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Catalyst Coatings Carriers Based on Boron-Silicon Glass Crystalline Compositions

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This research has examined the effect of using secondary carriers, which represent boron-silicate compounds, on the effectiveness of palladium oxide catalysts. The technology of applying such glass-ceramic coatings on primary carriers has described. A comprehensive analysis of the morphology of the obtained carriers and the surfaces of catalytically active compounds coating them was carried out. The effectiveness of the proposed method was experimentally confirmed. The influence of the secondary coatings composition on the degree of hydrocarbons oxidation on PdO catalyst was studied. The surface reaction rate constant and the mass transfer coefficient have been calculated for this process. The obtained values allow calculating the rational size of the reactor for the process of hydrocarbons oxidation in the low-temperature area with the condition of 95 % conversion degree.

1. Introduction

Internal combustion engines, waste processing systems and thermal power plants are causing significant environmental pressure on the ecology. A well-known and well-proven method for purification of exhaust gases from carbon monoxide, nitrogen oxides and hydrocarbons of incomplete combustion products is catalytic purification (Levenspiel, 1999). Thermomechanical performance characteristics of catalysts, along with their catalytic activity, are important factors that determine not only the efficiency but also the catalyst lifetime (Ved` et al., 2015). This paper is devoted to the thermochemical aspects of the formation of the catalytically active, mechanically strong and thermochemical sustainable coatings both on metals and ceramics.

The effective functioning of a catalyst in gas emissions purification processes is determined by its chemical activity, which is a function not only of its qualitative and quantitative composition, but also depends on the qualitative composition of the catalyst carrier. In many cases, when the catalyst carrier is a metal or ceramics, changes in the chemical composition of the carrier over a wide range are not possible, (Ponomarenko et al., 2016). There is a definite gap in researches concentrated on the deposition of catalysts on glass and ceramics with an intermediate glass-ceramic coating (Makhanov et al., 2015). This leads to the idea of creating an intermediate (secondary) catalyst carrier, localized on the surface of the primary carrier (metal or ceramic). Secondary catalyst carrier hosts on its surface the layer of catalytically active compounds (Krasnokutskiy et al., 2015). Such a multilayer system due to the possibility of varying over a wide range of qualitative composition of the intermediate coating overcomes drawbacks of bilayer systems ("carrier-catalyst") and provides the ability to control thermo-mechanical and catalytic properties of the catalytic coating (Krasnokutskiy et al., 2016).

The study aims to determine the effectiveness of operating characteristics catalysts in the processes of neutralization of gas emissions and identify the controlling factors by which is possible to increase the operating parameters on the basis of a comprehensive study of the surface structure of the carrier's catalytic coating, their morphology and morphology of the developed catalysts.

Thermomechanical stability and catalytic activity of catalysts in the purification of gas emissions of road transport, thermal power plants and waste-processing complex are determined by the qualitative composition

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of catalytic coatings catalysts (Krasnokutskiy et al., 2015). However, the catalytic activity is also determined by the promoting and modifying properties of the catalyst carrier. The promoting properties of the carrier are a function of its qualitative, quantitative composition, microstructure and thermal background. Experimental and theoretical studies of the composition of catalyst carrier allow finding such composition values, which will significantly increase the thermomechanical stability and catalytic activity of the catalysts (Krasnokutskiy et al., 2016). However, since the catalytic coatings carriers' materials are composed of ceramic or metallic, the composition of the carrier has significant limitations associated with carriers' mechanical and performance properties.

To work around the specified limitation the use of intermediate (secondary) carriers of glass-crystalline nature is offered. Secondary carriers are formed on the surface of the primary carrier (ceramic or metal) and then on the surface of the secondary carrier catalytically active coating layer is created. The above three-layer system allows overcoming the limitation of the composition of the catalyst support, which is an undeniable advantage (Makhanov et al., 2015). On the other hand, it should be noted that the three-layer system as well as the two-layer system of type "catalyst carrier" has the disadvantage due to thermal coefficient of linear expansion difference of carrier and coatings. This difference inevitably leads to mechanical stresses between the layers of the catalyst system and as a result of mechanical destruction under dynamic thermal operating parameters of catalytic neutralization units.

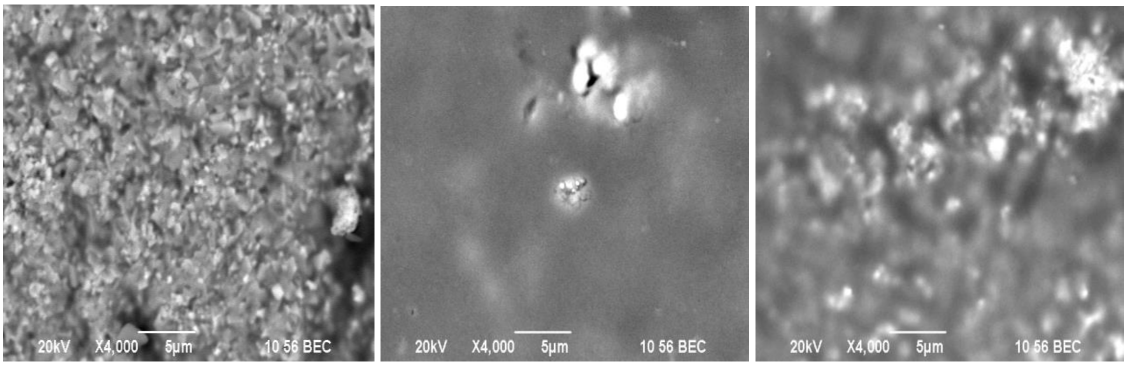
The use of secondary carriers of glass-crystalline nature allows avoiding the accumulation of critical thermomechanical stresses between the layers of the primary carrier, secondary carrier and layer of catalytically active components. This is due to the possibility of selection of the qualitative and quantitative composition of the glass-crystalline support, which allows obtaining an intermediate value of the coefficient of linear expansion of secondary carrier and allows the use of a secondary carrier as a thermal stress absorber between the primary carrier and the catalyst layers.

2. The surface morphology of the synthesized secondary carriers and catalyst layer

Synthesized secondary coatings in accordance with the proposed method are formed on the metal surface and are in the form of oxide system of amorphous or glass crystalline adhesion. The primary carrier is a foil of NiCrA alloy (the same as NiCr80/20, Ni80Cr20, Chromel A, N8, Nikrothal 8, Resistohm 80, Cronix 80, Nichrome V, HAI-NiCr 80). In this paper, the following compositions of oxide systems of the secondary carriers are investigated: manganese-boron-silicon (MBS), nickel-boron-silicon (NBS) cobalt- boron-silicon (CBS), scanning electron microscopy of surfaces of which is shown in Figure 1.

The coatings of all above compositions have high mechanical strength and adhesion to the metal surface and continuity. On the foil, surface coating was formed. Mechanical strength of coatings was studied visually in locations of multiple foils bends to almost zero radiuses. There are no cracks and chips on the surface of the coating in bends. Thermal stability of the catalytically active coating on the surface of the metal foil was demonstrated by carrying out thirty thermal cycles of 1,000 °C to room temperature; it was demonstrated no delamination of the coating from the support and cracks of the coating after such heat treatment.

Investigation of the structure of coatings was carried out by optical, scanning electron and atomic force microscopy.



a) *Ni-B-S,* b) *Co-B-S* c) *Mn-B-S*

Figure 1: Exterior of glass crystalline coatings scanning electron microscopy.

Nickel-containing coating is characterized by the absence of large-scale morphological formations such as canals, caverns and elevations (Figure 1a). The predominant surface structure is a fine-grained component that covers the entire surface of the carrier. The morphology of the NBS coating makes it possible to assume the abundance of the crystalline phase in its composition, which is confirmed in the results of the X-ray diffraction analysis, which indicates a large amount of NiO.

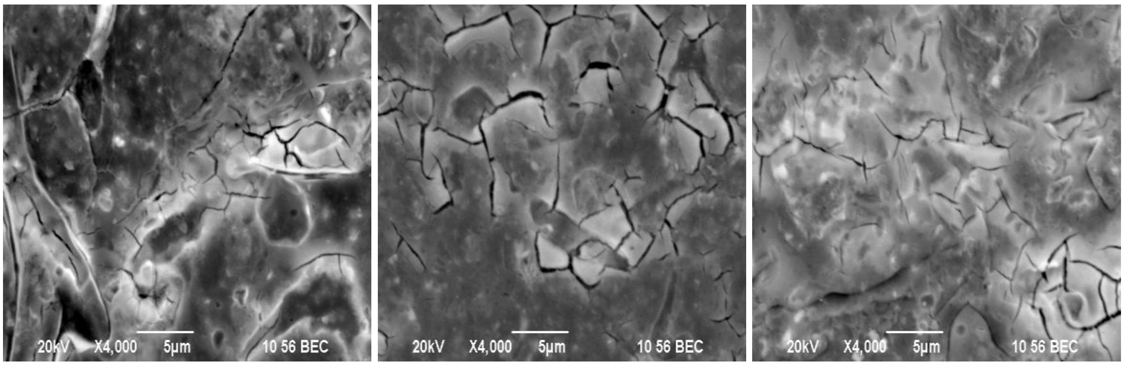
As seen from Figure 1b, the Co-containing coating has a continuous structure and completely covers the carrier from the foil of the NiCrA alloy. A characteristic feature of the CBS coating is the absence of granulation of the substance on the surface, which suggests the presence of a significant amount of the vitreous component in its composition and the almost complete absence of the crystalline component. But according to the results of X-ray diffraction analysis (Krasnokutskiy et al., 2016), the CBS coating has in its composition a significant amount of the crystalline phase represented by such components as Co_3O_4, CoB_2O_4, Co_2SiO_4 (γ-Co_2SiO_4, β-Co_2SiO_4). That fact can be explained by the formation of nanosized particles of these crystalline phases and their high wettability by the surrounding vitreous phase.

The Manganese-containing coating (Figure 1c) in its morphology occupies an intermediate position between CBS and NBS. On the one hand, the MBS coating exhibits continuity and the absence of a fine-grained structure, as in CBS. On the other hand, the MBS coating has a "proto-granularity", which means the presence of half-soluble microstructures, with a surface and edges that are well wetted by the surrounding vitreous phase, but which have a pronounced morphological differentiation with respect to the surrounding vitreous phase. The described morphology is represented by light structures in Figure 1c, X-ray diffraction analysis of the MBS coating substance indicates the presence of a crystalline phase in its composition.

The analysis of the results of scanning electron microscopy of synthesized surfaces, as well as the X-ray diffraction analysis of the secondary coating material, allows the coatings to be arranged in the following series:

- According to the solubility of the crystalline phase in the vitreous phase: CBS > MBS > NBS;
- According to the size of the elements of the microrelief: NBS > MBS > CBS;

In accordance with the proposed method on the surface of the secondary carrier, the catalytically active compound layers are formed. In the present study, as the catalytically active substance of palladium oxide, PdO is selected. Scanning electron microscopy of the resulting coatings is shown in Figure 2.



a) *Ni-B-S* b) *Co-B-S* c) *Mn-B-S*

Figure 2: Exterior of catalytically active compound PdO layers on surfaces of glass crystalline coating of compositions scanning electron microscopy.

Figure 2 shows that the catalytically active layer of palladium oxide completely shields the surface of the support structure of the secondary carrier, which means that the thickness of the palladium oxide (PdO) layer reaches up to 1 μm, which corresponds to the amount of applied palladium oxide.

Catalytic coatings of palladium oxide on all examined secondary carriers have a similar structure and features of morphology (Figure 2). All coatings from Figure 2 are characterized by the presence of a developed system of microcracks with a characteristic length of 5 μm.

Microcracks are formed at the time of the formation of the catalytic layer during the thermal decomposition of the precursor of palladium oxide.

The absence of any melting of the cleavage edges, roundness and smooth lines describing the morphology of surfaces in all the cases shown in Figure 2 indicates the absence of a vitreous component that can significantly affect the surface structure. The peculiar interest to the presence of the vitreous component in the secondary carriers is explained by its ability to wet and dissolve the palladium oxide, shielding it thus from the surrounding gas phase and reducing the catalytic activity. From the traces absence of the vitreous phase, we can conclude that the catalytic activities of the synthesized palladium-containing coatings are close in magnitude in the external diffusion region of the heterogeneous catalytic conversion process. The difference in the features of the process of catalytic conversion in the kinetic region will be determined by the promoting properties of the 3d transition metals that make up the secondary coating.

3. Determination of the catalytic activity of the composite coatings

The catalytic activity of the synthesized catalytic coatings in gas conversion processes was determined using a flow type bench model. Tests of the catalytic converters were carried out in benzene oxidation reactions. To determine the amount of gaseous components that are part of exhaust gases measuring devices "Infrakar" and "Oxy" were used. There are follow conditions for the determination of the catalytic activity: the linear velocity of the gas mixture is 1.5 m/s, the particle size of the catalyst is 5-10 mm, the heating rate is 10 C/min. The composition of the model mixture containing benzene is benzene (10 g/m^3) and air (everything else).

To determine the effect of the composition of the secondary carrier, each of sample was impregnated with catalytically active compounds PdO of the same qualitative and quantitative composition. Catalytic compositions obtained in such way were examined on research stand.

Figure 3 shows the temperature dependence of the conversion degree of the test compound - benzene - for coatings of the boron-silicon composition series.

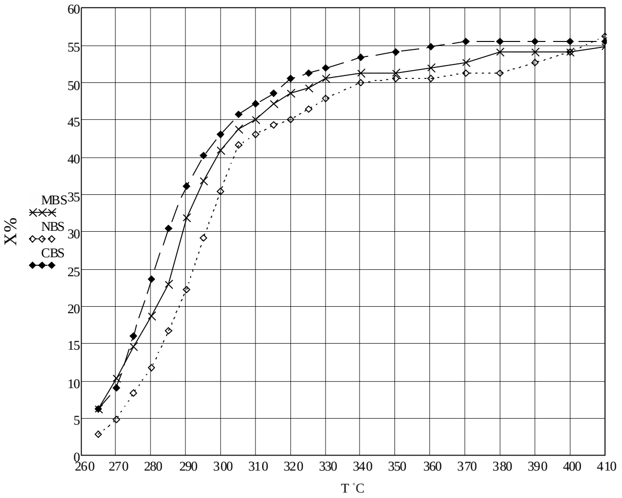


Figure 3: Temperature dependence of the benzene conversion degree X for coatings compositions of the MBS, NBS and CBS.

As shown by the experimental data presented in Figure 3, the temperature dependences of the degree of benzene conversion in cases of various compositions of secondary catalyst supports are close in magnitude.

Each graphical representation of experimental data given in Figure 3 has two sections: a low temperature section (corresponding to limitation of benzene conversion process by chemical processes on the surface of the catalytic coating) and high temperature section (corresponding to limitation of benzene conversion process by features of mass transfer in the system "gas stream - the catalytic surface coatings").

Numbers of available catalytic sites for adsorption and their energy distribution have an impact on the conversion temperature degree in low-temperature section.

At high-temperature section, all active centres participating in catalytic processes are about equivalent energetically and the key factor determining the completeness of benzene conversion to the final product CO_2 is the quantity and availability of active sites for molecules adsorbed starting substances.

The temperature dependence of the degree of benzene conversion to the final product carbon (IV) oxide has two stages of the heterogeneous catalytic process.

Separation set of data points into groups corresponding to the stages of benzene conversion, in accordance with (Ved' et al., 2015) allows determining some parameters. These parameters are the observed value of the activation energy, pre-exponential factor, value of mass transfer coefficient. The mass transfer coefficient is determined by methodology presented by Krasnokutskii and Ved' (2017) which takes into account two benzene oxidation mechanisms: catalytic mechanism on the surface of the catalytic converter and a radical thermal mechanism in the core gas flow.

Determination of the observed values of activation energy, pre-exponential factor and mass transfer coefficient was performed on the basis of concepts that benzene conversion process takes place not only on the surface of the catalyst by the catalytic mechanism but also in the gas flow by a radical chain mechanism (Krasnokutskiy et al., 2017).

The radical reaction rate in the gas flow is additionally influenced by such factors as the benzene concentration in a gas flow, flow structure and its mixing intensity. Taking into account these factors makes it possible to obtain an equation of benzene conversion rate in the carbon (IV) oxide, which takes into account heterogeneous catalytic process and benzene oxidation by a radical chain mechanism. In the integral form of this equation for limitation of benzene conversion process by chemical processes on the surface of the catalytic coating has the following form Eq(1).

$$X = 1 - exp\left(-\tau k_0 \frac{F}{V} C_{cat}^{a} C_0^{b} \mathrm{Re}^{c}\, exp\left(-\frac{E}{RT}\right)\right) \qquad (1)$$

where F is the catalyst area, m^2, E is the observed activation energy, J/mol, k_0 is the Arrhenius pre-exponential factor, m/s, R is the universal gas constant, J/K×mol, τ is the contact time, s, T is the actual temperature in the reaction zone, K, Re is the Reynolds number, C_{kat} is the surface concentration of the catalytically active compounds, kg/m^2, V is the reactor volume, m^3, C_0 is the initial concentration of benzene, mol/m^3, a, b, and c are constants.

The main performance indicators of benzene heterogeneous catalytic conversion process on the surface of the synthesized catalysts are given in Table 1 below.

Table 1: Performance indicators of benzene heterogeneous catalytic conversion process

Secondary carrier	Observed value of the activation energy, J/(mol×K)	Pre-exponential factor, m/s	The surface reaction rate constant at 320 °C, m/s	Length of the reactor on which 95 % conversion is reached at 320 °C in case of absence of external diffusion resistance, m	Mass transfer coefficient at 380 °C, m/s
NBS	193,000	4.8×10^{18}	49.8	0.17	0.0142
CBS	209,000	3.3×10^{20}	133.17	0.06	0.0159
MBS	166,000	2.6×10^{16}	59.85	0.14	0.0153

4. Analysis of experimental data

The catalytic coatings synthesized on the surface of the Ni-containing, Mn-containing and Co-containing secondary carriers are characterized by similar values of the degree of benzene conversion and respectively similar values of mass transfer coefficients in the high-temperature section. This fact is explained as follows. At high temperatures the entire heterogeneous catalytic process is limited by mass-transfer processes, so features of chemical kinetics at the catalyst surface did not affect mass transfer. Therefore only the coverage degree of the catalyst surface by active sites effects on the value of the mass transfer coefficient.

Indeed, the total absence of signs of melting and vitrification of the catalyst layer on the NBS coatings surface and the presence of crystal phase in it, as well as absence of signs of catalyst vitrification on the CBS and MBS surface coating, promotes more complete localization palladium oxide (PdO) on the surface and not in the deep layers of the secondary coatings, where it is much more difficult to access for the reactants from the gas phase. Thus the similarity of the surface structures of the catalyst layer on the secondary carriers indicates to similar values of surface concentration of palladium oxide and hence the mass-transfer coefficient and the degree of benzene conversion at high temperatures.

The difference between Ni-containing, Mn-containing and Co-containing coatings is the presence of different types of metal, which leads to differences in the physicochemical properties of the interaction of the catalyst layer with the secondary carrier. This is manifested, firstly, in the promoting properties of the secondary coating, and, secondly, in the morphology of the secondary carrier. According to electron microscopy scanning results of the secondary coatings, they have different characteristic particle size and crystalline phase and, consequently, the different specific surface area of the crystalline phase contacting the catalyst coating. The data of the kinetics of the benzene heterogeneous catalytic conversion process shown in Figure 3 correlate with the particle size of the crystalline phase: the smaller the particle size of the crystalline phase, the higher the catalytic activity of palladium oxide.

The only distinguishing characteristic of the coating CBS is the presence of cobalt oxide. This leads to the conclusion that the presence of cobalt oxide in the secondary carrier has a significant promoting effect on the catalytic properties of a palladium catalyst. Cobalt promotion is so strong that its significant effects on the surface of the catalyst layer even if the thickness of the coating of palladium oxide reaches 2 μm.

5. Conclusions

Conducted comprehensive study of surface morphology of catalysts and their catalytic activity in the oxidation of benzene revealed general patterns the structure and physicochemical properties of the surface of the secondary carrier that provides an increase in the chemical reaction surface rate constant and the mass transfer coefficient from the gas stream to the catalyst surface. There were obtained maximum values of the activation energy (209 J/(mol×K)), the surface reaction rate constant (133.17 m/s) and mass transfer coefficient (0.0159 m/s) on secondary carrier, which represents cobalt- boron-silicon, while the process of hydrocarbons oxidation in the low-temperature area. Features of the temperature dependence of the degree of benzene conversion for catalysts on various secondary carriers (Table 1) are explained by differences in the characteristics of the interaction of palladium oxide with NBS, CBS and MBS oxides systems on a chemical level at the moment of the formation of the catalytic coating. The experimental data shows that the promising ways to increase in constant speed at the given temperature can be:

- selection of the composition of the secondary carrier containing promoter components;
- selection of the composition of secondary carrier, the formation of which will form crystalline inclusions;
- selection of the secondary carrier composition with a maximum possible vitrification temperature to avoid the dissolution of the catalyst in the secondary carrier.

Catalytic converters manufactured on the basis of the proposed methodology are successfully used in waste treatment complexes and neutralizers of vehicle gas emissions (Makhanov B. at al., 2015).

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