Universal Multi-Functional Secondary Catalyst Carriers for Purification of Gas Emission of Thermal Power Equipments

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A method of deposition on the surface of metals or ceramics catalytically active compounds by attaching them to the intermediate glass crystalline coatings. The effect of the presence of 3d-transition elements in the intermediate coating to modify the activity of a palladium containing catalyst was studied. The basic indicators of the efficiency of non-isothermal heterogeneous catalytic conversion process of benzene depending on the types of transition metals which are part of the intermediate coating were studied. Comprehensive analysis of the morphology of a glass-intermediate secondary catalyst carriers and surface coating them with layers of catalytically active compounds was carried out, which allowed to estimate the effect of the characteristic features of the structure of the coating surface on the rate constant of the process of conversion and mass transfer coefficient.

1. Introduction

Catalysts neutralization of gas emissions are widely used in industry, in particular it is used in waste treatment complexes and for neutralization of exhaust gases of internal combustion engines. Operating conditions of catalysts are characterized by dynamic thermal and mechanical loads, nonuniformity of speed of catalytic reactions in different parts of the support surface due to inhomogeneity of hydrodynamic and thermal conditions in the axial and radial sections of block-converter. In such circumstances, long-term operation results in the destruction of the catalyst surface, the catalyst layer peeling from the carrier material, which is caused by differences in the values of the linear expansion coefficients of the system "catalyst carrier - catalytic layer". Significant influence on the activity of the catalyst in chemical processes of neutralization of gas emissions also provides qualitative and quantitative composition and the morphology of the catalyst support, experimental and theoretical study of the effect of which is the main objective of catalytic research.

2. Formulation of the problem

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.
The catalytic properties of materials are determined by factors such as chemical composition, crystal structure, macro- and microscopic structure. Efficiency of catalytic coatings also depends on the type, composition and characteristics of morphology of the catalyst support.
As the catalyst carrier in a vehicle and industry catalyst supports of different materials and different constructions are used. In order to increase the specific surface of metallic and ceramic carriers and increase the catalytic

properties of the finished catalyst, forming of the intermediate coating is widely used. On the surface of intermediate coating one or more metals or oxides of the platinum group (platinum, palladium, rhodium) as an active component is deposited.

Deposition of platinum group metals or oxides is mainly takes place from aqueous solutions of inorganic salts, followed by drying, calcination and partial or full chemical reduction of catalyst.

Formation of catalyst layer on a metal or ceramic surface by known means is associated with various drawbacks. In particular, for the reason that only a certain combination of catalyst material and carrier material to produce sufficient adhesion of the catalyst to the surface of the carrier material (metal or ceramic) under high temperature and thermally unstable operation of the catalyst can be used. The condition of certain ratio between the temperature coefficients of linear expansion in the system "catalyst carrier – catalytic" layer must be fulfilled, since cyclic temperature changes lead to thermal stresses which are proportional to the differences in the coefficient of linear expansion values of the catalyst and carrier which leads to the destruction of the coating. The destruction of the catalytic coating can also be caused by mechanical impact, abrasion and other factors.

To solve this problem, a method of managed formation of catalytically active centres of a complex micro relief on the surface of high-temperature alloys and ceramic materials (primary carrier) was developed. It is based on the idea of the chemical compositions and the new technology of forming the special amorphous or glass crystalline adhesives of thickness less than 1 micron (the secondary carrier) which are applied to surface of metals or ceramics (primary carrier) layers. Research has shown that the secondary coatings of any composition and of any value of the thermal coefficient of linear expansion do not have a mechanical effects on the primary carrier, the thickness of which only one order of magnitude greater than its covering layer, when the temperature is up to 1,000 °C.

Secondary carrier by means of structural viscosity relaxes thermal stress arising in it from the mechanical action of the primary metal carrier with increasing temperature due to the difference in coefficient of linear expansion. The catalytically active coating layers are deposited on the surface of the secondary glass-containing carrier with thickness considerably smaller than 1 micron and also do not cause thermal stresses in our proposed compositions of aggregate coatings.

Research has revealed that using the developed compositions of secondary carriers leads to activation of the catalyst and demonstration their satisfactory catalytic activity exhibited even in case of such primary carriers, which in the absence of the secondary coating of the carrier have an inhibitory effect on the catalytic activity.

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

Synthesized secondary coatings in accordance with the proposed method are formed on the foil 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-aluminum-boron (MAB), nickel-aluminum-boron (NAB) cobalt-aluminum-boron (CAB), 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 were formed. Mechanical strength of coatings was studied visually in locations of multiple foil bends to almost zero radius. It has been shown the lack of cracks and chips on the surface of the coating in a 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.
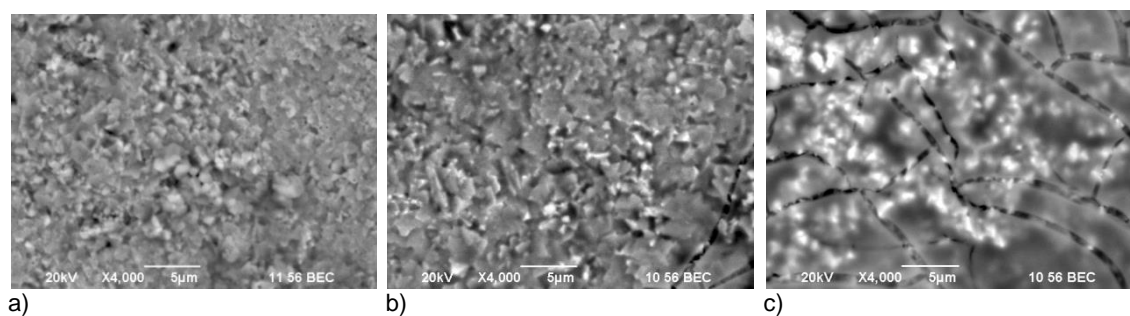

a)   b)   c)

Figure 1. Exterior of glass crystalline coatings: Ni-Al-B (a), Co-Al-B (b), Mn-Al-B (c). Scanning electron microscopy

As seen from Figure 1a Ni-containing coating is continuous, completely covers the carrier a foil of NiCrA alloy and has a granular surface structure containing a small amount of crystalline inclusions of alleged compositions of $Al_4B_2O_9$, $Al_5(BO_3)_6$, $Al_{13}B_4O_{33}$ (according to X-ray crystallography). Co-containing coating is also characterized by continuity and the absence of cracks developed at the micro level, and is different from the Ni-containing coatings by lack of crystalline inclusions (according to X-ray crystallography), as well as by presence of few light granular structures. Mn-containing coating is characterized by developed system of cracks and grooves at the micro level, the smoothness of the surface, which allows the identification of this covering as glass. It was confirmed by X-ray crystallography data. On the surface of the Mn-containing coating (Figure 1b) the significant bright droplet formations are also noticeable.

The typical height of the surface structure of the investigated coating element is from 1 to 2 µm.

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)   b)   c)
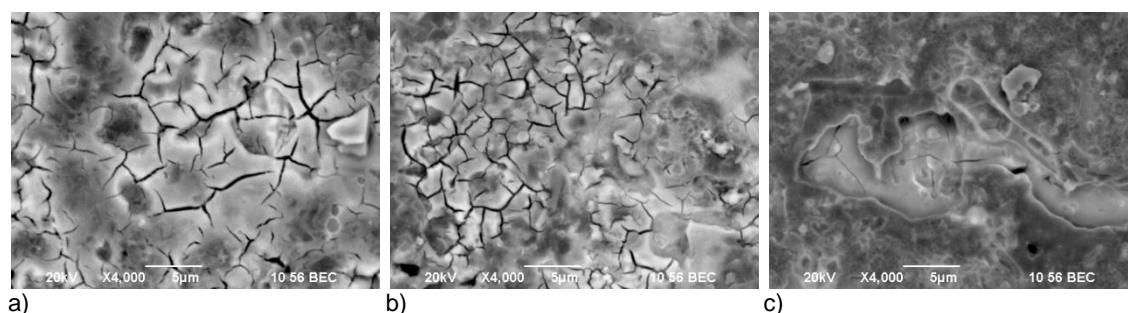
Figure 2. Exterior of catalytically active compound PdO layers on surfaces of glass crystalline coating of compositions Ni-Al-B (a), Co-Al-B (b), Mn-Al-B (c). Scanning electron microscopy

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 PdO layer reaches up to 1 µm, which corresponds to the amount of applied palladium oxide.

From Figure 2a follows that the use of Ni-containing glass crystalline phase as a secondary carrier for catalyst based on palladium oxide forms a continuous surface characterized by a developed system of microcracks and absence melted and smoothed cracks edges. Figure 2b shows that on the surface of Co-containing coating the layer of palladium oxide forms more dense network of cracks as compared to nickel-based system. This surface is also characterized by the presence of a small amount of rounding chips and cracks.

Figure 2c shows the structure of the surface of the catalyst layer of palladium oxide on the secondary Mn-containing carrier. The surface layer of palladium oxide completely shields the developed cracks system inherent to the structure of the secondary carrier surface. Catalytic surface is also characterized by clearly expressed with smooth lines of grooves edges, the lack of cracking, chipping, which indicates the active processes of glass transition at the moment the layer of palladium oxide catalyst formation and consequently possible redistribution of parts of palladium oxide from a coating surface to its bulk.

4. Determination of catalytic activity of the composite coatings

The catalytic activity of the synthesized catalytic coatings in gas conversion processes was determined using 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. Conditions for the determination of the catalytic activity are follows: the linear velocity of the gas mixture is 1.5 m/s, the particle size of the catalyst is 5×10 mm, 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 composition of the secondary carrier each of sample was impregnated with catalytically active compounds PdO of the same qualitative and quantitative composition. Obtained in such way catalytic compositions were examined on research stand.

Figure 3 shows the temperature dependence of the conversion degree of the test compound - benzene - for coatings of the aluminum-boron composition series.
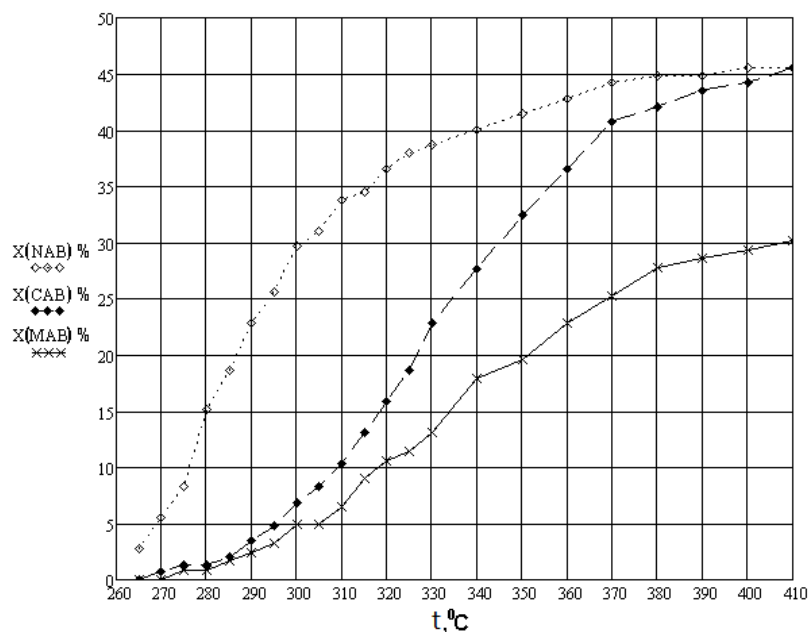
Figure 3. Temperature dependence of the benzene conversion degree X for coatings compositions of the MAB, NAB and CAB

As shown by the experimental data presented in Figure 3, the temperature dependence of the degree of benzene conversion in cases of various compositions of secondary catalyst supports have their own characteristics.

Each graphical representation of experimental data given on 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").

The change in the degree of conversion dependency on temperature in the low temperature section is influenced by such factors as the number of available catalytic sites for adsorption and their energy distribution.

At high temperature section all active centres participating in catalytic processes are about equivalent energetically therefore the key factor determining the completeness of benzene conversion in 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 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 to determine parameters such as the observed value of the activation energy and pre-exponential factor, as well as the value of mass transfer coefficient according to methodology presented by Krasnokutskii and Ved' (2013a) which takes into account two benzene oxidation mechanisms: catalytic mechanism on the surface of the catalytic converter and a thermal radical 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.

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 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:

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

where 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

The secondary carrier	The observed value of the activation energy, J/(mol×K)	The pre-exponential factor, m/s	The surface reaction rate constant at 320 °C, m/s	The 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
NAB	204,000	6.4×10^{19}	64.7	0.13	0.0118
CAB	165,000	1.7×10^{15}	5.1	1.68	0.0108
MAB	169,000	2.4×10^{15}	3.0	2.80	0.0054

5. Analysis of experimental data

The catalytic coatings synthesized on the surface of the Ni-containing and Co-containing secondary carriers are characterized by close values of the degree of benzene conversion and respectively close 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 to mass transfer. Therefore only the coverage degree of the catalyst surface by active sites affects on the value of the mass transfer coefficient.

Indeed, the total absence of signs of melting and vitrification of the catalyst layer on the NAB coatings surface and the presence of inclusions of crystal phase in it, as well as minor signs of catalyst vitrification on the CAB 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.

In the case of using Mn-containing secondary carrier the lowest values of benzene conversion rate and mass transfer coefficient are observed.

Significant scale of glass transition and melting of MAB surface secondary carrier compared to coatings NAB and CAB at the time of the catalytic coating PdO synthesis indicates migration of palladium oxide from the surface of the secondary carrier to its deep layers, as well as the wetting surface layer of PdO by liquid phase at the time of vitrification. This reduces the amount of available for the adsorption and acts of catalytic interaction active sites of the catalyst.

Features of the temperature dependence of the degree of benzene conversion for catalysts on various secondary carriers are explained by differences in the characteristics of the interaction of palladium oxide with NAB, CAB and MAB oxides systems on a chemical level at the moment of the formation of the catalytic coating. The experimental data shows that the significant increase in constant speed at the given temperature can be achieved by means of:

– Selection of the composition of secondary carrier containing a 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.

6. Conclusions

The results of these studies show the effectiveness of the use of secondary catalysts carriers synthesized by the newly developed method, which allows carrying out the process of the formation of the catalyst in a relaxed state. Synthesized secondary carriers effectively shield the layer of catalytic material on the possible inhibitory effect of the chemical components that are part of primary carrier of ceramic or metallic nature, modify and promote the catalyst layer, increase the life of the mechanical integrity of the catalytic coating in a cyclic thermal loads due to the damping properties of the secondary carrier.

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 provide increase in the chemical reaction surface rate constant and the mass transfer coefficient from the gas stream to the catalyst surface.

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