pure ceria is a poor oxide ion conductor (σ_{600°C}≈10⁻³ S/cm), and the ionic conductivity can be significantly enhanced by increasing the oxygen vacancies, which can be created by the doping of ceria with about 20% concentration of dopant, because such systems achieve the highest conductivity, but a further increase in the dopant concentration results in decreasing one. The highest conductivity for intermediate temperature application was found in Gd₀.₅Bi₀.₅₂Mn₀.₅₅Ce₀.₇₅O₂ (Table 1). In addition, it
was recently shown that the nature of manganese species in ceria may vary with the method of synthesis [8]. Moreover, after sintering Mn ions may be in solid solution with ceria, or as a segregated phase along the grains boundaries, or even on the surface of grains, therefore, the sintering mechanism of this system is a very complex phenomenon and requires further experiments.

![XRD patterns](image1.png)

**Figure 1.** XRD patterns (a), adsorption-desorption isotherms (b), pore size distributions (c), TEM microphotos (d), catalytic activity in CO oxidation (e), and impedance spectrum at 600°C in air of of sample 5 (Gd$_{0.05}$Bi$_{0.15}$Mn$_{0.05}$Ce$_{0.75}$O$_2$).

The catalytic activity of systems was determined in the model oxidation reaction of CO. The conversion of carbon monoxide increases with the increase in temperature, and the curves have S-shaped type (Fig. 4). The 100% oxidation temperature of CO was following, °C: 404 (sample 0), 424 (sample 1), 485 (sample 2), 464 (sample 3), 441 (sample 4), 395 (sample 5). The full conversion temperature is higher than the original reference sample. However, the parameter $T_{50\%}$ is lower than that of the sample 0. As expected the modification by Cu or Mn [4] has a good effect on the surface, increasing the catalytic activity. The sample 5 (Gd$_{0.05}$Bi$_{0.15}$Mn$_{0.05}$Ce$_{0.75}$O$_2$) has the lowest oxidation temperature. The systems
with the addition of zirconium had a conversion temperature higher by 100°C. When comparing the best catalyst with other systems based on ceria (Zr$_{0.12}$Y$_{0.08}$Ce$_{0.8}$O$_2$, La$_{0.12}$Y$_{0.08}$Ce$_{0.8}$O$_2$, etc. [9, 10]) under close test conditions, the catalytic activity of the developed system was higher (the temperature of complete oxidation of CO is lower by 50-100°C).

4. Conclusions
The investigation showed the expediency of using such catalysts in the oxidation of CO and these solid solutions could be used as the catalyst or support for the subsequent deposition of an active phase. As noted above, the catalytic activity and electrical conductivity for ceria based materials correlate with each other: sample Gd$_{0.05}$Bi$_{0.15}$Mn$_{0.05}$Ce$_{0.75}$O$_2$ had the best electrical conductivity associated with the ionic conductivity of oxygen [11, 12].

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