

Synthesis, structure and catalytic properties of nanodispersed cerium-containing compositions

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Abstract. Nanodispersed cerium dioxide and materials based on it are widely used by humanity: micro-and nanoelectronics, optical, protective anticorrosive coatings, solid oxide fuel cells, biomedical drugs, sensor devices, ceramics, polishing mixtures, abrasives, etc. Outstanding interest is the use of cerium-containing compositions as catalysts and their carriers for various processes: oxidation of CO, hydrocarbons and volatile organic substances(VOC), PROX-process, synthesis gas production, dehydrogenation of alcohols, Fischer-Tropsch synthesis, soot afterburning, oxidative destruction of organic compounds, catalytic neutralization of automobile emissions, due to their unique physicochemical properties: light redox transition Ce^{3+}/Ce^{4+} , oxygen storage capacity/capacity (OSC) and thermochemical stability.

On the front burner, the synthesis of multicomponent catalytically active cerium-containing compositions with a fluorite-like structure includes d-and f-elements. During the formation of solid solutions, crystallographic distortions resulting from the doping of cerium dioxide with ions of other metals lead to the generation of defects and vacancies, because of which there is an increase in the mobility of lattice oxygen, the formation of Ce^{3+} ions and, as a result, an increase in catalytic activity. Currently, questions about the optimal chemical composition of solid solutions, the influence of the nature of dopant ions on the dispersed and textural characteristics, as well as the catalytic activity of multicomponent cerium-containing solid solutions with a fluorite-like crystal lattice remain open. The available data on the genesis of the emerging catalytic compositions is ambiguous and in some cases contradictory, that urges the need conduct systematic research in this area.

Of particular interest is the use of multicomponent solid solutions as carriers of the active component (Pt, Pd, Ru, Au). These catalytic compositions are characterized by the formation of surface nanostructures resulting from the manifestation of the "metal-carrier" interaction effect. The resulting compounds have a higher activity and thermal stability contributing to the operational capabilities of the catalysts. In this regard, research in the field of synthesis of highly effective cerium-containing compositions for various catalytic processes is relevant.

The work aims to develop the physicochemical bases for the synthesis of highly efficient cerium-containing systems with specified functional properties for the processes of catalytic purification of industrial and automotive emissions from CO, CH₄, reduction NO, and afterburning of soot.

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The following tasks to be solved to achieve the set **goals**:

* investigation of the influence of the chemical background of CeO₂ on the catalytic properties of Pd/CeO₂ (the precursor is Pd(C₅H₇O₂)₂) in the oxidation reaction of CO.

* synthesis of bimetallic deposited Pd-Ag/CeO₂ catalysts using the heteronuclear carboxylate complex PdAg₂(OAc)₄(HOAc)₄. Study of the influence of the nature of the reaction medium on the chemical composition of the deposited component, the charge state of the components and the catalytic activity in the CO oxidation reaction.

* method of synthesis of a solid solution of Zr_{0,2}Ce_{0,8}O₂ by co-precipitation of poorly soluble compounds of the corresponding metals with subsequent heat treatment, study of their thermal stability.

* study of the "composition-structure-catalytic activity" relationship for the isostructural series of compounds M_{0,1}Zr_{0,2}Ce_{0,8}O_{2-δ}, where M = Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm, Er, Lu, by directional changes in the composition of the studied compounds by the M-cation (dopant). The choice of a dopant based on the studies of crystallographic, dispersed, textural characteristics and catalytic activity of synthesized materials in the CO oxidation reaction.

* study of the architecture of nanostructures of the "metal-carrier" interaction of compositions M/Pr_{0,1}Zr_{0,2}Ce_{0,8}O_{2-δ}, where M = Pd, Pt, Ru, and their catalytic properties in the oxidation reaction of CO, CH₄, CO+NO and afterburning of soot.

* synthesis of MnO_x-CeO₂ and MnO_x-ZrO₂-CeO₂ nanocomposites by co-deposition of peroxo compounds of the corresponding metals, study of thermal stability, electronic profile of the surface of synthesized materials and catalytic activity in the CO oxidation reaction.

* synthesis of gold-containing catalysts deposited on Pr_{0,1}Zr_{0,1}Ce_{0,72}O_{2-δ} and MnO_x-CeO₂. Identification of the influence of the nature of the carrier, the precursor and the conditions of heat treatment on the catalytic properties in the CO oxidation reaction.

* method of synthesis of Sn_xCe_{1-x}O_{2-δ} solid solutions, determination of their catalytic activity in CO oxidation and CH₄ deep oxidation reactions.

* synthesis of a block highly porous catalyst of a cellular structure with a cerium-containing catalytically active coating and determination of their activity in reduction NO reactions.

Scientific novelty:

1. The provisions of the directed synthesis of fluorite-like cerium-containing compositions that allow controlling the crystal structure, defectiveness, dispersed, textural characteristics and catalytic properties in redox processes by iso- and heterovalent doping of cerium dioxide with d- and f-element ions are theoretically substantiated.

2. It is shown that in the synthesis of the bimetallic Pd-Ag/CeO₂ catalyst of CO oxidation using the precursor of the heteronuclear carboxylate complex PdAg₂(OAc)₄(HOAc)₄, the determining factor allowing to regulate the ratio of catalytic active components on the CeO₂ surface: Pd-Ag bimetallic alloy nanoparticles, Pd⁰ clusters, Pd_xCe_{1-x}O_{2-δ}, PdO and Ag⁰ surface solid solution is the chemical nature of the thermolysis gas medium.
3. It was found that the effect of γ-radiation on the Pd/CeO₂ catalyst leads to a change in the content of weakly bound oxygen forms, which contributes to an increase in activity due to the intensification of the exchange of lattice and weakly bound oxygen forms by the spillover mechanism.
4. When analyzing the dependence of the catalytic activity of fluorite-like solid solutions of the isostructural series of compounds M_{0,1}Zr_{0,18}Ce_{0,72}O_{2-δ}, where M = Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm, Er, Lu, on the ionic radius of the dopant (M-cation), it was found that the most active in the oxidation reaction of CO is the catalytic composition Pr_{0,1}Zr_{0,18}Ce_{0,72}O_{2-δ}.
5. The effect of a strong metal-carrier interaction was found for the catalysts M/Pr_{0,1}Zr_{0,18}Ce_{0,72}O_{2-δ}, where M - Pt, Pd, Ru, which is a consequence of the electronic and chemical interaction of the metal obtained by the reduction of precursors - acetylacetonates Pt, Pd, Ru, impregnated on the carrier, and the surface of Pr_{0,1}Zr_{0,18}Ce_{0,72}O_{2-δ}.
6. The region of formation of fluorite-like Mn_xCe_{1-x}O₂ solid solutions in the MnO_x-CeO₂ bicomponent system synthesized by the method of co-deposition of cerium and manganese peroxo compounds has been determined. It is shown that doping with Zr⁴⁺ ions of the MnO_x-CeO₂ composition increases its thermal stability.
7. The region of formation of fluorite-like solid solutions Sn_xCe_{1-x}O₂, where x < 0 - 0.15, is established with the co-deposition of Sn⁺² and Ce⁺³ ions in an aqueous isopropanol medium. It is shown that the highest catalytic activity in CO oxidation reactions and deep CH₄ conversion is shown by a solid solution of Sn_xCe_{1-x}O₂.

Practical significance:

1. The parameters of synthesis of a solid solution of Zr_{0,2}Ce_{0,8}O₂ with a fluorite-like crystal structure by the hydroxide method, the filtration coefficients of a suspension of cerium and zirconium hydroxides depending on the temperature and pH of the medium were determined, and the limits of thermal stability of solid solutions of Zr_{0,2}Ce_{0,8}O₂ were established.
2. Highly active catalytic compositions M/Pr_{0,1}Zr_{0,18}Ce_{0,72}O_{2-δ}, where M - Pd, Pt, Ru, have been synthesized for CO oxidation reactions, deep CH₄ conversion, NO reduction and soot oxidation. The obtained research results can be used in the development of new and improvement of existing catalysts for the purification of industrial gas mixtures and automobile emissions.
3. For the process of low-temperature oxidation of CO, a catalyst 0.05 wt.% Au/Pr_{0,1}Zr_{0,18}Ce_{0,72}O_{2-δ} has been developed, the precursor of the active component of which is the dispersion of Au

nanoparticles obtained by radiation-chemical reduction in the $\text{HAuCl}_4/\text{H}_2\text{O}/\text{AOT}/\text{isooctan}$ system, where AOT is bis (2-ethylhexyl)sodium sulfosuccinate.

4. A method has been developed for the synthesis of solid solutions of $\text{Sn}_x\text{Ce}_{1-x}\text{O}_2$ with a fluorite-like crystal structure exhibiting high catalytic activity in the oxidation reaction of CO and CH_4 (RF Patent No. 2688945).

5. A method has been developed for producing highly permeable cellular block catalysts with a catalytically active coating in the form of a solid solution $\text{Pr}_{0,1}\text{Zr}_{0,18}\text{Ce}_{0,72}\text{O}_{2-\delta}$ (RF Patent No. 2564672)

6. Conducted tests of the activity of the deposited catalyst 0.5 wt. Pd/CeO₂ /VPYAM in the oxidation reaction of CO showed that the complete conversion of CO occurs at a temperature of 145 ° C, and in the presence of an industrial catalyst PK-505 (0.5 wt. % Pd/Al₂O₃) produced by the Redkin Catalyst Plant at a temperature of 200 ° C, which indicates the advantage of the developed catalyst.