VARIOUS PHYSICOCHEMICAL AND TECHNOLOGICAL PROCESSES

Catalytic Properties of Complex Oxide Coatings on Foamed Nickel

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Abstract—Effect of the Ni/NiO composite support on the properties of catalytic systems based on cerium oxide and lanthanum manganite with various dopants was studied.

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Complex-oxide catalysts on supports made of a highly porous cellular material (HPCM), e.g., foamed nickel with an intermediate aluminum oxide layer [1–9] are used in the industry for purification of gases to remove toxic substances, such as carbon monoxide, hydrocarbons of varied nature, and nitrogen oxides [10, 11]. In some cases, an economic variety of catalysts of this kind can be used, which is produced on a preliminarily oxidized nickel surface [12] without an intermediate Al_2O_3 layer. The catalytic activity of complex oxides most strongly depends on the nature of the underlying surface. In particular, it has been shown that the catalytic system based on silver-doped lanthanum manganite with a perovskite-type structure on a Ni/NiO support makes it possible to effectively oxidize oxygen-containing compounds, e.g., ethanol [13]. As catalytic coatings on HPCMs can be used complex oxides with a structure of not only perovskite, $La_{1-x}M_xMnO_{3+y}$, but also fluorite, $Ce_{1-x}M_xO_{2-\delta}$, where $M = Ag$, Cs, Sr, and Cu, and also other compositions [14, 15]. Depending on the nature of doping elements, their introduction can differently affect the catalytic activity of compositions.

The goal of the present study was to examine the catalytic activity of complex-oxide coatings deposited on the Ni/NiO composite in the reaction of carbon monoxide oxidation. A unified doping parameter was set for all the samples under study: x was chosen to be 0.25. The data obtained can be used to select the optimal, as regards

practical application, support–catalyst systems whose catalytic activity is affected to the maximum positive extent by the synergic interaction between the support and the catalytic coating. The stability under cyclic working conditions was roughly assessed for systems of this kind.

EXPERIMENTAL

A dense oxide layer was produced on foamed-nickel supports (highly porous permeable cellular material [2, 6]) with cell size of 2–3 mm (coarsely porous) and $0.2-0.3$ mm (finely porous) by oxidation of an HPCM in a furnace in air at 500 and 650°C for the finely and coarsely supports, respectively. To obtain a dense solid layer of nickel oxide, finely and coarsely porous samples of foamed nickel were kept until their mass increased by 1 and 0.25%, respectively. The oxidation process was monitored by the gravimetric method and also with an optical microscope (Olympus BX 51) and AURIGA CrossBeam scanning electron microscope with an attachment for local energy-dispersive analysis. The control, operation monitoring, and analysis of the data obtained were made with an Analysis Station, AURIGA series, Version 3.7 software package.

Complex oxides were synthesized on the surface of the support from the following starting reagents: cerium(III) nitrate hexahydrate $Ce(NO₃)₂·6H₂O$, manganese(II) nitrate tetrahydrate $Mn(NO₃)₂·4H₂O$,

strontium(II) nitrate $Sr(NO₃)₂$, and copper(II) nitrate trihydrate Cu(NO₃)₂·3H₂O, all of analytically pure grade; lanthanum(III) nitrate hexahydrate $La(NO_3)_3.6H_2O$, cesium nitrate $CsNO₃$, and silver nitrate, all of chemically pure grade. The synthesis was performed by pyrolysis of polymer-salt compositions [16–18], with polyvinyl alcohol (PVA) of 11/2 brand [GOST (State Standard) 10779–78] as the polymeric component.

To prepare an aqueous solution, a PVA powder was dissolved in water in a prescribed amount 3, 5, or 10 wt %). The heating on a water bath was performed to complete dissolution of PVA, with water added instead of its evaporated amount when necessary. Then, the finished polymer solution was added to solutions of salt mixtures calculated for obtaining a particular complex oxide. The relative amounts of salts and the polymer were chosen on the basis of the stoichiometric ratio [16] for the pyrolysis reaction yielding carbon dioxide, water, and molecular nitrogen as gaseous products. Samples of the nickel HPCM were submerged in the resulting working solution and impregnated to saturate their moisture capacity. Then the samples were removed, the excess amount of a solution were allowed to flow down, and dried in air for 24 h. After that the samples were annealed at 50°C for 4 h. Then, the catalyst deposition procedure was repeated and then the samples were again annealed, now at 650°C. When necessary, subsequent layers of a complex oxide were deposited to reach a mass fraction of the coating relative to the mass of the entire formulation equal to 9 to 15% for the finely porous support and 9 to 11% for the coarsely porous support. To obtain reference samples, powdered complex oxides of an appropriate composition were obtained by evaporation of working polymer-salt solutions in a porcelain pan on an electric hotplate. After water was removed, pyrolysis was performed and its products were annealed in an electric furnace under the conditions corresponding to those in which complex oxide coatings are synthesized.

The specific surface area of the samples under study was determined on a Micromeritics TriStar 3029 automated sorption installation by using the volume variant of the BET sorption method. The specific surface area was calculated from the isotherm of lowtemperature sorption of nitrogen vapor. The morphology of the resulting materials was examined with the abovementioned scanning electron microscope.

The phase composition of the samples was determined by X-ray phase analysis on a DRON-6 automated X-ray diffractometer. The X-ray diffraction patterns were obtained with Cu K_a radiation (λ = 1.5418 Å) at 20 angles in the range $20^{\circ} - 80^{\circ}$ at a scanning rate of 2 deg min⁻¹. The crystallographic parameters were calculated and the phase composition was analyzed on the basis of Peak Find and PDwin4 software packages, with phases identified using the ICDD database [19].

The catalytic activity of the samples was measured for the reaction of carbon monoxide oxidation in a flow type reactor, in which conditions as close as possible to the ideal-displacement mode were realized. Before the beginning of an experiment, the reactor was filled with a catalyst on a support or catalyst grains 2.4–2.6 mm in size when a study was performed for a powder sample. After that the reaction mixture was delivered. The contents of CO and oxygen in the gas mixture did not exceed 0.2 and 3 vol %, respectively, at a gas flow rate of $0.017 \text{ dm}^3 \text{ s}^{-1}$ and specific load on a catalyst of $100 000$ h⁻¹. The mixture was set using gas cylinders with N_2 and CO (content of CO 0.2 vol $\%$, with the inert filler N₂ the rest). The content of carbon oxide in the starting reaction mixture was set and that in the final mixture was monitored with a Testo-350 XL electronic gas analyzer. Experimental data were obtained with stepwise heating of the reaction zone.

RESULTS AND DISCUSSION

Catalytic layers based on perovskite $(La_{1-x}M_xMnO_{3\pm y})$ and fluorite ($Ce_{1-x}M_xO_{2-\delta}$), where $M = Ag$, Cs, Sr, Cu, were produced by pyrolysis of polymer-salt composition on foamed-nickel supports. After complex-oxide coatings of perovskite systems were synthesized on a Ni/NiO composite support, their phase composition was analyzed both directly on the surface of the support and upon mechanical detachment of the catalytic layer from the support. The X-ray diffraction pattern obtained directly from the surface of a catalyst-coated support shows analytical peaks associated both with nickel itself and with its oxide; in addition, highest intensity reflections from the perovskite phase proper are well seen. The diffraction pattern of the catalytic layer detached from the support shows reflections related to the metallic and oxidized nickel, which are firmly adherent in the composite to the catalytic coating.

For example, the $La_{1-x}M_xMnO_{3+y}$ catalytic coating is heterogeneous and contains, in addition to the perovskite phase, metallic silver, in agreement with the previously obtained data [20]. Silver is only partly incorporated

Composition of a catalyst	Phases observed ^a	
$La_{0.75}Ag_{0.25}MnO_{3\pm y}$	$LaMnO_3$, Ag	
$La_{075}Cs_{025}MnO_{3\pm\nu}$	LaMnO ₃	
$La_{0.75}Sr_{0.25}MnO_{3\pm y}$	LaMnO ₃ , SrCO ₃ , MnO ₂	
$Ce_{0.75}Ag_{0.25}O_{2-\delta}$	$CeO2$, Ag	
$Ce_{0.75}Cu_{0.25}O_{2-\delta}$	CeO ₂ , CuO	
$Ce_{0.75}Cs_{0.25}O_{2-\delta}$	CeO ₂	

Table 1. Phase composition of supported samples preliminarily detached from the substrate

^a LaMnO₃ are solid solutions based on LaMnO_{3±*y*}, and CeO₂, those based on $CeO_{2-\delta}$.

into the perovskite structure. The phase composition of complex oxide samples detached from a support is presented in Table 1. All the X-ray diffraction patterns have peaks associated with metallic nickel Ni, its oxide, and the main phase of the catalyst. It should be noted that presence of phase impurities frequently positively affects the catalytic activity. This refers, in particular, to systems including silver. When copper is introduced into a catalyst based on cerium oxide, the second phase, copper oxide CuO, is also formed [21, 22], which improves the catalytic activity in redox reactions. In this case, copper oxide itself is also actively involved in the oxidation of substances by oxygen. The stabilization of CuO and the absence of a noticeable reduction of this oxide by carbon-containing substances are provided by the transfer of oxygen from the ambient medium by cerium oxide, which enables reverse oxidation of copper oxide partly reduced in the catalytic cycle. Thus, the problem of obtaining on an oxidized support a composite including the main phase (solid solution based on perovskite or cerium dioxide) and impurities improving the catalytic activity was successfully solved.

Method of pyrolysis of polymer-salt compositions was also used to synthesize, for comparison purposes, also powdered samples of $La_{0.75}Ag_{0.25}MnO_{3\pm\nu}$, $La_{0.75}Sr_{0.25}MnO_{3\pm y}$, $Ce_{0.75}Ag_{0.25}O_{2-\delta}$, and $Ce_{0.75}Cu_{0.25}O_{2-\delta}$. An analysis of the phase composition of the powdered samples demonstrated that $La_{0.75}Ag_{0.25}MnO_{3\pm\nu}$, $Ce_{0.75}Ag_{0.25}O_{2-\delta}$, and $Ce_{0.75}Cu_{0.25}O_{2-\delta}$ samples, as well as supported samples, are heterogeneous and contain the same impurity phases as the supported complex oxides. In the given case, the presence of a substrate had no effect on how the phase composition of the complex oxide system was formed. Only the complex oxide $La_{0.75}Sr_{0.25}MnO_{3+\nu}$ was single-phase when synthesized as a powder, in contrast to the case of a coating. A possible reason for the heterogeneity of the $La_{0.75}Sr_{0.25}MnO_{3\pm v}$ coating is that the components of the complex oxide are localized on different parts of the surface of the support (are separated), and just this circumstance leads at a comparatively low temperature of synthesis to its incompleteness.

Table 2 lists the specific surface areas of the Mi/NiO/ catalytic coating composites obtained in the study. It should be taken into account that the fact that specific surface areas of the supported catalysts are comparatively small follows from the catalyst/support mass ratio. The largest specific surface area among all the samples was observed complex oxide coatings of composition $La_{0.75}Cs_{0.25}MnO_{3±*v*}$. This is due to the presence of a partly

Fig. 1. Electron micrographs of the catalytic layer in the Nicoarse/NiO/La_{0.75}Cs_{0.25}MnO₃ composite. Magnification: (a) ×30 and (b) ×3000.

Fig. 2. Conversion α of carbon monoxide for complex oxides Ce_{0.75}Mn_{0.25}O_{2– δ} used as catalysts vs. temperature *T*. (a) Supported samples: (*1*) oxidized support without a catalytic coating, (2) Ce_{0.75}Cu_{0.25}O_{2–δ}, (3) Ce_{0.75}Cs_{0.25}O_{2–δ}, (4) Ce_{0.75}Ag_{0.25}O_{2–δ}; (b) powdered samples: (1) Ce_{0.75}Ag_{0.25}O_{2–δ}, (2) Ce_{0.75}Cs_{0.25}O_{2–δ}, (3) Ce_{0.75}Cu_{0.25}O_{2–δ}.

Fig. 3. Conversion α of carbon monoxide for complex oxides used as catalysts vs. temperature *T*. (a) Supported samples: (*1*) oxidized support without a catalytic coating, (2) La_{0.75}Sr_{0.25}MnO_{3±*y*}, (3) La_{0.75}Cs_{0.25}MnO_{3±*y*}</sub>, (4) La_{0.75}Ag_{0.25}MnO_{3±*y*}</sub>; (b) powdered samples: (*I*) oxidized support without a catalytic coating, (2) La_{0.75}Cs_{0.25}MnO_{3 ± *y*}, (3) Ce_{0.75}Cs_{0.25}O_{2–δ}.

amorphized phase in complex oxide layers, demonstrated by electron microscopy (Figs. 1a and 1b). The first complex oxide layer directly adjacent to the surface of nickel oxide was denser and had a nanocrystalline structure. It provided a god adherence of the higher lying layers to the support. Figure 1b shows a complex oxide layer situated between cells of the foamed-nickel support. This partly amorphized catalytic layer had a branched structure with a set of pores and channels proving its gas permeability. The specific surface area of catalysts on the coarsely porous nickel could be larger because it possessed a substantial free space for an amorphized complex oxide to be formed. Simultaneously, the permeability to gases under the catalysis conditions was preserved.

The catalytic activity of complex oxide coatings of composition $La_{0.75}M_{0.25}MnO_{3\pm y}$ (M = Sr, Cs, Ag) and $Ce_{0.75}M_{0.25}O_{2-\delta}$ (M = Cu, Cs, Ag), deposited on a finely porous support, in the reaction of carbon monoxide oxidation depended on the nature of the dopants being introduced (Fig. 2a). Naturally, the catalyst support itself had a substantially lower catalytic activity (Fig. 2a), but affects the catalytic coating in various ways. For example, the presence of a support affected comparatively weakly the catalytic activity exhibited in the test reaction of carbon monoxide oxidation by cerium oxide with a structure of the fluorite type upon introduction of copper and cesium into the catalyst. At the same time, the presence of an underlying surface significantly diminished the activity of the silver-including system.

Samplea	$S_{\rm sp}^{\rm b}$, m ² g ⁻¹	
	1	2
Ni _{fine}	0.20	
Ni _{fine} /NiO	0.20	
$\text{Ni}_{\text{fine}}/\text{NiO}/\text{La}_{0.75}\text{Cs}_{0.25}\text{MnO}_{3\pm y}$	2.16	13.81
$\text{Ni}_{\text{fine}}/\text{NiO/L}a_{0.75}\text{Ag}_{0.25}\text{MnO}_{3\pm\text{v}}$	0.57	11.15
$Ni_{\text{fine}}/NiO/Ce_{0.75}Cu_{0.25}O_{2-\delta}$	1.52	12.51
$\mathrm{Ni}_\mathrm{coarse}$	0.11	
Ni _{coarse} /NiO	0.10	
$\mathrm{Ni_{coarse}/NiO/La_{0.75}Cs_{0.25}MnO_{3\pm\nu}}$	0.51	4.43
$\mathrm{Ni_{coarse}/NiO/La_{0.75}Ag_{0.25}MnO_{3\pm\gamma}}$	0.25	2.54
$\mathrm{Ni_{coarse}/NiO/Ce_{0.75}Cu_{0.25}O_{2-8}}$	0.58	6.27

Table 2. Specific surface areas of the samples obtained

^a Ni_{coarse} is coarsely porous foamed nickel (cell diameter 2–3 mm), and Ni_{fine} is finely porous foamed nickel (cell diameter $0.2-0.3$ mm).

 b Column 1 presents the total specific surface area of the whole catalytic system, and column 2, the specific surface area of the complex oxide coating proper.

The activity of the corresponding complex oxides can be arranged for the powdered samples with respect to dopants in the following order: $Ag > Cu > Cs$ (Fig. 2b). For the supported catalysts this series has the form: Cu > $Cs > Ag$ (Fig. 2a).

A similar situation was observed for the system of catalysts based on doped lanthanum manganite with a perovskite-type structure (Fig. 3a). Silver-doped perovskite introduced silver had a substantially lower catalytic activity in the presence of a support. The catalytic activity of silver-containing compositions in the reaction of CO oxidation commonly exceeds that with strontiumdoped lanthanum manganite [13]. Thus, having analyzed two systems with catalytic coatings of different structural types, we can conclude that silver particles are passivated when deposited on the Ni/NiO composite. It should be assumed that, for silver-containing systems to retain their catalytic activity, it is necessary to obtain an intermediate layer based on aluminum oxide, in agreement with the results of earlier studies $[13]$. As regards the influence exerted by the structural type of the main phase on the catalytic activity of supported systems, it should be noted that the perovskite-based supported catalyst is advantageous (Figs. 2a and 3a). A possible reason is that silver is partly incorporated into the perovskite structure [13], with additional catalytic centers generated, in contrast to the system based on cerium oxide, in which silver is found only in the metallic state. As evidence confirming that silver does not dope the fluorite-type structure serves the fact that the lattice parameters of cerium dioxide remain unchanged. The introduction of an alkaline-earth element (strontium) and an alkali element (cesium) into supported lanthanum manganite gives nearly the same result because the catalytic activities of these compositions are close (Fig. 3a). This makes possible in economic regard to use the less expensive strontium for doping. The activities of supported catalysts of two different structural types upon introduction of cesium were also found to be close to each other (Fig. 3b).

The working stability of catalysts is important for their practical application. A primary test of cycling loading of catalysts, with their intermediate cooling, makes it possible to select in a rather simple way the most promising of them. Sufficiently active supported catalytic composites with the $Ce_{0.75}Cu_{0.25}O_{2-\delta}$ and $La_{0.75}Ag_{0.25}MnO_{3±*v*} coatings were chosen for a primary$ testing. The latter system was studied despite the observed passivation of metallic silver in the case of nickel oxide as an intermediate layer. A supported catalyst was placed in a tubular furnace and a gas mixture containing CO, oxygen, and nitrogen (CO concentration was 0.2 vol % passed trough, with a load on the catalyst of about 100 000 h–1. The experiment was performed with the temperature stepwise raised from 25 to 700°C and the conversion of CO measured in the process. Then, the supported catalyst was cooled in the furnace to room temperature in the same medium, after which the cycle of heating and cooling in the reaction medium was repeated. It was found in these experiments (Figs. 4a and 4b) that there was no significant decrease in the catalytic activity and the catalysts are suitable for further tests. An electronmicroscopic analysis of silver-doped perovskite samples demonstrated that uniform distribution of the finely dispersed silver phase over the perovskite surface remains unchanged upon cyclic tests. The size of silver particles, which appear to be lighter in the electron micrographs, did not change significantly (Fig. 5).

On being subjected to cyclic tests, the supported catalyst $Ce_{0.75}Cu_{0.25}O_{2-\delta}$ was more stable, compared with the similar powdered sample (Fig. 6). In this case, there presumably appears an additional stabilizing effect of the support on the heterogeneous catalyst.

Fig. 4. Working stability of catalysts deposited on a nickel HPCM: (a) $Ce_{0.75}Cu_{0.25}O_{2-\delta}$ and (b) $La_{0.75}Ag_{0.25}MnO_{3+y}$. (a) Conversion and (*T*) temperature.

Fig. 5. Electron micrographs of the catalytic layer in the Nifine/NiO/La_{0.75}Ag_{0.25}MnO_{3±*y*} composite. (a) Before the catalytic study, magnification \times 14 000; (b) after cyclic tests in CO oxidation, magnification \times 15 000.

CONCLUSIONS

The results of the study demonstrated that using the economical Ni/NiO composite support results in a decrease in the catalytic activity of complex oxides containing silver as a dopant. Presence of nickel oxide as an intermediate layer in the supported system results in that the catalytic activity of complex oxides based on lanthanum manganite is nearly independent of the nature of a dopant, whereas for compositions based on cerium dioxide, the activities are arranged as regards the dopants in the following order: $Cu > Cs > Ag$.

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Fig. 6. Conversion α of carbon monoxide in 6th cycle of testing of the catalyst of composition $Ce_{0.75}Cu_{0.25}O_{2-\delta}$ vs. temperature *T*. Sample: (*1*) deposited on foamed nickel and (*2*) in the form of powder.

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