

Catalyst Coatings Carriers Based on Aluminium-Silicon Glass Crystalline Compositions

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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

Road transport and waste-processing complexes are the main consumers of catalysts produced in the world. Both in post-combustion exhaust gas systems of internal combustion engines and systems of catalytic exhaust gas purification of waste treatment complexes the dynamically changing parameters of the flowing out the catalyst gas flow takes place. Changes in temperature can reach up to 200 K, and the gas flow rates changing of up to 50 % of the average speed. These conditions lead to mechanical destruction not only the catalyst surface but also the catalyst carrier, which reduces the effective lifetime functioning of purification systems. 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 and quantitative composition of catalyst carrier. In many cases, when the catalyst carrier is a metal or ceramics, changes in chemical composition of the carrier over a wide range are not possible. 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. Such a multilayer system due to the possibility of varying over a wide range of qualitative and quantitative 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.

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.

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 as well known by qualitative and quantitative composition of catalytic coatings. However, not least the catalytic activity is also determined by the promoting and modifying properties of 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 to find such composition values, which will significantly increase the thermomechanical stability and catalytic activity of the catalysts. However, since the catalytic coatings carriers' materials have ceramic or metallic nature, 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 to overcome limitation of composition of the catalyst support, which is undeniable advantage. 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 to mechanical destruction under dynamic thermal operating parameters of catalytic neutralization units.

The use of secondary carriers of glass-crystalline nature allows to avoid 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 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.

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-silicon (MAS), nickel-aluminum-silicon (NAS) cobalt-aluminum-silicon (CAS), 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.

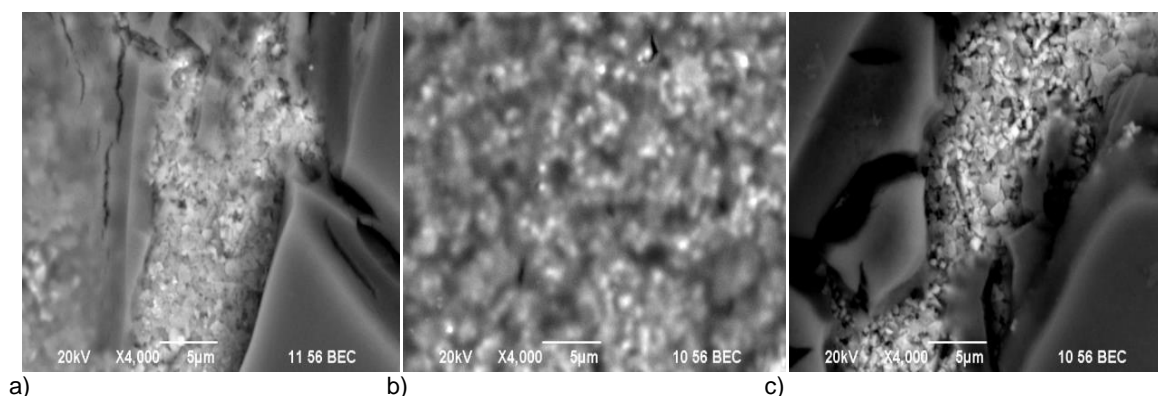


Figure 1: Exterior of glass crystalline coatings: Ni-Al-S (a), Co-Al-S (b), Mn-Al-S (c). Scanning electron microscopy.

As seen from Figure 1b Co-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 $\text{Co}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, $\text{Co}_3\text{Al}_2(\text{SiO}_4)_3$ (according to X-ray crystallography). Ni-containing coating is characterized by large structural elements such as channels and elevations. The width of the channel is from 5 to 15 μm . The edges of the channels and cracks are characterized by sharp corners and the absence of melting traces. Such a structure is characteristic of crystalline coatings, which is confirmed by X-ray analysis of NAS coating. The NAS coating contains the following crystalline components $\text{Ni}_{10.3}\text{Al}_{11.3}\text{Si}_{2.4}\text{O}_{32}$, $\text{Ni}_{27}\text{Al}_{13.9}\text{Si}_{5.1}\text{O}_{48}$,

$\text{Ni}_{12.48}\text{Al}_7\text{Si}_{4.5}\text{O}_{32}$, $\text{Ni}_3\text{Al}_2\text{SiO}_8$. Mn-containing coating is characterized by large structural elements such as channels and elevations. The width of the channel is from 5 to 15 μm . The edges of the channels and cracks are characterized by sharp corners and the absence of melting traces. Such a structure is characteristic of crystalline coatings, which is confirmed by X-ray analysis of MAS coating. The MAS coating contains the following crystalline $\text{Mn}_{0.86}\text{Al}_{1.14}(\text{SiO}_4)\text{O}$, $\text{Mn}_{1.9}\text{Al}_{3.8}\text{Si}_{8.3}\text{O}_{24}$, $\text{Mn}_3\text{Al}_{12}(\text{SiO}_4)_3$, $\text{Mn}_{46}(\text{Al}_{92}\text{Si}_{100}\text{O}_{384})$.

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.

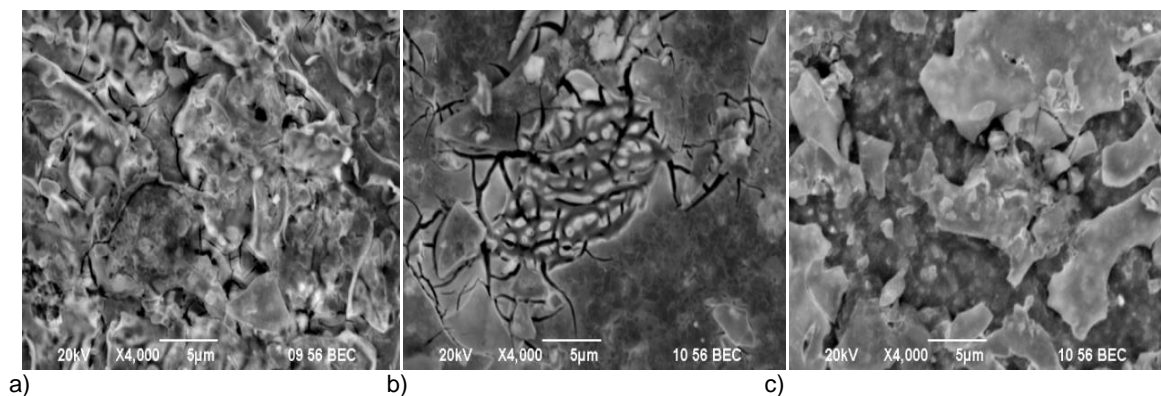


Figure 2: Exterior of catalytically active compound PdO layers on surfaces of glass crystalline coating of compositions Ni-Al-S (a), Co-Al-S (b), Mn-Al-S (c). Scanning electron microscopy.

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. PdO layer completely fills the cracks and channels of a secondary coating and forms aggregates ranging in size from 5 to 25 μm on the surface. The catalytic surface is characterized by a expressed sharp edges and chipping and by lack of roundness and melted faces and edges.

An exterior surface of the examined catalysts indicates to the absence of a vitrification in the moment of palladium oxide layer formation, resulting in little or no migration of PdO into the interior of the secondary carrier. It allows to assume about close gas emissions conversion rate values on all (MAS, NAS, CAS) synthesized surfaces in conditions of the external diffusion inhibition.

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 5x10 mm, heating rate is 10 $^{\circ}\text{C}/\text{min}$. 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.

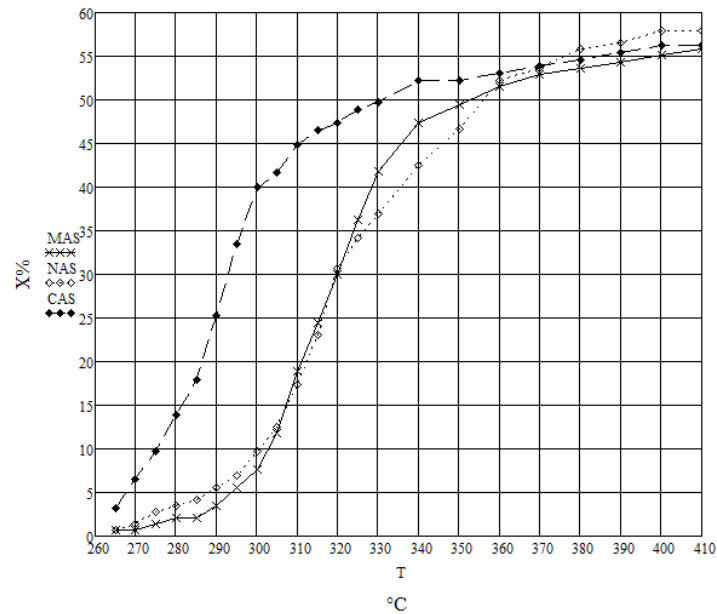


Figure 3: Temperature dependence of the benzene conversion degree X for coatings compositions of the MAS, NAS and CAS.

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 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 centers 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:

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

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/Kxmol, 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, $\text{J}/(\text{mol K})$	The pre-exponential factor, m/s	The surface reaction rate constant at $320\text{ }^\circ\text{C}$, m/s	The length of the reactor on which 95% conversion is reached at $320\text{ }^\circ\text{C}$ in case of absence of external diffusion resistance, m	Mass transfer coefficient at $380\text{ }^\circ\text{C}$, m/s
NAS	177,000	4.1×10^{16}	10.3	0.83	0.0161
CAS	197,000	1.6×10^{19}	64.5	0.13	0.0156
MAS	206,000	1.6×10^{19}	10.3	0.83	0.0152

5. 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 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 NAS coatings surface and the presence of inclusions of crystal phase in it, as well as absence of signs of catalyst vitrification on the CAS 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 use of Co-containing secondary carrier the highest conversion rate value is observed at low temperatures, which corresponds to limitation of heterogeneous catalytic conversion process by stage of the surface chemical kinetics. By the condition of experimental study the palladium content on all the above carriers is equal. Also with the help of surface morphology analysis and kinetic analysis of the experimental data of heterogeneous catalytic conversion at high temperatures it is shown no migration of palladium into the interior of the secondary carrier. The only distinguishing characteristic of the coating CAS 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 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 $2\text{ }\mu\text{m}$.

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

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 NAS, CAS and MAS 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.

References

- Beutel, T.W. and Dettling, J.C. and Hollobaugh, D.O. and Mueller, T.W., 2009. Pt-Pd diesel oxidation catalyst with CO/HC light-off and HC storage function. US Patent 7576031.
- Ohno, K., Kunieda, M. and Ido, T., 2012, Honeycomb structure and exhaust gas conversion apparatus. EP Patent 2127725.
- Khalyeyev A.B., Koshchii V.A., Rovenskii R.O., Ved' O.V. and Krasnokutskiy Ye.V., 2012, A method of manufacturing a catalytic converter. UA Patent 69861. (in Ukrainian).
- Krasnokutskiy E. V., Makhanov B. B., Ved' V. E., Satayev M. I., Ponomarenko A. V., Saipov A. A., 2016, Universal multi-functional secondary catalyst carriers for purification of gas emission of thermal power equipments, *Chemical Engineering Transactions*, 52, 277-282 DOI:10.3303/CET1652047
- Krasnokutskii E.V., Ved V.E., 2013a, Substantiating Reaction Mechanism of Thermocatalytic Benzene Conversion, *Theoretical Foundations of Chemical Engineering*, 47, 1, 60-65, DOI: 10.1134/S004057951301003X.
- Krasnokutskiy Ye., Ved V., Kuznetsova M., 2015. Modelling of Effective Thickness of the Catalyst Support Porous Layer. CAPE Forum 2015. Computer Aided Process Engineering. Book of Abstracts, University of Paderborn. Paderborn, Germany 71.
- Krasnokutskiy Ye.V., Ved' V.Ye., Ponomarenko A.V. and Koshchii V.A., 2013b, Stand for the study of kinetic and gasdynamic parameters of catalytic gas cleaning processes. *Intehrovani tekhnolohiyi ta enerhozberezhennya*, 2, 126-131. (in Russian).
- Levenspiel, O., 1999, *Chemical Reaction Engineering*, Wiley. New York, USA.
- Makhanov B., Satayev M., Krasnokutsky Ye., Ved V., Saipov A., 2015, New Type of Harmful Gas Emissions Catalytic Converter, *Industrial Technology and Engineering*, 4, 5-18.
- Ngk Insulators, Ltd., 2008, Use of a honeycomb structure in an exhaust gas converter system. EP Patent 1384507.
- Richards, R., 2006, *Surface and nanomolecular catalysis*. Boca Raton, FL, CRC/Taylor & Francis.
- Tovazhnyanskii L.L., Ved' V.E., Koshchii V.A., Rovenskii A.I., Krasnokutskii E.V., 2013, Mobile Thermocatalytic Waste Processing Complex, *Chemical Engineering Transactions*, 35, 907-912, DOI: 10.3303/CET1335151.
- Tovazhnyanskii L.L., Ved' V.E., Koshchii V.A., Rovenskii A.I., Meshalkin V.P., Krasnokutskii E.V., 2011, Effectiveness of Operation of Sewerage System of Mobile Complex of Thermocatalytic Waste Treatment, *Theoretical Foundations of Chemical Engineering*, 45, 6, 838-841, DOI: 10.1134/S0040579511060169.
- Ved' V. E., Krasnokutskiy E. V., Satayev M. I., Ved' A. V., Saipov A. A., 2016, Calculation of the operation parameters of the catalytic converters of the harmful gas impurities, *Chemical Engineering Transactions*, 52, 91-96 DOI:10.3303/CET1652016
- Ved' V., Tovazhnyanskiy L., Krasnokutskiy Ye., Koshchii V., 2015, Modelling Of Hydrocarbons Catalytic Conversion Process, *Chemistry & Chemical Technology*, 9, 1, 101-106.