

Application of NiO sublayer in catalytic systems on the basis of complex oxides

Russkikh O.V.*, Chezganov D.S., Chumak N.A., Ostroushko A.A.
Ural Federal University, Ekaterinburg, Russia
*corresponding author: olga.v.russkikh@mail.ru

Introduction

Protection of the environment especially atmosphere from industrial and transport emissions is one of the most important problems of nowadays. Scientists and technologists are looking for a solution of this problem by reducing pollution in different ways, one of which is the catalytic purification of exhaust gases.

Complex oxide compositions on the basis of lanthanum manganite and cerium dioxide are among perspective materials used as catalysts for carbon-containing substances oxidation. Complex oxides coated on different supports are more convenient for practical use. Highly porous cellular materials (for example, nickel foam) or cordierite are often used as carriers. Intermediate layer is coated directly on carriers before catalytic layer for catalytic system creation. Aluminum oxide is used for this purpose nowadays. The possibility of replacement of aluminum oxide to nickel oxide was investigated in the present work. This replacement would reduce the cost of the complete catalytic system.

Materials and Methods

Complex oxide catalysts were synthesized by pyrolysis of polymer-salt compositions [1]. This method allows to receive both superfine oxide powders and oxide coatings on foam nickel carrier (support). Surface morphology was investigated by electron microscopy method with the help of working station AURIGA (CrossBeam, Carl Zeiss NTS). Specific surface area of received catalysts was measured by low-temperature nitrogen sorption on analyzer TriStar 3020. Phase content was defined by means of X-ray diffractometer Bruker D8 ADVANCE ($\text{CuK}\alpha$, $\lambda = 1,5418 \text{ \AA}$).

Catalytic activity was estimated in two reactions: oxidation of diesel soot and carbon oxide (II). The experiments of diesel soot oxidation were run in open reactor at 300°C. Catalyst and diesel soot were taken in ratio 4/1, and grinded for receiving dense contact between them. The experiments of carbon monoxide oxidation were run in a flow-type reactor. Initial CO concentration was 2000 ppm, flow rate 1 l/min, temperature was varying from 50-700°C with a step 50°C.

Results and Discussion

Intermediate layer NiO was obtained by annealing of foam nickel carrier at 650°C in air during 2 hours. Carrier retained its mechanical strength in this conditions and NiO with a thickness about 1 μm (measured by electron microscope) was formed. Then the catalytic layer was formed in two-step process. At the first step crystalline complex oxide is formed (investigated by electron microscope) and its growth centers were on NiO crystals. At the second step complex oxide in amorphous state is formed in cavities. Amorphous part (mechanically stable in gaseous flow) is riddled by the system of micro pores and micro channels providing a more complete contact of catalyst and exhaust gases.

Specific surface area of foam nickel carrier was equal to 0.1 m^2/g , and that of complex oxide coating – 10-13 m^2/g . Phase composition of powder and coated oxide samples was the same. Both complex oxides with Ag were heterogeneous, metal silver was the second phase. Sample $\text{Ce}_{0.75}\text{Cu}_{0.25}\text{O}_2$ contained CuO as the second phase.

The catalytic activity of complex oxides $\text{La}_{0.75}\text{Me}_{0.25}\text{MnO}_3$ (Me=Sr, Cs, Ag) and $\text{Ce}_{0.75}\text{Me}_{0.25}\text{O}_2$ (Me=Cu, Cs, Ag) coated on foam nickel carrier (support) depended on the nature of the input dopants. Foam nickel carrier had a significantly lower catalytic activity. But it had a noticeable effect on catalytic activity of complex oxide coatings. Thus catalytic activity for powder samples $\text{Ce}_{0.75}\text{Me}_{0.25}\text{O}_2$ (Me=Cu, Cs, Ag) in carbon oxide (II) oxidation decreases in dopant number $\text{Ag} > \text{Cu} > \text{Cs}$. While this dopant number looked like $\text{Cu} > \text{Cs} > \text{Ag}$ for coated samples. For the system $\text{La}_{0.75}\text{Me}_{0.25}\text{MnO}_3$ (Me=Sr, Cs, Ag) with perovskite structure a similar dependence was observed. Catalytic activity of $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3$ was much smaller than expected [3]. Comparing two catalytic coatings with different structural type we supposed that passivation of silver particles occurs when Al_2O_3 intermediate layer is replaced to NiO. High catalytic activity of $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3$ coated on foam nickel carrier with Al_2O_3 intermediate layer was confirmed in [2].

Figure 2 (a) shows the morphology of annealed foamed nickel carrier, (b) morphology of complex oxide $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3$ coated on foam nickel carrier with NiO used as intermediate layer. Nanoscale metal silver particles are equally distributed on the surface of complex oxide, which retains after carrying out experiments of carbon oxide (II) oxidation at 700°C. We suppose that this distribution promotes high catalytic activity because of high stable surface of silver nanoscale particles.

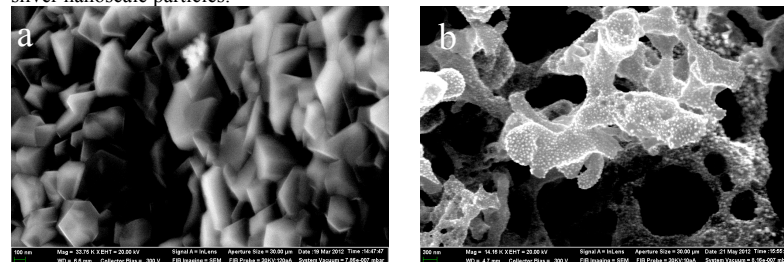


Figure 2. SEM photos a) NiO coat (magnification $34 \cdot 10^3$; 20 kV) b) $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3$ coat on foam nickel carrier (after oxidation experiments, magnification $14 \cdot 10^3$; 20 kV).

Significance

Complex oxides $\text{La}_{0.75}(\text{Ag}, \text{Sr})_{0.25}\text{MnO}_3$ and $\text{Ce}_{0.75}(\text{Ag}, \text{Cu})_{0.25}\text{O}_2$ were synthesized both as superfine oxide powders and oxide coatings on foam nickel carrier (support). Their phase state, morphology, specific surface and catalytic activity were investigated. Replacements of intermediate layer is possible for $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ complex oxide coating. Coated complex oxides are more stable during exploitation in comparison with powder ones. Substitution of La^{3+} or Ce^{4+} to Cs or Ag leads to increase of catalytic activity in oxidation of diesel soot, and to Cu or Ag leads to increase of catalytic activity in oxidation of carbon oxide (II).

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References

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