Multifunctional nanomaterials based on ceria solid solution

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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 copper, manganese, zirconium, gadolinium, and bismuth 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 (and, as a rule, these data for ceria correlate with explanations of dependencies). Thus, in order to realize an effective process, a crystalline structure with a sufficiently high concentration of oxygen defects is necessary, and an increase in the magnitude of OSC and the number of defects are possible by doping ceria with various oxides.

The present study purpose was the preparation of solid solutions based on doped ceria and subsequent investigation of their physicochemical properties.

2. Materials and Method

Ce(NO₃)₃·6H₂O, Bi(NO₃)₃·5H₂O, Gd(NO₃)₃·6H₂O, Cu(NO₃)₂·3H₂O, ZrO(NO₃)₂·7H₂O, Mn(NO₃)₂·4H₂O (Acros Organics) were used as metal precursors. 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 (in one experiment after dissolution acetylacetone was added). 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 100 MPa. Then they were sintered at 1000 or 1150°C (T_sint) 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 900°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 GdₓBi₀.₂₋ₓCe₀.₈ₓO₂ and CuₓMn₀.₁₋ₓ(Zr₀.₁₄)Ce₀.₈ₓO₂ were evaluated. According to TG-DSC, the first solid solution is stable up to 1000°C (because of Bi evaporating process after 1050°C) and the second is up to 1400°C. Thus, further obtaining dense ceramics was achieved at temperatures of 1000 and 1150°C, respectively. Typical characteristics for, as will be shown later, the most active samples are shown in Table 1.

| Sample                  | d_{XRD} (nm) | S_{BET} (m²/g) | T(100% conversion of CO, °C) | σ_{600°C} (S/cm⁻¹) |
|-------------------------|--------------|----------------|-----------------------------|---------------------|
| Gd₀.₀₈Bi₀.₁₅Ce₀.₈ₓO₂    | 8            | 23             | 404                         | 0.005               |
| Cu₀.₀₈Mn₀.₀₂Ce₀.₈ₓO₂    | 9            | 79             | 215                         | 0.002               |
| Cu₀.₀₈Mn₀.₀₂Zr₀.₁Ce₀.₈ₓO₂ | 8            | 31             | 310                         | 0.008               |

According to XRD (Figure 1a), samples have single-phase with fluorite structure (Fm3m, JCPDS-34-0394). Thus, in all cases the solid substitutional solution is formed in which the dopants enter the ceria lattice. In contrast to XRD results, which afford information, related to the cation sublattice, Raman spectroscopy of the catalysts is dominated by oxygen lattice vibrations. The strong band at 460 cm⁻¹ is attributed to the F₂g Raman vibration mode of the cubic fluorite structure phase, which also suggests that dopant ions have been incorporated into the ceria lattice to form solid solutions, and the broad band at 590 cm⁻¹ is attributed to the oxygen vacancies generated by the partial substitution of dopant ions to Ce⁴⁺ [1, 2].

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 10 nm for all samples, which corresponds to the individual particles according to TEM (Figure 1d-f).

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 (σ_{600°C}=5·10⁻³ S/cm) was found in Gd₀.₀₈Bi₀.₁₅Ce₀.₈ₓO₂ (in series of GdₓBi₀.₁₅Ce₀.₈ₓO₂ systems), and σ_{600°C}=8·10⁻³ S/cm was in Cu₀.₀₈Mn₀.₀₂Zr₀.₁Ce₀.₈ₓO₂ (in series of CuₓMn₀.₁₋ₓ(Zr₀.₁)Ce₀.₈ₓO₂ systems) (Table 1). These results demonstrate that co-doping with the optimum ratio can improve the conductivity of ceria based electrolytes. When compared with other electrolytes, sintered even at a higher temperature, the electrical conductivity of the developed systems is comparable or higher than samples doped by REE [3-6] at 600°C.
Figure 1. XRD patterns (a), adsorption-desorption isotherms (b), pore size distributions (c), TEM microphotos (d, e, f), and catalytic activity in CO oxidation (g) of calcined powders. Gd$_{0.05}$Bi$_{0.15}$Ce$_{0.8}$O$_2$ – black line, photo d; Cu$_{0.08}$Mn$_{0.02}$Ce$_{0.9}$O$_2$ – red line, photo e; Cu$_{0.08}$Mn$_{0.02}$Zr$_{0.1}$Ce$_{0.8}$O$_2$ – blue line, photo f.

The catalytic activity of synthesized nanopowders was determined in the model oxidation reaction of CO. Figure 1g shows the increase in temperature the conversion of carbon monoxide increases, while the curve has the S-shaped type. Among the all samples, the same mentioned samples
Gd$_{0.05}$Bi$_{0.15}$Ce$_{0.8}$O$_2$, Cu$_{0.08}$Mn$_{0.02}$Ce$_{0.9}$O$_2$, and Cu$_{0.08}$Mn$_{0.02}$Zr$_{0.1}$Ce$_{0.8}$O$_2$ had 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. [7-9]) 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: samples Gd$_{0.05}$Bi$_{0.15}$Ce$_{0.8}$O$_2$, Cu$_{0.08}$Mn$_{0.02}$Ce$_{0.9}$O$_2$, and Cu$_{0.08}$Mn$_{0.02}$Zr$_{0.1}$Ce$_{0.8}$O$_2$ had the best electrical conductivity associated with the ionic conductivity of oxygen [10].

Acknowledgments

This research was supported by Russian Science Foundation (No. 17-73-10331). This work was partially conducted within the framework of budget project No. 075-00746-19-00 (XRD).

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