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CO Oxidation over Pd/MeO_x/M Catalysts, where MeO_x/M Carrier is Prepared by Plasma Spraying (MeO_x: Al₂O₃, Al₂O₃-CeO₂, Al₂O₃-MnO₂; M: Ni-Al/Stainless Steel)*

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Abstract

The activity in the CO oxidation reaction of MeO_x/M and Pd/MeO_x/Ni-Al/stainless steel (SS) catalysts where MeO_x: Al₂O₃, Al₂O₃-CeO₂, Al₂O₃-MnO₂ carrier is applied to Ni-Al/SS (grids made of SS with an evaporated Ni-Al layer) was studied. Samples, in which grids made from fechril and nichrome were used, were prepared for comparison. It was demonstrated that intermediate Ni-Al coating itself serving to increase adhesion of oxides to a metal substrate exhibited the catalytic activity. The most active samples activated and not activated by palladium were determined according to the results of catalytic trials. All catalysts were characterized by X-ray phase analysis, scanning electron microscopy methods. The most active Pd/Al₂O₃/Ni-Al/SS sample was additionally studied by scanning electron microscopy (SEM) with local analysis.

Kew words: CO oxidation, catalysts, Al₂O₃, Al₂O₃-CeO₂, Al₂O₃-MnO₂, plasma application, [Pd(NH₃)₄](NO₃)₂, scanning electron microscopy (SEM), X-ray phase analysis

INTRODUCTION

The issue of air pollution associated with the active use of auto transport and the development of chemical industry is one of the most crucial eco-problems in the modern world. Emissions of automobile exhaust gasses make the

greatest contribution into air pollution. The problem is constantly compounded by high growth rates of stock of vehicles with a limited throughput of urban highways. On average in Russia, the contribution of motor transport into atmospheric pollution is 40–45 %, and in large cities – up to 90 % [1].

The use of catalytic neutralizers of automobile exhaust gases widely used in developed countries with 1970s is a solution of this problem. A modern catalytic neutralizer represents a catalytic or metal honeycomb block, on the

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surface of which a catalytic active layer is applied to. Wholesale catalytic neutralizers are most often manufactured based on ceramic blocks that can easily be destroyed resulting from local overheating, water contamination or mechanical shock. Mechanical carriers compete with ceramic honeycomb blocks owing to high thermal conductivity, thermal shock resistance, mechanical strength, thermal shock resistance and an opportunity to easily give them the desired geometric shape form [3, 4]. Secondary carriers based on aluminium, silicon and zeolites applied to metal blocks by impregnation lose an adhesive strength with the majority carrier and flake off, therefore, the elaboration and study of preparation methods of catalysts applied to metal catalysts with high mechanical strength and thermostability and their study are relevant [5]. Plasma application of catalytic coatings may be one of the promising methods [6]. Plasma spray technology of various coatings is well developed [7], and the major research objective consists in the fact that to determine through the selection of suitable precursors of catalytically active substances and conditions of their application, which factors (nature and properties of precursors, plasmochemical spraying conditions) affect the activity of the synthesized catalysts.

The selection of carriers in our case was made based on the results published in the literature and data of our own works. Thus, fechrals and stainless steels X15U5 and X20H10T were used in [8–12].

The selection of initial oxides for plasmochemical application of the active layer to thermostable alloys was made by us based on literature data and the results of our own works [10, 11, 13].

Thus, coatings over a metal film carrier used in [11] contained in their composition: Al, Al_2O_3 , Cr_2O_3 , WO_3 , CuO and the sum of REE oxides. Herewith, the activity of catalysts obtained by the plasmochemical method was comparable with that of the samples obtained by the traditional impregnation method [14].

The purpose of this article is to present the results on catalytic properties of the samples synthesized by plasma spraying on grids made of stainless steel and the same catalysts activated by palladium. The catalytic properties were

determined in a model of the CO oxidation reaction. Earlier [15, 16], similar catalysts were tested in the reaction of deep oxidation of methane and CO oxidation.

EXPERIMENTAL

Catalysts preparation

Catalysts preparation consisted of several stages. Grids made from stainless steel 12X18H10T and from fechrals and nichrome were subjected to abrasive blasting with silicon carbide powder. To better concatenate the oxide coating with a stainless grid a sublayer of heat-sensitive PT-Yu10N powder (90 % Ni, 10 % Al) was applied to, a thickness of the sublayer is $\sim 30\ \mu\text{m}$. The surface of stainless steel after covering with PT-Yu10N powder is rough, has greater adhesion in relation to oxides powders than stainless steel surface without the sublayer. Coatings made of Al_2O_3 , $\text{Al}_2\text{O}_3\text{--CeO}_2$, $\text{Al}_2\text{O}_3\text{--MnO}_2$ were applied by the plasma method from the corresponding powders of oxides and mechanical mixtures of individual oxides into three passes of the plasma torch from each side. Fractions of the powders with the sizes of particles oxides of 30–50 μm , optimum for plasma coating, were used for applying coatings. Argon and 5 % hydrogen were used as a plasma forming gas. According to the literature, the temperature of the plasma, was $\sim 10\ 000\ ^\circ\text{C}$ [17]. After applying palladium, oxidation of applied Ni–Al sublayer to NiO, active in deep oxidation, may occur [18], therefore, catalytic activity of Ni–Al/SS and Pd/Ni–Al/SS samples was also studied by us.

Palladium was applied by the impregnation method from a solution of $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$, the samples were later dried at $110\ ^\circ\text{C}$ for 2 h and then calcined in air at $500\ ^\circ\text{C}$ for 3 h.

Catalytic trials

Catalytic characteristics of samples in the CO oxidation reaction were determined in a flow type setup using the initial gas mixture of composition: 1 % CO + 99 % air. A sample weight of the catalyst for testing was $(3.40 \pm 0.03)\ \text{g}$ with a volume of $\sim 2\ \text{cm}^3$. A tubular reactor with an

inner diameter of 10 mm was made of Pyrex glass. The flow rate of the gas mixture was 300 mL/min. Contact time is ~0.4 s, the temperature range 50–500 °C. The concentration of CO before and after reaction was determined by chromatographic separation of the mixture on a packed column filled with zeolite CaA (3 m) and using a thermal conductivity detector. Nitrogen included in the reaction mixture was used as an internal standard.

After the release of the catalytic activity to the stationary phase *i. e.*, obtaining three chromatograms close by value $P^{\text{CO}}/P^{\text{N}_2}$ for the initial reaction mixture (IRM) and a mixture after the reactor (MAR) at the same temperature, conversion degrees of CO (X_{CO}), % were calculated according to the formula

$$X_{\text{CO}} = \frac{(P_{\text{IRM}}^{\text{CO}} / P_{\text{IRM}}^{\text{N}_2}) - (P_{\text{MAR}}^{\text{CO}} / P_{\text{MAR}}^{\text{N}_2})}{P_{\text{IRM}}^{\text{CO}} / P_{\text{IRM}}^{\text{N}_2}}$$

where $P_{\text{IRM}}^{\text{CO}}$ is CO peak area in the initial reaction mixture, $P_{\text{IRM}}^{\text{N}_2}$ is N₂ peak area in IRM, $P_{\text{MAR}}^{\text{CO}}$ is CO peak area in MAR, $P_{\text{MAR}}^{\text{N}_2}$ is N₂ peak area in MAR.

The activity was assessed according to the temperatures of reaching 50 % of the conversion degree ($T_{50\%}$) and the conversion degree at 500 °C.

Characterization of samples

The phase composition of oxide carriers was determined by the powder diffractometry method on a Bruker D8 Advance diffractometer using CuK_α radiation with a step of 0.05° and signal accumulation time of 2 s, a voltage of 40 kV, the strength of current of 40 μA. Registration of the diffracted radiation was carried out using a Lynxeye position sensitive detector (Bruker).

For the study, the applied oxide layer was removed from the stainless steel grid. The resulting powder was ground in an agate mortar and applied to an amorphous substrate (SiO₂). Decoding the diffractograms obtained was performed using the ICDD PDF-2 powder diffraction database of 2006. Calculation of the size of CSR was performed in the TOPAS 4.2 program (Bruker AXS). The fundamental parameter (FP) method was used in the calculations.

The study of the morphology and composition of samples surface was carried out using a JSM-6610LV JEOL scanning electron microscope (SEM) equipped with an X-ray microanalysis spectrometer (INCAx-Act Oxford Instruments).

RESULTS AND DISCUSSION

Characteristic of samples

The mass of applied Na–Al sublayer and oxides was determined by weighting of samples after abrasive blasting of the initial grid made of stainless steel, applying the sublayer and oxides (Table 1).

Stainless steel samples, as well as nichrome and fechrall samples with various contents of the sublayer from ~6 to 22 mass % were taken for study.

Depending on the oxide nature (oxides mixture) and metal matrix, the following is observed (see Table 1). Aluminium oxide is applied on a system of sublayer/metal grid with a high sticking coefficient: weight gain of 29.2, 30.2 and 43.8 mass % for SS, nichrome and fechrall, respectively, Al₂O₃–CeO₂ and Al₂O₃–MnO₂ are applied much worse: thus, Al₂O₃–CeO₂ gives a weight gain of only 10.0 % (75 % Al₂O₃ and 25 % CeO₂), Al₂O₃–MnO₂ – 7.2 % (75 % Al₂O₃ and 25 % MnO₂). A low degree of application of mixtures of oxides can be explained by different melting points of the oxides and different dynamics of their plasma heating.

Catalytic activity

The results of activity determination of MeO_x/Ni–Al/SS catalysts are presented in Fig. 1 and Table 2.

As follows from the data of Table 2 the oxide catalysts prepared by the method of plasma deposition and the grid made of stainless steel itself not containing palladium are inactive in CO oxidation reaction. By the conversion degree (X) at 500 °C catalysts over (Ni–Al)/SS in CO oxidation make up a row: Ni–Al (85 %) > Al₂O₃–CeO₂ (76 %) > Al₂O₃–MnO₂ (74 %) > Al₂O₃ (64 %) > SS (2 %). The value of $T_{50\%}$ for the best sample of Ni–Al/SS is 420 °C. A low

TABLE 1

Characteristics of samples after applying the sublayer and oxides on metal carriers

Sample Nos.	Samples	Mass of the applied Ni-Al layer*, mass %	Mass of the applied MeO _x layer, mass %
1	Ni-Al/SS	21.7	—
2	Al ₂ O ₃ /Ni-Al/SS	19.0	29.2
3	Al ₂ O ₃ -CeO ₂ /Ni-Al/SS	17.6	10.0
4	Al ₂ O ₃ -MnO ₂ /Ni-Al/SS	17.5	7.2
5	Al ₂ O ₃ /Ni-Al/nichrome	8.8	30.2
6	Al ₂ O ₃ /Ni-Al/fechral	5.7	43.8

* From the mass of the entire sample.

activity of catalysts prepared by the plasma method can be explained by the low specific surface of the applied layer. The problem can be solved through the development of the surface of oxides by various thermochemical treatments. Thus, Ni-Al/SS sample is active due to both dispersion of Ni-Al alloy at plasma appli-

cation and nickel oxidation to NiO that is the third oxide (after Co₃O₄ and CuO) by the activity in CO oxidation out of the activity row of IV period transition metal oxides [19]. A relatively high activity of Ni-Al alloy may be driven by the formation of NiO-Al₂O₃ system at air oxidation when calcining at 500 °C and the formation of NiAl₂O₄ spinel [20].

The study results of the grid material on the conversion degree of CO are presented in Fig. 1, b.

By the conversion degree (X) at 500 °C, Al₂O₃/metal grid catalysts make up a row: Al₂O₃/Ni-Al/SS (64 %) > Al₂O₃/Ni-Al/nichrome (21 %) > Al₂O₃/Ni-Al/fechral (3 %). Such an activity can mainly be explained by smaller amounts of applied Ni-Al sublayer on nichrome and fechrals carriers (see Table 1).

Activation of oxide samples activated by palladium on stainless steel substantially increases their activity. The trial results in CO oxidation reaction of Pd/MeO_x/Ni-Al/SS samples activated by palladium are given in Fig. 2, a and Table 3. It can be seen that the Pd-modified oxide catalysts and the grid itself

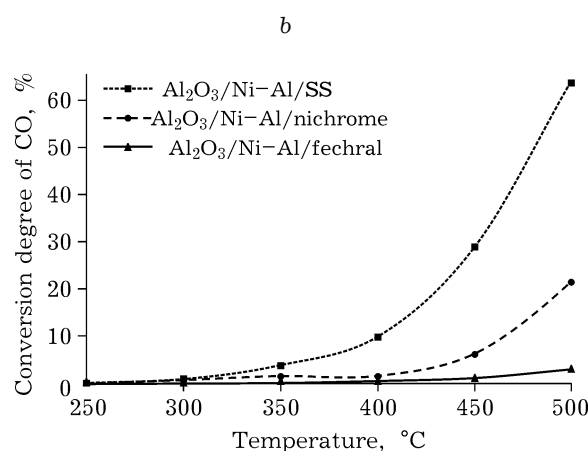
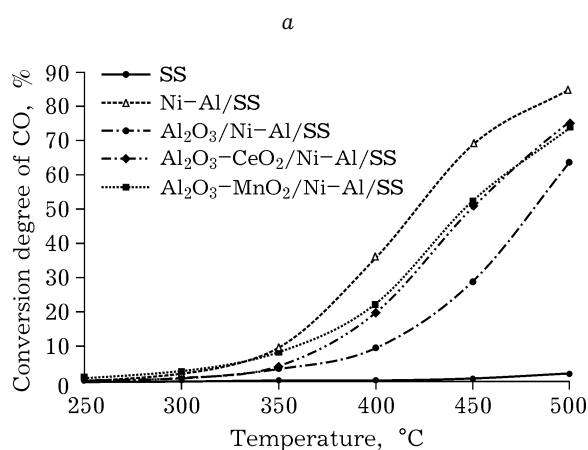


Fig. 1. Effect of the nature of the secondary oxide (a) and metal (b) carriers on the catalytic activity of the samples not activated by palladium in CO oxidation reaction.

TABLE 2

Catalytic characteristics of oxide catalysts prepared by plasma spraying on stainless steel (SS)

Catalysts	$T_{50\%}$, °C	X, %
SS	—	2
Al ₂ O ₃ /Ni-Al/SS	478	64
Al ₂ O ₃ -CeO ₂ /Ni-Al/SS	447	76
Al ₂ O ₃ -MnO ₂ /Ni-Al/SS	445	74
Ni-Al/SS	420	85

Note. $T_{50\%}$ — temperature of reaching $X = 50\%$, X — conversion degree at 500 °C.

made of stainless steel are active in CO oxidation reaction. By the half reaction temperature $T_{50\%}$, the Pd-modified catalysts make up a row: Pd/Al₂O₃/Ni-Al/SS (135 °C) > Pd/Al₂O₃-MnO₂/Ni-Al/SS (141 °C) > Pd/Ni-Al/SS (147 °C) > Pd/Al₂O₃-CeO₂/Ni-Al/SS (156 °C) > Pd/SS (164 °C). A high catalytic activity of Pd/Al₂O₃/Ni-Al/SS catalyst can be explained by the fact that the Al₂O₃ content in this sample is higher (29.2 %) than in other catalysts. According to the literature data, precisely applying Pd over Al₂O₃ yields the most active catalysts for deep oxidation.

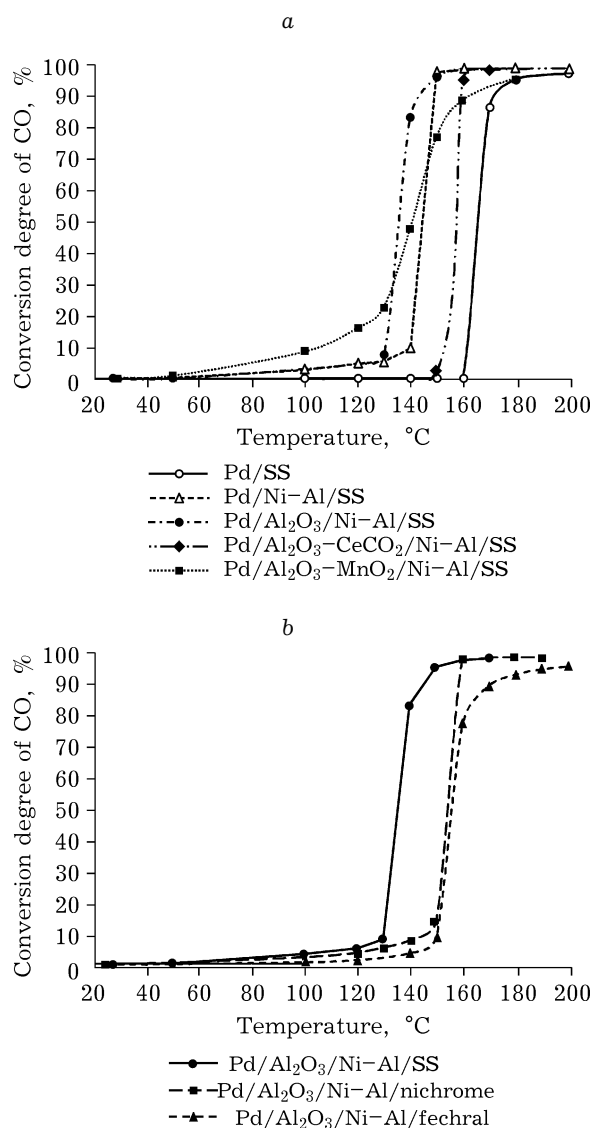


Fig. 2. Effect of the nature of the secondary oxide (a) and metal (b) carriers on the catalytic activity of the samples activated by palladium (Pd content of 0.25 %) in CO oxidation reaction.

TABLE 3

Catalytic characteristics of oxide catalysts activated by palladium (0.25 mass % Pd)

Catalysts	$T_{50\%}$, °C	X at 200 °C, %
Pd/SS	164	98
Pd/Al ₂ O ₃ /Ni-Al/SS	135	100
Pd/Al ₂ O ₃ -CeO ₂ /Ni-Al/SS	156	100
Pd/Al ₂ O ₃ -MnO ₂ /Ni-Al/SS	141	98
Pd/Ni-Al/SS	147	100

By the temperature of the half reaction $T_{50\%}$, Pd-modified catalysts, Pd/Al₂O₃/Ni-Al/metal grid make up a row in CO oxidation: Pd/Al₂O₃/Ni-Al/SS (135 °C) > Pd/Al₂O₃/Ni-Al/nichrome (152 °C) > Pd/Al₂O₃/Ni-Al/fechral (155 °C) (see Fig. 2, b).

Study of catalysts by physical methods

The data obtained by the X-phase analysis method of coatings removed from the stainless steel surface are given in Table 4.

It was demonstrated by X-ray phase analysis of powders obtained from mechanically remote oxide coating that joint mixed phases that are spinels or solid solutions of Al₂O₃-MnO₂ and Al₂O₃-CeO₂ were not detected. Nevertheless, joint plasma spraying of mixtures of oxides affects the structure of the phases that are applied and dimensions of coherent scattering regions (CSR). Thus, plasma application of individual Al₂O₃ leads to the formation on the surface of γ -Al₂O₃, alongside with corundum; moreover, the size of CSR for the latter is 17 nm. Upon applying of a mixture of Al₂O₃-CeO₂, the X-ray particle size of γ -Al₂O₃ is close to 23 nm. It should be noted that nickel or its nickel-aluminum intermetallic compounds is detected in all samples. The phases formed have a relatively small CSR size. But judging by activity, the specific surface of these phases is low, which testifies agglomeration (the formation of particle aggregations). It is interesting that a small part of Al₂O₃ in the form of γ -Al₂O₃ with a relatively small CSR size is present in catalysts obtained upon plasma application of corundum. Apparently, air injection with the formation of water vapours

TABLE 4

Phase composition and the sizes of coherent scattering regions (CSR) of the detected phases

Samples	Phase composition	CSR, nm
Pd/Al ₂ O ₃ · CeO ₂ /Ni-Al/SS	α-Al ₂ O ₃	>100
	γ-Al ₂ O ₃	23±1
	CeO ₂ cubic	90±10
	Ni cubic	36±2
Pd/Al ₂ O ₃ /Ni-Al/SS	α-Al ₂ O ₃	>100
	γ-Al ₂ O ₃	17±2
	Ni cubic	34±3
Pd/Al ₂ O ₃ · MnO ₂ /Ni-Al/SS	α-Al ₂ O ₃	>100
	γ-Al ₂ O ₃	22±1
	Ni cubic	37±1
Pd/Ni-Al/SS	Ni ₅ Al ₃ orthorhombic	27±1
	Ni cubic	20±1

capable of interacting with molten corundum and a partial formation of γ-Al₂O₃ with a small CSR size occurs in the jet of the plasma gas

(5 % H₂ in Ar). Why herewith the specific surface of the applied layer does not increase is unclear, but one can suggest that this happens

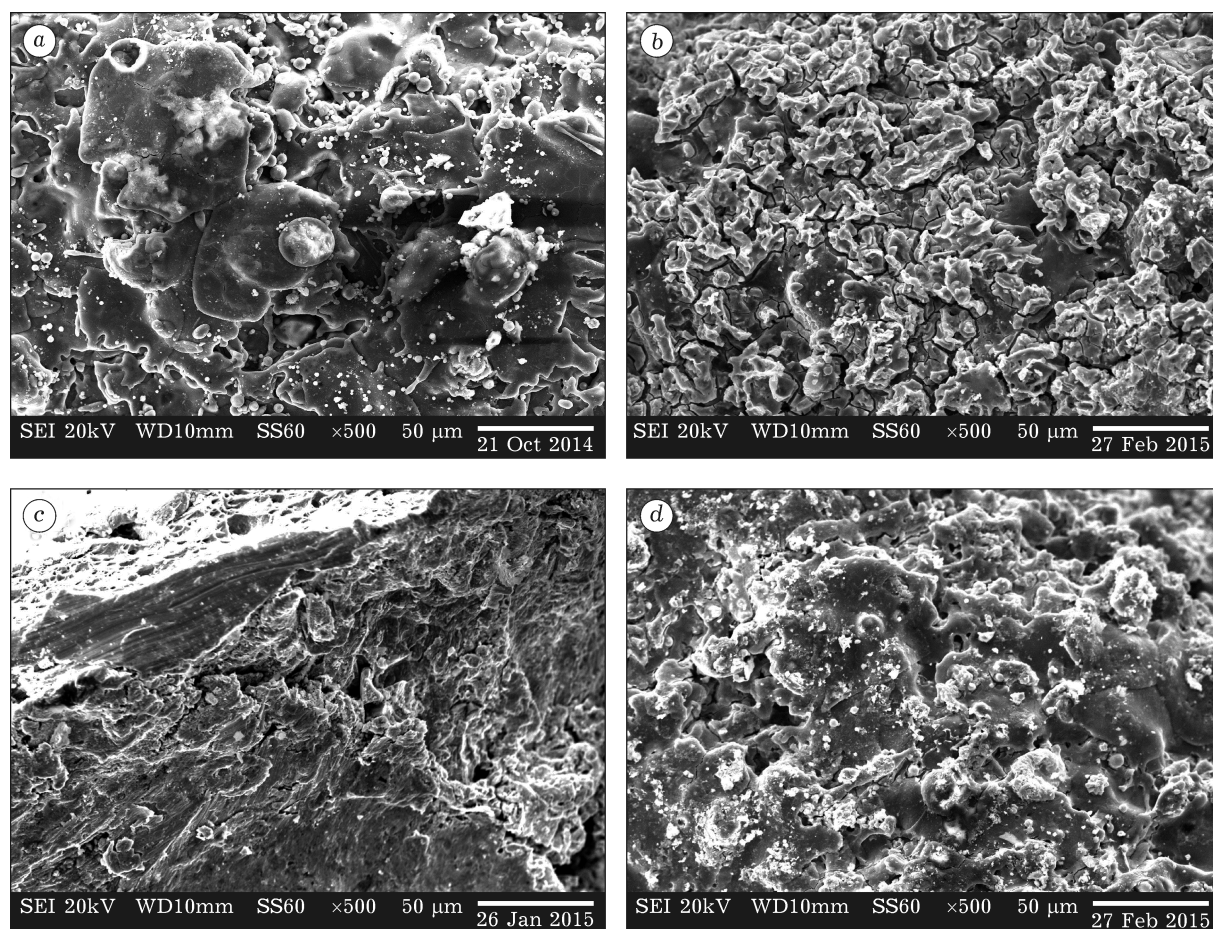


Fig. 3. Micrographs of catalysts Pd/MeO_x/Ni-Al/SS: a – Pd/Al₂O₃/Ni-Al/SS, b – Pd/Al₂O₃-MnO₂/Ni-Al/SS, c – Pd/Ni-Al/SS, d – Pd/Al₂O₃-CeO₂/Ni-Al/SS. 500× magnification.

due to particles splice (agglomeration) of primary particles of $\gamma\text{-Al}_2\text{O}_3$.

The process of grid applying of oxides is characterized by the fact that oxides particles in the plasma jet are melted and cause local submelting of the sublayer and its interaction with particles by hitting the grid elements covered by Ni–Al sublayer. Herewith, micropores with a size of several microns (roughness) are formed, but the pores of the nanoscale range disappear due to melting of the particles. As a result, if a sample of the oxide were porous, its surface abruptly drops after applying plasma. From here it follows that plasma effects on characteristics of the applied oxide are mostly determined by its nature. The availability of micropores in the applied oxides can be explained by the fact that there remain gaps between particles after the impact and the dispersion of molten particles of the surface of the sublayer or of the already applied oxide particle. Dispersion of large particles occurs, and smaller ones (1–5 μm) are formed, which is seen in images obtained using a scanning electron microscope.

Electron microscopic studies of the samples

The structure of oxide layers in Ni–Al sublayer was determined by scanning electron microscopy (SEM) methods (Fig. 3). Aluminium oxide (see Fig. 3, a) forms the most uniform coating consisting of frozen particles of Al_2O_3 melts that contains a small number of pores. Resulting from particles collision of molten Al_2O_3 with the substrate, diffuence and the formation of tapered particles with the diameters of 70–100 μm occur, with the initial particle size of 30–50 μm , as well as the formation of spherical particles with the sizes of 1–5 μm happens. A similar coating comes out upon spraying $\text{Al}_2\text{O}_3\text{--CeO}_2$ (see Fig. 3, d): ordered coatings are formed, however, there are more pores in them than in Al_2O_3 , smaller pores (1–3 μm) are present, there are significantly more particles with the sizes of 1–10 μm . The availability of many small particles and pores is apparently due to different melting points (2044 $^\circ\text{C}$ for Al_2O_3 and 2400 $^\circ\text{C}$ for CeO_2) and the possibility of transition of CeO_2 into Ce_2O_3 in the reduced plasma. The formation of cracks for $\text{Al}_2\text{O}_3\text{--MnO}_2$ coatings (see Fig. 3, b)

apparently takes place resulting from the difference in the coefficients of linear expansion (compression) when freezing of the system components. A nickel-aluminium sublayer forms fine grained coating with a small number of pores but, rough, therefore, oxide layers are well kept on it.

Elements mapping on the surface at a magnification of 10 000 times (Fig. 4) demonstrates that the location of oxygen and aluminium coincide, moreover, the ratio of these elements is close to that in Al_2O_3 . The palladium concentration (4 %) in the investigated fragment far exceeds its average concentration in the catalyst, which is clear, since EMF analysis correlates the palladium concentration only to a specific fragment of the surface layer, not to the entire mass of the catalyst.

Spherical Al_2O_3 particles are observed on the sample surface. Spherical particles with the sizes of 1–3 μm are formed during the impact of Al_2O_3 melts with the surface of the Ni–Al sublayer. The sphere surface is rough and the most defective at the periphery. Palladium is concentrated precisely in there, additionally, in the

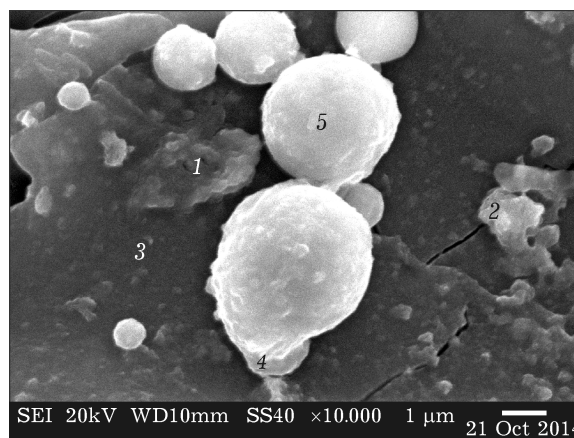


Fig. 4. Local composition of Pd/ Al_2O_3 /Ni–Al alloy sample. 10 000 $\times$ magnification.

Local microanalysis of the composition of the surface of Pd/ Al_2O_3 /Ni–Al alloy catalyst, %

	O	Al	Ni	Pd
1	41	35	3	21
2	30	42	5	23
3	47	52	–	1
4	45	50	–	5
5	47	51	–	2

areas with oxidized Ni–Al alloy. Thus, the amount of oxygen determined in point 1 (see Fig. 4) is more than enough for the availability of Al_2O_3 and NiO and PdO oxides in this area. Calculations of the ratios of oxygen and metal in point 2 lead to the conclusion that the oxygen available in this area is not enough even for complete oxidation of the available aluminium, *i. e.* there are aluminium oxide, nickel-aluminium alloys, zero-valent nickel and zero-valent palladium in this point. Aluminium oxide and 1 % palladium form the basis in point 3.

CONCLUSION

Catalysts not activated by palladium make up a row by the conversion degree of CO at 500 °C: Ni–Al (85 %) > Al_2O_3 – CeO_2 (76 %) > Al_2O_3 – MnO_2 (74 %) > Al_2O_3 (64 %) > SS (2 %).

Palladium activated samples make up the activity row by $T_{50\%}$: Pd/ Al_2O_3 /Ni–Al/SS (135 °C) > Pd/ Al_2O_3 – MnO_2 /Ni–Al/SS (141 °C) > Pd/Ni–Al/SS (147 °C) > Pd/ Al_2O_3 – CeO_2 /Ni–Al/SS (156 °C) > Pd/SS (164 °C).

According to XPA, all samples have components that were found in the initial powders. Joint Al_2O_3 – MnO_2 and Al_2O_3 – CeO_2 phases were not detected, but nickel-aluminum intermetallic phases were found.

Since the systems obtained by plasma applications are quite complex, it is difficult to explain the facts obtained. Apparently, many reasons affect phase transformations: differences in the phase and fractional composition of powders initial for application, flow rate of the plasma-forming gas and its composition, interaction with the sublayer. In any case, it can be seen that by varying influencing factors on the system, one may change coating properties, including catalytic.

The data obtained allow concluding that by developing the surface, primarily of the sublayer using chemical methods (for example, by leaching) or by changing the powder composi-

tion before plasma spray, one can substantially increase the catalyst activity in CO oxidation reactions and deep oxidation of hydrocarbons.

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