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Effect of rare-earth element oxides (La_2O_3, Ce_2O_3) on the structural and physico-chemical characteristics of Pd/Al_2O_3 monolithic catalysts of nitrogen oxide reduction by methane

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Abstract

It is shown that introduction of additives of rare-earth element oxides (La_2O_3, CeO_2) enables regulating the structural and functional characteristics of Pd/Al_2O_3-catalysts (applied on ceramic monoliths of honeycomb structure) of nitrogen oxide reduction by methane. Modifying additives provide increase of thermal stability of porous structure of both highly dispersed Al_2O_3, as the second support, and the catalyst as a whole.

Contribution of La_2O_3 and CeO_2 in increasing the thermal stability is of an additive nature, and lanthanum oxide shows the higher efficiency than cerium one. According to X-ray phase analysis data, stabilizing action is conditioned by occurrence of rare-earth element oxides into lattice of Al_2O_3, which retards diffusional processes leading to phase transitions of low-temperature crystalline modifications of alumina into high-temperature ones with a low specific surface. For the catalyst samples modified with La_2O_3 an effect of thermal activation is observed, which is revealed by increase in catalytic activity as a result of annealing at 850 °C. Such a phenomenon, as shown by means of X-ray photoelectron spectroscopy technique, can be explained via stabilization of palladium in singly charged state in the form of groups of $Pd^+O_2^-$ and corresponding increase in concentration of active centers.

Keywords: Cordierite; Second support; Aluminium oxides; Rare-earth element oxides (La_2O_3; Ce_2O_3); Palladium; Reduction of NO; Methane; Structure

1. Introduction

Removal of nitrogen oxides from industrial and automotive exhaust gases belongs to the main tasks of environment protection. One of the ways of solving this problem is reduction of NO_x by lower alkanes. Use of methane as reducing agent is of a considerable interest since it is cheap and well spread feedstock.

Reaction $NO + CH_4$ in the oxygen-free medium is used at decontamination of exhaust gases of automobiles working on methane [1] as well as gas emissions of factories producing nitric acid [2]. Concerning this reaction in focus are granulated catalysts based on transition metal oxides [3] and ion-exchanged zeolites [4], among which beyond comparison are those containing precious metals due to their high efficiency and activity, chemical and thermal stability, resistance to catalytic poisons [3,5,6].

Reduction of nitrogen monoxide by methane, like most of processes for purification of gas exhausts, proceeds, as a rule, in the external diffusion or the external transition mode. Therefore, an optimum design of catalysts for such processes are ceramic monoliths of honeycomb structure, in which the active component is applied on the external surface of support and, thus, is completely accessible for the catalytic reaction to proceed. Due to the small thickness of walls of a monolithic framework the efficiency of applied component is increased, which enables to reach a higher efficiency in catalyst work and considerably reduce the consumption of expensive active component.

At present, synthetic or natural alumosilicate-cordierite [1,7], with a low specific surface, not exceeding 0.2–0.4 m^2/g, are most frequently used in order to form honeycomb structure. Increase in the specific surface of such materials is usually achieved by the application of second support – Al_2O_3, MgO, ZrO_2 and other thermostable oxides – on the original

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monolithic matrix [1]. Aluminium oxides of certain crystalline modifications (having a sufficient specific surface, chemical and thermal stability) are most often used as the second support for gas purification catalysts.

In order to prevent sintering and transition of low-temperature forms of alumina into high-temperature ones with a low specific surface a chemical modification of second support with rare-earth element oxides (REEO: CeO_2, La_2O_3, Y_2O_3, Nb_2O_3, etc.) is used in many cases [8–11]. At the same time, there is no common point of view concerning mechanism of the action of these modifying additives. Most often, increase in thermal stability, as a result of modifying, is attributed to formation of mixed surface phases (such as $LaAlO_3$), which protect the bottom layers of the second support against transformations.

It is known also, that introduction of some rare-earth element oxides enables controlling the properties of low-percent catalysts based on platinum group metals. The most detailed studied is an effect of the REEO upon the properties of platinum in catalysts of deep oxidation of alkanes [12]. Introduction of cerium oxide into the structure of alumo-platinum catalyst was found to stabilize platinum in an oxidized state, probably as $PtO_xMe_nO_m$ [13], and as a result, to increase dispersion of applied platinum and thermal stability of the catalyst. Atomic catalytic activity of platinum oxidized sites (Pt^{n+}) for the deep oxidation reactions is lower than that of Pt^0 [14], but due to augmentation of total number of active sites an increase in specific catalytic activity is reached, which is not affected by overheatings [15].

Increased activity of palladium-containing catalysts, modified with lanthanum and cerium oxides, concerning red-ox reactions is noted in [16]. Promoting action of cerium dioxide in such catalysts is usually attributed to high oxygen storage capacity (OSC) of CeO_2 [17]. Due to interactions between lanthanum oxide and palladium the high catalytic activity of $Pd–La_2O_3/Al_2O_3$ composites in three-way conversion reactions ($CO/NO_x/C_nH_m$) is kept even after annealing at 1000 °C despite substantial decrease in a specific surface [18].

However, the rare-earth element oxides can also cause an inhibitory effect on activity of palladium-containing catalysts. It was found in [19] that introduction of cations of Ce^{4+} into composition of alumo-palladium catalyst leads to substantial decrease in its activity for carbon monoxide oxidation by oxygen (from air), though at the same time an enhancement of thermal stability of catalyst was proposed to took place due to interactions between cerium dioxide and palladium.

In this work studied is an effect of lanthanum and cerium oxides on structural characteristics and physico-chemical properties of alumo-palladium catalysts of high-temperature reduction of nitrogen oxide by methane with the purpose of finding out a way of regulating their activity and thermal stability.

2. Experimental

In this work, ceramic monoliths of honeycomb structure were used as a framework of catalysts. These blocks, made of synthetic cordierite ($2Al_2O_3 \cdot 2MgO \cdot 5SiO_2$), have the following characteristics: value of linear expansion thermal coefficient 1.0×10^{-6} deg^{-1}, wall thickness 0.2 mm, size of cells 1.2 mm × 1.2 mm, open porosity 43–48%, predominant size of pores 1–3 μm. Said material of the framework provides a long-term work in the mode of thermocycling, which becomes apparent in resistance to destruction under the action of thermal shock.

To form the layer of aluminium oxide as a second support on the original monolith surface (or to synthesize Al_2O_3 as pure phase) aqueous solutions of nitrate and oxynitrate of aluminium $Al(NO_3)_3 \cdot 9H_2O$, $Al(OH)_2NO_3 \cdot H_2O$ and their corresponding mixtures at various ratios of the components as well as colloidal solutions of aluminium salt mixtures (prepared as a result of addition of ammonia buffer solution) were used. $Al(NO_3)_3 \cdot 9H_2O$ was of industrial manufacturing whereas $Al(OH)_2NO_3 \cdot H_2O$ was synthesized by us according to [20]. Compositions of precursors are presented in Table 1.

In order to modify Al_2O_3 with REEO (La_2O_3, CeO_2) corresponding nitrates of rare-earth elements ($La(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$) were added to the impregnating solution.

The application procedure was carried out via impregnation of monoliths by aqueous solutions of corresponding salts followed by drying in air at 150–200 °C and calcination at 550 °C (to form phases of interest of applied components on the monolithic surface). In some cases the second support was formed as a MgO phase (solutions of $Mg(CH_3COOH)_2$ were used).

Catalyst samples were prepared by a successive application of second support – γ-Al_2O_3 or MgO – with/without modifying additives of rare-earth element oxides and active component – palladium – onto the original ceramic monolith.

Palladium was applied by the impregnation procedure using the palladium nitrate solution at a concentration (per Pd) of 0.5 g/ml followed by drying at 120–200 °C and calcinating in air at 550 °C. The palladium content in prepared catalyst samples was of 0.4 wt.%.

The phase composition was studied by the method of X-ray diffractometry (DRON-3M) in monochromatized Cu Kα radiation using curved graphite monochromator on diffracted beam. Shootings were taken in the mode of a step scanning in the range of angles 10–80° 2θ, and also with recording the diffraction curves on the band. The apparent size of aluminium

Table 1
Effect of precursors on the specific surface of Al_2O_3

No. of sample	Original precursors	Concentration of ammonia (mol/l)	Specific surface of Al_2O_3 (m^2/g)
1	$Al(OH)_2NO_3 \cdot H_2O$	0	24
2	$Al(NO_3)_3 \cdot 9H_2O$	0	55
3	$Al(NO_3)_3 \cdot 9H_2O$, $Al(OH)_2NO_3 \cdot H_2O$	0	103
4	$Al(NO_3)_3 \cdot 9H_2O$, $Al(OH)_2NO_3 \cdot H_2O$	0.6	121
5	$Al(NO_3)_3 \cdot 9H_2O$, $Al(OH)_2NO_3 \cdot H_2O$	1.3	153
6	$Al(NO_3)_3 \cdot 9H_2O$, $Al(OH)_2NO_3 \cdot H_2O$	2.4	179

The samples are calcinated at 550 °C.

oxide crystals was calculated by the Sherrer formula, $L = k\lambda/B\cos\theta$.

X-ray photoelectron spectra were recorded using Kratos Analitical SERIES 800 XPS X-ray photoelectron spectrometer with Mg Kα (1253.6 eV) radiation. Prior to registration of spectra catalyst samples were applied onto polymeric band. Error in measurement of electron bonding energy did not exceed 0.1 eV.

The specific surface was determined by the method of heat desorption of argon with gas chromatography control.

The total acidity of catalyst samples surface was measured using thermally programmed desorption of ammonia (TPDA) technique.

The catalytic activity measurements were carried out at volume flow of 80 cm^3/min, space velocity GHSV of 20,000 h^{-1} using monolith fragment with a diameter of 7–8 mm, height of 6–7 mm and weight of 0.3 g. Concentrations of reactants were CH_4—1.0 vol.%; NO—4.0 vol.%.

The catalytic activities in the reaction $CH_4 + NO$ were evaluated by a conversion of methane. CO_2, N_2 and H_2O were primarily detected as products. In the temperature range, corresponding to 30–70% of NO conversion, nitrous oxide (N_2O) was produced as well. Maximum concentration of N_2O reached 30% of NO amount consumed in the course of reaction. N_2O selectivity did not depend upon catalyst composition and was dependent on run's temperature only. At 70% of NO conversion and beyond N_2 was the only nitrogen-containing product.

3. Results and discussion

The major components, used to form the layer of the second support in the form of an aluminium oxide on the surface of ceramic monoliths, are aluminium nitrates of various compositions. As shown from Table 1, surface area of Al_2O_3 depends substantially on precursor composition. Aluminium oxide samples prepared from either $Al(NO_3)_3{\cdot}9H_2O$ or $Al(OH)_2NO_3{\cdot}H_2O$ have the lowest surface areas. Aluminium oxide with considerably extended surface is formed when a mixture of salts mentioned was used in the course of synthesis. Increase in concentration of ammonia buffer (NH_4OH) in the solution of salt mixture also results in the increase of Al_2O_3 surface area. When preparing catalyst samples, buffer solution ($Al(NO_3)_3{\cdot}9H_2O$:$Al(OH)_2NO_3{\cdot}H_2O$ = 1:2) at concentration of ammonia 2.4 mmol/l, providing the most extended surface area (Table 1, sample No. 6), was used. Noteworthy is that such a colloidal solution has a good adhesion towards ceramic block matrices.

Here presented are the results of studies of thermal stability and structural characteristics of alumina samples, synthesized according to procedure mentioned above, as well as those, modified with rare-earth element oxides (La_2O_3, CeO_2).

As shown from Table 2, thermal stability of non-modified Al_2O_3 (sample No. 1) is limited by the temperature of 850 °C. At higher temperatures a drastic decrease in surface area is observed, which is attributed to the transition of alumina into crystalline modifications with lower specific surface. Modification of aluminium oxide with REEO in the course of preparation of second support in some cases results in decrease in the specific surface (sample Nos. 3–6) as compared to non-modified alumina (sample No. 1). However, after raising the temperature of annealing from 550 to 700 °C an increase in specific surface for these samples (Nos. 3–6) is observed followed by decrease when further heating (above 700 °C). The most distinct is thermo-stabilizing effect at 1000 °C: surface areas of modified with REEO samples (Nos. 2–6) as compared to pure aluminium oxide are much higher. For instance, specific surface of pure alumina (sample No. 1) decreases from 176 to 10 m^2/g (by more than 17 times) as a result of raising the temperature of annealing from 550 to 1000 °C, whereas surface area of sample modified with La_2O_3 (No. 2) decreases from 176 to 86 m^2/g (by two-fold only).

Table 2
Effect of modifying additives of rare-earth element oxides (CeO_2, La_2O_3) on the thermal stability of Al_2O_3

No. of the sample	Content of modifying additives (wt.%)		Specific surface (m^2/g) after annealing at various temperatures			
	CeO_2	La_2O_3	550 °C	700 °C	850 °C	1000 °C
1	0	0	176	167	142	10
2	0	2.0	176	153	142	86
3	0	5.0	132	144	112	62
4	5.0	0	166	180	130	20
5	5.0	2.5	124	160	124	69
6	2.5	5.0	142	149	112	56

When analyzing data of the Table 2, it can be concluded that lanthanum oxide enhances the thermal stability of low-temperature crystalline modifications of alumina more strongly than cerium dioxide. Noteworthy is that simultaneous introduction of cerium and lanthanum oxides does not result in the synergistic effect: the thermal stability of mixed systems ($La_2O_3 + CeO_2$)/Al_2O_3 (Nos. 5 and 6) does not exceed the thermal stability of La_2O_3/Al_2O_3 (No. 2).

Structural characteristics of alumina samples – non-modified and modified with REEO – calcinated at various temperatures are illustrated by X-ray diffractograms in Figs. 1 and 2.

Fig. 1 presents X-ray diffractograms of non-modified Al_2O_3 samples calcinated at various temperatures. Character of curve 1 gives the basis to conclude that aluminium oxide, prepared at 550 °C, is X-ray amorphous with particle sizes of less than 2 nm (though according to [21] 550 °C—the temperature of forming the phase of γ-Al_2O_3). Such a predominance of amorphous state can be explained by a presence of nitrate-anions stabilizing this structure in the samples [11]. Formation of the crystalline structure, as follows from curves 2–4 in Fig. 1, takes place at higher temperatures, which can be attributed to a complete withdrawal of nitrate-anions. In the diffractogram of the sample, calcinated at 700 °C (curve 2), there are wide diffraction maximums, for which parameter 2θ corresponds to 20°, 37°, 44° and 68°. Evaluation of grain size for the half-width of diffraction maximum at 68° gives a value of $L \approx 2$ nm. With an increase of temperature of annealing to 800 °C (curve 3), the width of diffraction maximums decreases, maximums themselves are

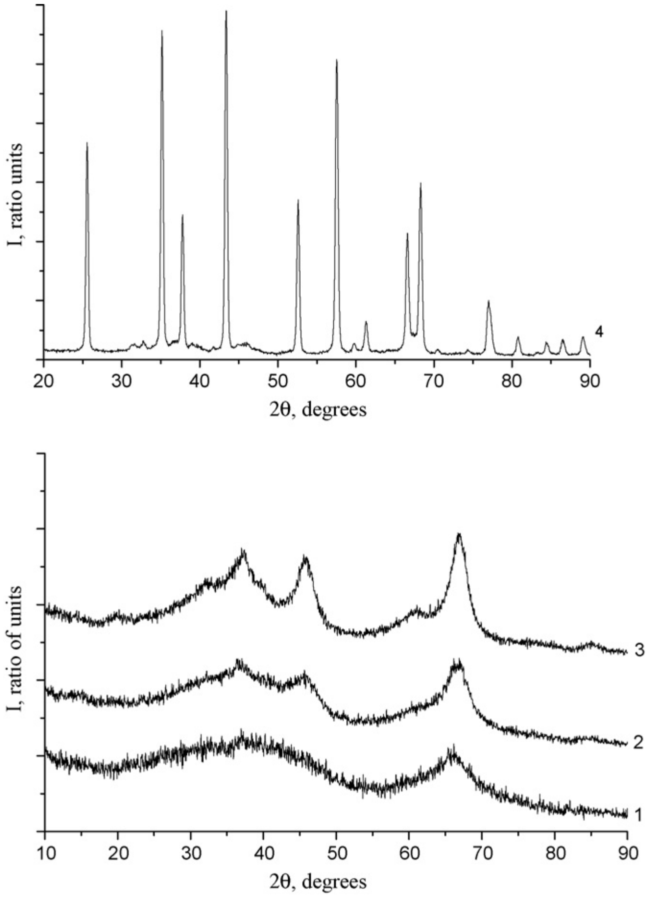

Fig. 1. X-ray diffractograms of the sample Al_2O_3 calcinated at temperatures: (1) 550 °C; (2) 700 °C; (3) 850 °C; (4) 1000 °C.

disintegrated and revealed are the reflexes pertaining to γ-Al_2O_3 ($2\theta = 19.32°$, 37.50°, 39.50°, 42.50°, 45.50°, 61.0° and 67.5°). Decrease of diffraction curve width corresponds to growth of grain size of Al_2O_3 to the value of $L \approx 4$ nm. At temperature of annealing of 800 °C a corundum is formed which can be ascertained by revealing of corresponding reflexes pertaining to $2\theta = 25.5°$, 35.1°, 37.8°, 43.3°, 52.6°, 57.5°, 59.7°, 61.2°, 66.5° and 68.3°.

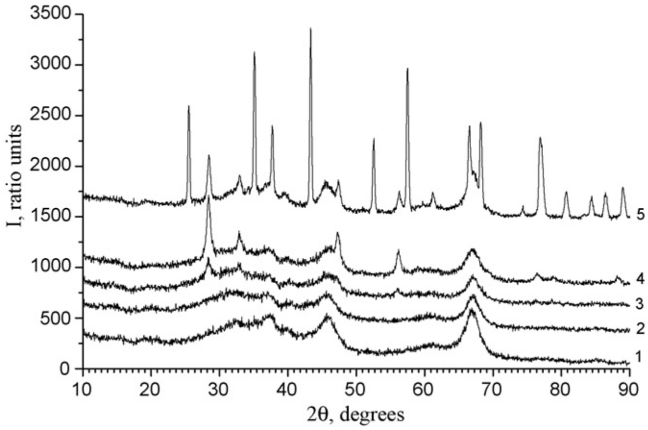

Fig. 2. X-ray diffractograms of the samples of second support modified with rare-earth element oxides after annealing at 1000 °C: (1) Al_2O_3/2% La_2O_3; (2) Al_2O_3/5% La_2O_3; (3) Al_2O_3/(5% La_2O_3 + 2.5% CeO_2); (4) Al_2O_3/(2.5% La_2O_3 + 5% CeO_2); (5) Al_2O_3/5% CeO_2.

The samples modified with lanthanum and cerium oxides were found to be X-ray amorphous after annealing at 550, 700 and 850 °C. Only weak broad halos at double angles with centers at 28.6° and 38.5° as well as broad weak reflex at 65.9°, conforming to structural motive of γ-Al_2O_3, were observed in corresponding diffractograms—similar to that one (and therefore not presented here) for non-modified aluminium oxide (Fig. 1, curve 1).

The most apparent is the crystallization of components, composing systems studied, at 1000 °C (Fig. 2). For example, diffractogram, corresponding to lanthanum-containing sample after annealing at 1000 °C (Fig. 2, curve 1), is similar to that one for non-modified (850 °C) highly dispersed phase of γ-Al_2O_3 (Fig. 1, curve 3). Increase in content of La_2O_3 from 2% (Fig. 2, curve 1) to 5% (Fig. 2, curve 2) results in decrease in intensity of characteristic bands of γ-Al_2O_3. For the samples, modified with mixture of REEO (Table 2, Nos. 5 and 6), reflexes, typical for CeO_2, are revealed ($2\theta = 28.4°$, 32.8°, 47.4°, 56.2°, 76.5°, 78.9° and 88.4°) in addition to the background of aluminium oxide spectrum (as shown from diffractograms 3 and 4, Fig. 2).

Annealing the samples of CeO_2/Al_2O_3 at 1000 °C results in formation of cerium oxide phase simultaneously with transition of fraction of γ-Al_2O_3 into corundum α-Al_2O_3 (as was observed for non-modified alumina), which explains the lower value of specific surface of cerium-containing sample (Table 2, No. 4) as compared to La_2O_3/Al_2O_3 after annealing at 1000 °C (Table 2, Nos. 2 and 3).

Therefore, introduction of either lanthanum oxide alone or together with cerium oxide retards transition of low-temperature γ-Al_2O_3 into high temperature α-Al_2O_3, thus stabilizing porous structure of second support. Similarity of diffractograms of pure alumina sample (Fig. 1) and those modified with lanthanum oxide (Fig. 2) gives the basis for the conclusion that stabilizing action of La_2O_3 is conditioned by occurrence thereof into Al_2O_3 lattice which retards diffusional processes leading to phase transitions.

In order to assess the effects of nature and content of second support on catalytic activity, catalyst samples, which are substantially different concerning acid–base properties, containing the same loadings of an active component (0.4 wt.% Pd) and different loadings of second support (Al_2O_3 or MgO), were prepared. Catalytic activities of the samples prepared were characterized by temperature of 50% of CH_4 conversion. As for the non-modified sample, an extreme dependence of activity on the second support content is observed (Fig. 3, curve 1). With an increase in Al_2O_3 content from 0 to 1.6% a decrease in reaction temperature by 60 °C takes place. However, further increase in alumina content leads to monotonous increase in temperature of 50% of CH_4 conversion in CH_4 + NO reaction, and at concentrations of 9.7% and above an effect of second support is leveled, though specific surface of catalyst increases monotonously from 0.4 to 24 m^2/g.

Such an effect of second support on activity of palladium catalysts can be attributed to surface acidic properties. It was found, by means of TPDA technique, that increase in Al_2O_3

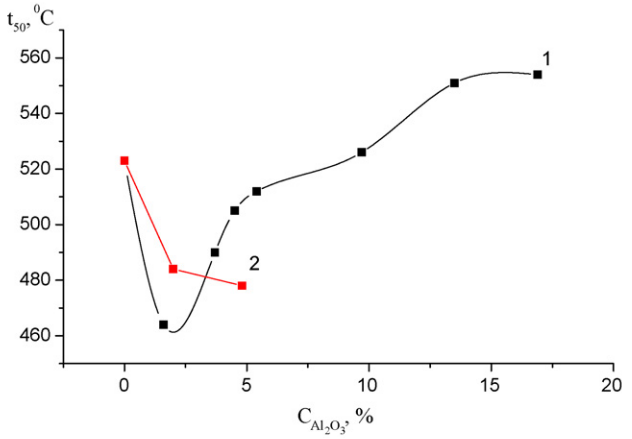

Fig. 3. Dependence of temperature of 50% conversion of CH_4 in the reaction of $CH_4 + NO$ on the content of second support: (1) Al_2O_3; (2) MgO.

content results in an increase in concentration of acid sites (to 0.24 mmol/g). An increased acidity of surface can contribute to the increase in bonding strength of carbon-containing structures [22] – products of CH_4 interaction with the surface of metal catalysts – and, as consequence, decrease in methane oxidative conversion rate [23,24]. To confirm this, the given is in Fig. 3 (curve 2) relationship between catalyst activity and content of the second support not having surface acidity—magnesium oxide: growth of content of MgO in the catalyst composition is steadily accompanied with the increase of its activity for the reaction ($CH_4 + NO$).

Experimental findings, mentioned above, indicate that there is a specific favorable (concerning catalytic activity) range of contents of Al_2O_3 as a second support for alumo-palladium catalysts of nitrogen oxide reduction by methane. Further, the content of the second support in catalyst samples was 1.6 wt.%.

Fig. 4 shows experimental relationships allowing to evaluate an effect of REEO on activity and thermal stability of the samples of alumo-palladium catalysts in nitrogen oxide reduction with methane.

Increase in temperature of preliminary annealing of the catalyst, not containing REEO, from 550 to 850 °C results in a shift of relationships of $x = f(t)$ to higher temperatures (Fig. 4a). Further increase of temperature of annealing results in a sharp decrease of activity: a complete conversion of methane over catalyst sample, calcinated at 1000 °C, is not achieved. Such a phenomenon is obviously explained by decrease of surface area due to the transition of highly dispersed Al_2O_3 into crystalline modifications with lower specific surface, as was shown above.

Comparing dependencies given in Fig. 4, we can see that introducing the REEO in alumo-palladium catalyst results in some decrease of activity, which is revealed by rising of temperature of 50% conversion by 10–30 °C. On the other hand, modified catalysts are more thermally stable: raise in temperature of annealing from 550 to 1000 °C for non-modified sample is accompanied by an increase in reaching the temperature of 50% conversion of methane by 122 °C ($\Delta t = 122$ °C) whereas for the catalysts modified with REEO $\Delta t = 38$ °C–45 °C. Moreover, for the catalyst samples modified

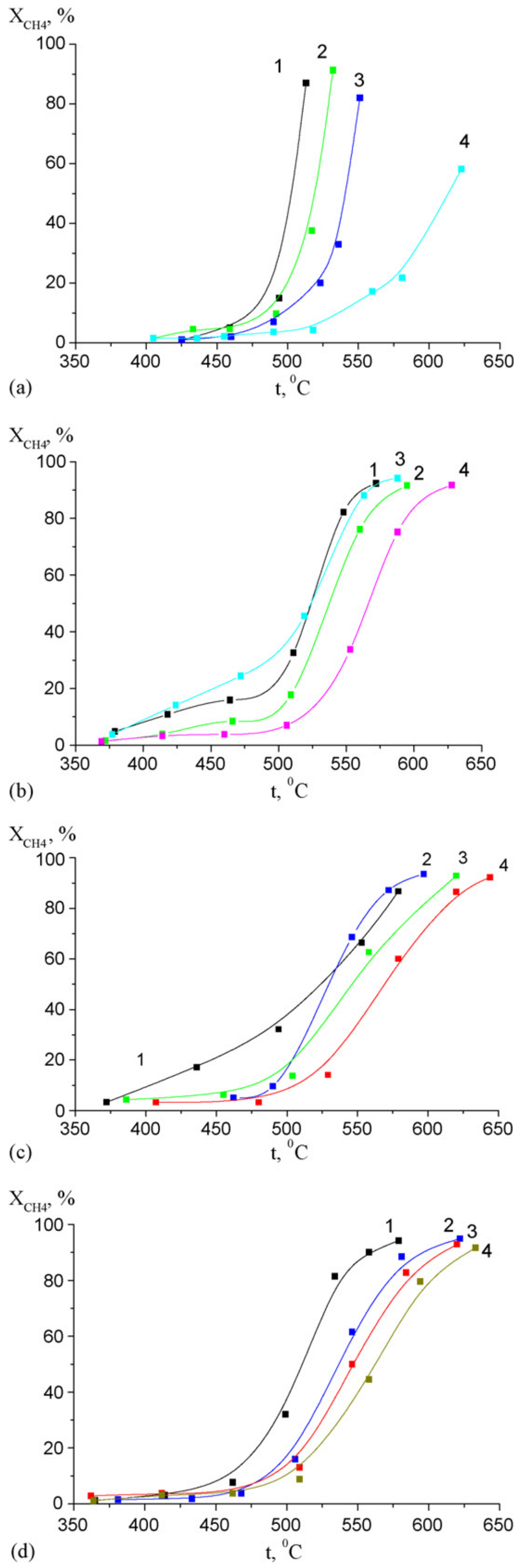

Fig. 4. Temperature dependences of methane conversion by nitrogen monoxide over the non-modified (a) and modified with 5% La_2O_3 (b), 5% CeO_2 (c), 2.5% CeO_2 and 2.5% La_2O_3 (d) alumo-palladium catalysts calcinated at: (1) 550 °C; (2) 700 °C; (3) 850 °C; (4) 1000 °C.

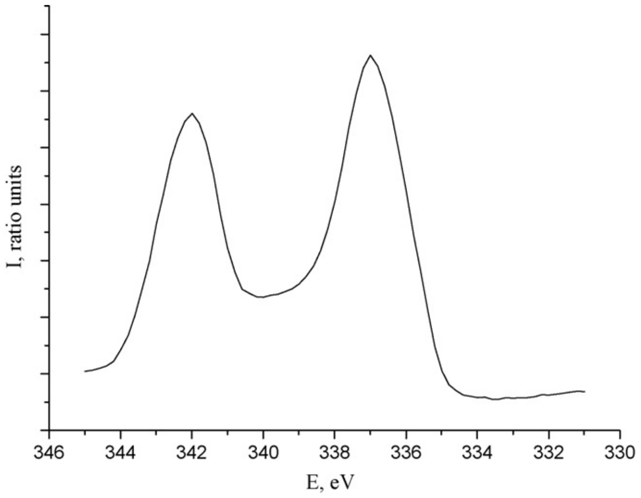

Fig. 5. XPS-spectrum of Pd_{3d} electrons in alumo-palladium catalyst (sample No. 1, Table 3).

with La_2O_3 an effect of thermal activation was observed. This effect (Fig. 4b, curves 2 and 3) is revealed by an increase in catalyst activity as a result of raising the temperature of annealing from 700 to 850 °C ($\Delta t = -14$ °C).

Fig. 5 shows XPS spectrum, typical for all studied catalyst samples, characterizing valency state of palladium. Shape of this spectrum – doublet $3d_{5/2}$ and $3d_{3/2}$ – gives a basis for the conclusion that each of the samples studied is characterized by the presence of palladium of only one valency state.

Table 3 summarizes X-ray photoelectron spectroscopy data concerning catalysts studied. The valency state of palladium, as we can see, changes depending on conditions of preparation and treatment of catalysts.

In the freshly prepared catalyst (sample No. 1) palladium is in the oxidized form, its valency state is close to Pd^{4+} (PdO_2) [25]. After catalysis run under conditions of complete conversion of reagents (sample No. 2) reduction of catalyst sample takes place. The valency state of palladium in the sample after catalysis run is characterized by a little degree of oxidizing and is close to metal state, and bonding energy $3d_{5/2}$ of electrons is in total by 0.3 eV different as compared to bonding energy in metal palladium (335.0 eV). Such a difference may be attributed to agglomerated form of metallic palladium (Pd^0). An initial increase in catalyst activity in running time (as was observed) may be taken as an argument in favor of reduction of palladium oxide by reaction gas mixture. This conclusion agrees with the data concerning higher atomic catalytic activity of Pd^0 as compared to Pd^{n+} [26].

The value of bonding energy $3d_{5/2}$ of palladium electrons in catalyst modified by lanthanum oxide (sample No. 3) conforms to the degree of oxidation of Pd^{2+} (PdO) [25]. Probably, the lower activity of given catalyst, as compared to non-modified one, is conditioned by difficulties in its reduction in the course of catalytic process.

The valent state of palladium in the sample No. 4, modified by lanthanum oxide and calcinated at 850 °C, can be referred to the state of Pd^{1+}—intermediate between Pd^{2+} and Pd^0. This assumption follows from the form of XPS spectrum, representing a well revealed doublet of $3d_{5/2}$ and $3d_{3/2}$ of electron states of palladium, and agrees with the data of the paper [26] concerning an assumption of formation of complex compounds of cerium and palladium oxides, in which palladium is stabilized in singly charged state in the form of groups of $Pd^+O_2^-$. In sample Nos. 5 and 6 palladium is also mostly in the metallic state (Pd^0).

Proposed assignment allows to explain an effect of thermal activation, observed for La_2O_3-containing catalyst, and an absence thereof for the sample, modified with CeO_2, in which the palladium ions due to low red-ox potential of cerium oxide more easily transforms into metal state (see Table 3). It seems obvious that stabilization of palladium in state of Pd^{1+}, due to electrostatic forces of mutual repulsion between particles charged of the same kind, results in atomic dispersion of an active component, whereas metal palladium (Pd^0) particles tend to aggregate. Though atomic catalytic activity of Pd^{n+} can be lower than that one for Pd^0 (similarly to platinum catalysts [14]), specific catalyst activity increases because of increase in concentration of active sites due to dispersion of an active component.

4. Conclusions

It is shown that characteristics of porous structure of a layer of highly dispersed Al_2O_3 (as a second support of alumo-palladium catalyst) applied on a surface of ceramic monoliths of honeycomb structure, are dependent on the composition of precursors—aluminium nitrates. The samples prepared from a buffer solution, containing $Al(NO_3)_3 \cdot 9H_2O$ and $Al(OH)_2NO_3 \cdot H_2O$ at a weight ratio of salts of 1:2,

Table 3
XPS data concerning catalyst samples

No. of the sample[a]	Content of REEO in Al_2O_3 (wt.%)		Temperature of annealing (°C)	Energy of bonding of electrons (eV) for element electron states			
	CeO_2	La_2O_3		Pd $3d_{5/2}$	O 1s	Si 2p	Al 2p
1	0	0	550	337.0	532.2	102.4	74.5
2	0	0	550	335.3	531.9	102.6	74.2
3	0	0.15	550	336.1	531.9	102.6	74.1
4	0	0.15	850	335.8	531.9	102.5	74.0
5	0.15	0	550	335.0	532.1	102.7	74.1
6	0.15	0	850	335.0	531.8	102.4	74.0

[a] 1: freshly prepared sample; 2–6: after catalysis run.

respectively, have the most extended specific surface. Increase of concentration of the ammonia buffer from 0 up to 2.4 mol/l results in an increase in specific surface of Al_2O_3.

Thermal stability of the porous structure of Al_2O_3, synthesized using mentioned above procedure, is limited by 850 °C. At the further heating, the specific surface of an alumina coating is sharply reduced. Modifying of the second support with rare-earth element oxides (La_2O_3, CeO_2) enhances its thermal stability. Contribution of La_2O_3 and CeO_2 is of an additive nature, and lanthanum oxide shows the higher efficiency than cerium dioxide. According to X-ray phase analysis data, stabilizing action of La_2O_3 is conditioned by occurrence thereof into lattice of Al_2O_3, which retards the diffusional processes leading to phase transitions of γ-Al_2O_3 into α-Al_2O_3 with low specific surface.

Dependence of activity of alumo-palladium catalyst on content of second support in nitrogen oxide reduction with methane is found to be of extreme kind. Maximum of activity was observed for catalyst sample with 1.6 wt.% of Al_2O_3. Increase in Al_2O_3 content above an optimal value results in a decrease in catalytic activity which is attributed to an increase in surface acidity.

Catalytic activity of said catalysts decreases somewhat after modification with rare-earth element oxides, whereas REEO enhance their thermal stability.

For the catalyst samples modified with La_2O_3 an effect of thermal activation is observed, which is revealed by increase in catalytic activity as a result of annealing at 850 °C. Such a phenomenon, as shown by means of X-ray photoelectron spectroscopy technique, can be explained via stabilization of palladium in singly charged state in the form of groups of $Pd^+O_2^-$ and corresponding increase in concentration of active centers.

References

[1] J. Kašpar, P. Fornasiero, N. Hickey, Catal. Today 77 (2003) 419–449.

[2] S.O. Soloviev, Ya.P. Kurylets, B.D. Zhygailo, et al. Khimicheskaya Promyshlennost (Russian Chemical Industry) 4 (2002) 48–52.

[3] M. Iwamoto, Stud. Surf. Sci. Catal. 130 (2000) 23–48.

[4] M.D. Fokema, J.Y. Ying, Catal. Rev. 42 (2001) 1–29.

[5] M.W. Kumthekar, U.S. Ozkan, J. Catal. 171 (1997) 45–54.

[6] M. Rashidzadeh, M.H. Peyrovi, R. Mondegarian, React. Kinet. Catal. Lett. 69 (2000) 115–122.

[7] R.J. Farrauto, R.M. Heck, Kinet. Catal. 39 (1998) 646–652.

[8] D.L. Trimm, Appl. Catal. 7 (1983) 249–282.

[9] M.F.M. Zwinkels, S.J. Jaras, P.J. Menon, T.A. Griffin, Catal. Rev. -Sci. Eng. 35 (1993) 319–325.

[10] H. Arai, H. Fukuzava, Catal. Today 26 (1995) 217–221.

[11] E.M. Moroz, J. Appl. Chem. 69 (1996) 1764–1776.

[12] V.A. Drozdov, P.G. Tsyriulnikov, V.V. Popovskyi, Kinet. Catal. 27 (1986) 162–166.

[13] D.P. Ju, P.G. Tsyriulnikov, E.N. Kudria, Kinet. Catal. 43 (2002) 410–414.

[14] R. Burch, D.J. Crittle, M.J. Hayes, Catal. Today 47 (1999) 229–234.

[15] V.A. Drozdov, P.G. Tsyriulnikov, V.V. Popovskyi, Kinet. Catal. 27 (1986) 721–725.

[16] T. Miki, T. Ogava, M. Haneda, et al. J. Phys. Chem. 94 (1990) 6464–6467.

[17] A. Hadi, I.I. Yaacob, Catal. Today 96 (2004) 165–170.

[18] D.H. Kim, S.I. Woo, J.M. Lee, Catal. Lett. 70 (2000) 35–41.

[19] A.N. Zakharov, L.N. Burenkova, V.A. Voblikova, J. Appl. Chem. 65 (1992) 2211–2216.

[20] S.A. Soloviov, Ya.P. Kurylets, S.N. Orlyk, Theor. Exp. Chem. 39 (2003) 50–54.

[21] H.R. Ismatov, A.B. Abdulaiev, J. Appl. Chem. 43 (1970) 668–670.

[22] T. Osaki, T. Mori, J. Catal. 204 (2001) 89–97.

[23] J.H. Bitter, K. Seshan, J.A. Lercher, J. Catal. 183 (1999) 336–343.

[24] I. Balint, A. Miyazaki, K. Aika, Appl. Catal. B 37 (2002) 217–229.

[25] K.S. Kim, A.F. Grossmann, N. Winograd, Anal. Chem. 46 (1974) 197–200.

[26] J.Z. Shyu, K. Otto, W.L.H. Watkins, et al. J. Catal. 114 (1988) 23–33.