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Abstract

Dissertation topic: Cerium-containing solid solutions for ecological catalysis.

Relevance of the research. Currently, the urgent problem facing humanity is environmental protection. According to the sixth UN report "Global Environment Outlook" (GEO-6), dedicated to the topic "Healthy Planet - Healthy People", air pollution is the main factor in the occurrence of pathologies of various genesis, which is due to an increase in greenhouse gas emissions (CO_2, CH_4, H_2O, N_2O), as well as emissions of SO_2, CO, hydrocarbons (CH_x), volatile organic compounds (VOCs) entering the atmosphere as a result of the extraction, processing and consumption of fossil fuels (energy, metallurgy, chemical and petrochemical industries, motor transport). One of the ways to solve this problem is the use of catalytic purification of gas emissions, the essence of which is the conversion of toxic components into less harmful ones. In this regard, the urgent task is to search for new highly effective and improve existing catalytic compositions. Of greatest practical interest in this area are cerium-containing systems with easy redox transition Ce^{+3}/Ce^{+4} and high oxygen storage capacity, which contributes to the manifestation of activity in such processes as oxidation of CO, CH_x, VOCs, soot afterburning, methane conversion, hydrogen production from ethanol and other processes. As a rule, cerium-containing materials are obtained by doping cerium dioxide with ions of d- and f-elements, which can lead to the formation of fluorite-like substitution solid solutions that can be used not only as catalysts, but also as carriers of the active component - nanoparticles of Pt, Pd, Au, Ag metals. The advantages of using cerium-containing compositions are the manifestation of their own catalytic activity and an increase in the dispersion of the applied active component. Despite the large number of studies conducted in the field of synthesis of cerium-containing compositions and study of their properties, questions about the formation of catalytically active fluorite-like solid solutions, which include 2 or more components, still remain open, which necessitates additional studies in this area. Based on the analysis of literature data, the following dopant ions were selected for the studies: Mn^{2+}, Zr^{4+}, Sn^{2+}, Cu^{2+}, Bi^{3+}, Sm^{3+}, Nd^{3+}, Gd^{3+}.

The aim of the work is to develop catalysts based on fluorite-like cerium-containing solid solutions for environmental catalysis processes, in particular, CO and CH_4 oxidation reactions.

Objectives of the work:

1. Study of the influence of chemical history of cerium dioxide on dispersion, textural characteristics, electronic state of components and catalytic activity of cerium dioxide in CO and CH_4 oxidation reactions. Synthesis of PdO_x/CeO_2 catalyst (precursor – $Pd(C_5H_7O_2)_2$), study of electronic state of components, catalytic activity in the reaction of complete CH_4 oxidation.

2. Synthesis of bicomponent solid solutions $Ce_xMn_{1-x}O_{2-\delta}$. Clarification of the region of formation of solid solutions $Ce_xMn_{1-x}O_{2-\delta}$: ratio of components Ce:Mn, temperature and duration of calcination. Synthesis of solid solutions $Ce_{0.80}Mn_{0.15}Me_{0.05}O_{2-\delta}$, where Me – Cu, Bi. Characterization of the obtained compounds by methods of physicochemical analysis, determination of catalytic activity in CO and CH_4 oxidation reactions. Study of the catalytic

properties of $PdO_x/Ce_{0.80}Mn_{0.20}O_{2-\delta}$ and $PdO_x/Ce_{0.80}Mn_{0.15}Me_{0.05}O_{2-\delta}$, where Me is Cu, Bi, in the reaction of complete oxidation of CH_4.

3. Synthesis of solid solutions $Ce_xSn_{1-x}O_2$, characterization of the obtained materials, determination of catalytic activity in the oxidation reactions of CO and CH_4. Study of the possibility of using the synthesized compositions $Ce_{0.90}Sn_{0.10}O_2$ and $Ce_{0.80}Sn_{0.10}Zr_{0.10}O_2$ as a carrier of the active component - Ni for the production of synthesis gas by the oxygen conversion method of CH_4.

4. Synthesis of multicomponent solid solutions $Ce_{0.72}Zr_{0.18}Bi_{0.05}Me_{0.05}O_{2-\delta}$, where Me is Nd, Sm, Gd. Characterization of the obtained compounds, determination of catalytic activity in the reaction of CO oxidation. Study of the correlation "composition – property – catalytic activity".

Scientific novelty:

1. The influence of the history of obtaining cerium dioxide, namely the precipitation method, the nature of the precipitant (NH_4OH, $(NH_4)_2CO_3$, $H_2C_2O_4$) on the dispersion, morphology and textural characteristics, the electronic state of the components and the catalytic activity in the oxidation reaction of CO and CH_4 is shown. The highest catalytic activity is characteristic of cerium dioxide obtained using $(NH_4)_2CO_3$, which is due to a combination of factors: the presence of lamellar morphology, a developed porous structure, as well as a high content of Ce^{+3} and weakly bound forms of oxygen.

2. It was found that fluorite-like solid solutions $Ce_{0.80}Mn_{0.20}O_{2-\delta}$ and $Ce_{0.80}Mn_{0.15}Cu_{0.05}O_{2-\delta}$ exhibit high catalytic activity in the reaction of complete oxidation of methane due to the synergistic effect of redox transitions Ce^{+3}/Ce^{+4}, $Mn^{+2}/Mn^{+3}/Mn^{+4}$ and Cu^{+}/Cu^{+2}.

3. It was shown that the introduction of zirconium in an amount of 10 mol. % into the composition of the bicomponent solid solution $Ce_{0.90}Sn_{0.10}O_2$ is accompanied not only by an increase in thermal stability, but also by an increase in catalytic activity when used as a carrier of the active component - Ni for the production of synthesis gas by the oxygen conversion of CH_4.

4. The presence of a correlation between the catalytic activity of the multicomponent fluorite-like solid solution $Ce_{0.72}Zr_{0.18}Bi_{0.05}Me_{0.05}O_{2-\delta}$, where Me is Nd, Sm and Gd, and the ionic radius of the rare-earth dopant is shown: the catalytic activity increases with decreasing ionic radius in the series Nd (0.99 Å) → Sm (0.97 Å) → Gd (0.94 Å). The most active composition in the CO oxidation reaction is the solid solution $Ce_{0.72}Zr_{0.18}Bi_{0.05}Gd_{0.05}O_{2-\delta}$.

Theoretical and practical significance:

1. The formation region of bicomponent solid solutions $Ce_xMn_{1-x}O_{2-\delta}$ was refined depending on the manganese content (0-50 mol.%), temperature (400-800°C) and calcination duration (2-8 h).

2. Highly active catalytic systems $PdO_x/Ce_{0.80}Mn_{0.20}O_{2-\delta}$ and $PdO_x/Ce_{0.80}Mn_{0.15}Cu_{0.05}O_{2-\delta}$ were synthesized for the reaction of complete oxidation of CH_4, the activity of which exceeds the activity of the reference sample PdO_x/Al_2O_3.

3. A method for synthesizing fluorite-like solid solutions $Ce_xSn_{1-x}O_2$, which exhibit catalytic activity in the oxidation reaction of CO and CH_4 (patent No. 2688945) was proposed.

The results of this work are of interest for the development of catalysts and their carriers in the processes of cleaning gas mixtures from CO, CH_4 and obtaining synthesis gas by the method of oxygen conversion of CH_4.

Thesis to be defended:

1. Results of the study of the influence of cerium dioxide history, namely the precipitation method, the nature of the precipitant (NH_4OH, $(NH_4)_2CO_3$, $H_2C_2O_4$) on the morphology, textural characteristics, electronic state of the components and catalytic activity in CO and CH_4 oxidation reactions. Results of the study of the physicochemical and catalytic properties of PdO_x/CeO_2 in the CH_4 oxidation reaction.

2. Results of the study of the formation region of $Ce_xMn_{1-x}O_{2-\delta}$ solid solutions, study of the physicochemical properties and determination of the catalytic activity in CO and CH_4 oxidation reactions. Results of the study of the physicochemical and catalytic properties of $PdO_x/Ce_{0.80}Mn_{0.20}O_{2-\delta}$ and $PdO_x/Ce_{0.80}Mn_{0.15}Me_{0.05}O_{2-\delta}$, where M is Cu, Bi in the reaction of complete oxidation of CH_4.

3. Results of the study of the physicochemical and catalytic properties of solid solutions $Ce_xSn_{1-x}O_2$ in the oxidation reactions of CO and CH_4, the effect of introducing zirconium into the bicomponent solid solution $Ce_{0.90}Sn_{0.10}O_2$ on the properties of the resulting material, as well as the possibility of using solid solutions as a carrier of the active component - Ni for obtaining synthesis gas by the method of oxygen conversion of methane.

4. Results of the study of the physicochemical properties and catalytic activity of multicomponent solid solutions $Ce_{0.72}Zr_{0.18}Bi_{0.05}Me_{0.05}O_{2-\delta}$, where M is Nd, Sm, Gd in the CO oxidation reaction.