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Adsorption Catalytic Neutralization of Exhaust Gases from Diesel Engines

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Abstract

The basic aspects of environmental protection from hazardous gaseous impurities present in the exhaust gases of diesel engines are considered. Approaches used for the development of fundamental investigation of adsorbents and catalysts for afterburning CO and hydrocarbons are outlined. Results of the investigation of adsorption capacity of zeolites BEA and Y types with respect to heavy hydrocarbons (decane and toluene) obtained with the help of the gravimetric microanalyzer TEOM are presented. It is shown that both zeolites possess comparable capacities with respect to toluene, while the presence of mesopores in BEA zeolite determines its substantially larger adsorption capacity with respect to decane. For Pd/Al_2O_3 catalysts as example, the effect of the nature of precursor of active component and treatment conditions on the activity of the catalysts in the oxidation of CO is considered. It is demonstrated that in the case of the mass fraction of deposited chloride components up to 0.25–0.5 % atomically dispersed forms of palladium are formed; they are responsible for the high activity of palladium catalysts.

Key words: diesel engines, neutralizers, exhaust gases, afterburning catalysts, adsorbents, zeolites, TEOM

INTRODUCTION

The modern level of motor transport threatens to turn from the achievement of progress into ecological disaster for the inhabitants of megalopolises. Tens millions personal automobiles fill the streets of cities and highways, traffic jams many kilometres long every now and then, enormous amount of fuel is burnt improperly, air is poisoned by automobile exhaust gases; in many cities their amount exceeds total emissions from industrial enterprises. Unlike for foreign countries, the growth of the Russian motor stock proceeds under the conditions of substantial lag of home and second-hand foreign cars in ecological parameters and lag of motor fuel used in Russia from the world level [1].

Each automobile emits about 200 different components with exhaust gases into the atmosphere. Exhaust gases contain carbon monoxide CO, hydrocarbons C_xH_y, nitrogen oxides NO_x, benzo(a)pyrene, aldehydes. Due to incomplete combustion of fuel in car engines, a part of hydrocarbons is transformed into soot containing tarry matter. The amount of soot and tar formed is especially high when a driver forces the engine and decreases the ratio of air to fuel in order to obtain so-called rich mixture [2].

In diesel engines, hydrocarbons C_xH_y partially remain in combustion chamber due to the heterogeneity of the mixture, that is, the flame shuts down in a very rich mixture where air is deficient due to incorrect turbulence, low temperature of poor spraying. Hydrocarbons get oxidized in the air and interact with nitrogen oxides; toxic compounds can be formed. Some of them are carcinogenic and cause cancer in humans after long-term contact [3].

During a long time within which the problem of air pollution with automobile exhaust gases exists, many methods were developed that allow one to decrease the amount of exhaust gases or to decrease heir toxicity. Neutralization of worked out gases in the outlet system became a widespread method. In this case, toxic vapour going out from engine cylinders gets mitigated before it is emitted into the atmosphere. Mitigation of exhaust gases with the help of catalysts occurs in devices called catalytic neutralizers [4]. Neutralizers are mounted into the exhaust system of engine without any changes and provide efficient purification from the major toxic components within a broad temperature range for worked out gases (150–900 °C).

The basic element of automobile converter (neutralizer) is a catalytic reactor, usually made as a monolith of block-honeycomb structure, which provides optimal hydrodynamic conditions of gas flow and high efficiency of the interaction of impurities with the catalyst. The first sample of a catalytic block-honeycomb converter was developed in the USA as early as in the middle of the 60es of past century, and in middle 1970es the neutralizers of this kind had become widely used in motorcar construction practice in the world [5].

Screens, compensators and other elements that are used in different designs of neutralizers usually play auxiliary functions and serve to solve partial problems.

As a rule, a modern neutralizer is a ceramic or metal block of honeycomb structure with catalytically active layer deposited on the inner surface of its channels [6]. This allows one to increase the catalyst surface, decrease the consumption of expensive metals (Pt, Pd, Rh) and prevent recrystallization and sintering of the active component at high temperature. Particle size of the metal supported catalysts to a high extent depends on the type of the support used. Supports are usually synthetic (active coal, silica gel, Al_2O_3, aluminosilicate, MgO, ZrO_2) and more rarely natural (natural clay, pumice, diatomite, asbestos) solids with highly developed specific surface and porosity [7].

The problem of catalyst deactivation is essential in automobile catalysts because catalytic materials are subjected to high temperatures under variable conditions. The action of high temperatures promotes a decrease in support surface and sintering of precious metals, which, in turn, leads to the loss of the catalytic activity. Catalysts can also get poisoned in the presence of some pollutants; glaring examples are sulphur and phosphorus [8, 9]. Sulphur is initially present in fuel in the form of mercaptanes and thiophenes; it is transformed into SO_2 and SO_3. The latter compounds are strong catalytic poisons for the majority of oxides. In this connection, it appears impossible yet to completely reject precious metals in catalytic compositions because these metals are stable against sulphur oxides.

Thus, the major attention in this paper is paid to the development of adsorbents and catalytic systems based on palladium to suppress the emission of diesel engines (CO, hydrocarbons).

COLD START PROBLEM: ADSORPTION OF HYDROCARBONS ON ZEOLITES

As we have already mentioned, the problem of exhaust neutralization is generally reduced to the removal of CO, hydrocarbons and nitrogen oxides from the exhaust gases. While catalysts are active towards the transformation of NO_x and CO within a broad temperature range, hydrocarbon oxidation starts at a temperature above 120–150 °C. For this reason, so-called cold start problem arises. To solve it, zeolites are used in world practice; their amount in afterburning catalysts can reach 40 mass % [10].

During the first minutes of engine operation, non-burnt hydrocarbons are captured in the porous matrix of zeolite. During further heating of the catalytic converter, non-burnt hydrocarbons get liberated from zeolites and are oxidized on the catalyst. In this connection, the developers of neutralizers face the problem to choose a zeolite so that a number of requirements due to the specificity of afterburning catalyst operation could be met.

To study adsorption properties of zeolites, different gravimetric devices are used in practice. One of the most suitable devices is a Rupprecht and Patashnik TEOM 1500 PMA (USA). The basic principle of TEOM (Tapered Element Oscillating Microbalance) operation is the principle of pendulum, the form of which is implemented in a cone reactor with the sample under test at the end. Changes of the mass of pendulum (sample) cause a square change of oscillation frequency, which is recorded with the help of optics in the real time mode (Fig. 1). The use of TEOM procedure, unlike other gravimetric techniques, allows one to achieve a 100 % contact of reaction flow with the weighed portion of the sample. In addition, this method provides a high sensitivity to mass ($5 \cdot 10^{-6}$ g) and high frequency of recording in the automatic mode (up to 10 measurements per second).

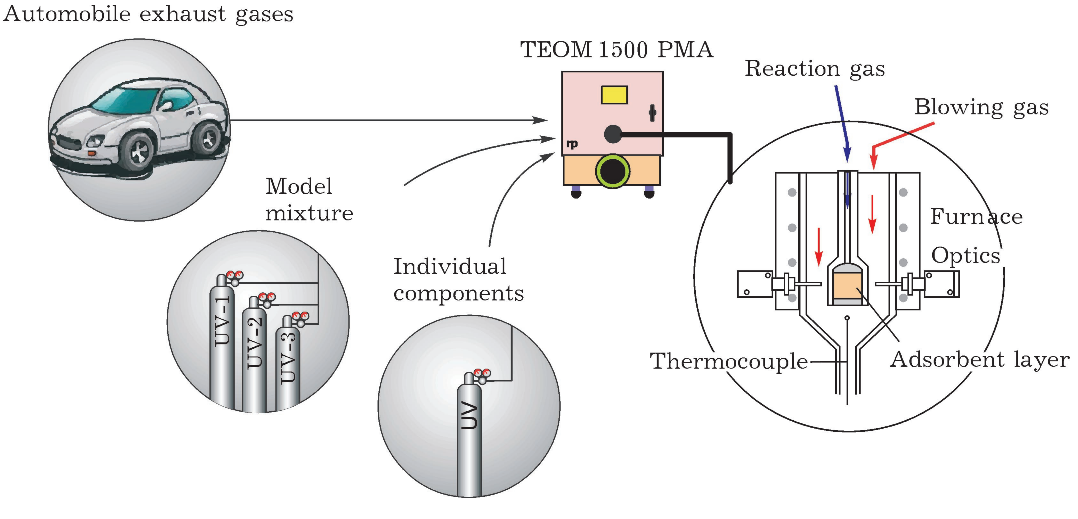

Fig. 1. Gravimetric microanalyzer TEOM and the areas of its application in the development and investigation of catalytic converters of exhaust gases.

Initially developed for measuring the concentration of solid particles in the air [11], the gravimetric microanalyzer TEOM has been used successfully for more than 10 years to study adsorption, diffusion, as well as deactivation and regeneration of catalysts [12–14].

In addition, TEOM microanalyzer has occupied important position in monitoring solid particles of automobile exhaust along with the investigation and development of new adsorbents and materials for automobile neutralizers [15]. This device is included in the complex of analytic equipment used for stand tests of experimental samples of afterburning devices mounted on real automobiles. In addition, TEOM has won active application in laboratory tests at the stage of choosing adsorbents and investigating their characteristics. For this purpose, one can use either model mixtures imitating real automobile exhaust or individual components which are of the highest interest for investigation (see Fig. 1).

TABLE 1

Texture characteristics of initial zeolite samples of BEA and Y types

Parameters	BEA	Y
Specific surface, m^2/g	585	790
Total pore volume, cm^3/g	0.31	1.40
Volume of micropores, cm^3/g	0.24	0.21
Concentration of micropores, %	78	15

In the work, we present the results of the investigation of zeolite samples of structural types BEA and Y; their texture characteristics are listed in Table 1. All zeolite samples were preliminarily calcined at 600 °C directly before the start of experiment.

Non-branched decane and toluene were used as model hydrocarbons that are usually present in the exhaust gases of diesel automobiles. The concentration of decane vapour in the flow of carrier gas (air) was 1200 ppm, and toluene 500 ppm. Adsorption of hydrocarbon vapour was carried out at a temperature of 30 °C. Desorption was performed using two methods: at 30 °C and through rapid heating of the sample to 250 °C in air flow.

Two experimental curves on decane adsorption (at 30 °C) and desorption in air flow at an-

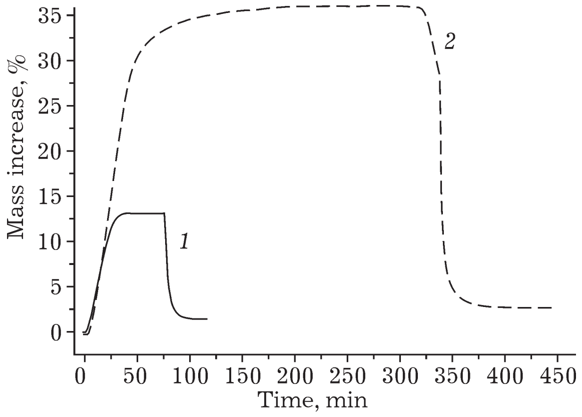

Fig. 2. Adsorption (30 °C) AND DESORPTION **(250** °C) of decane on zeolites of BEA (*1*) and Y (*2*) types.

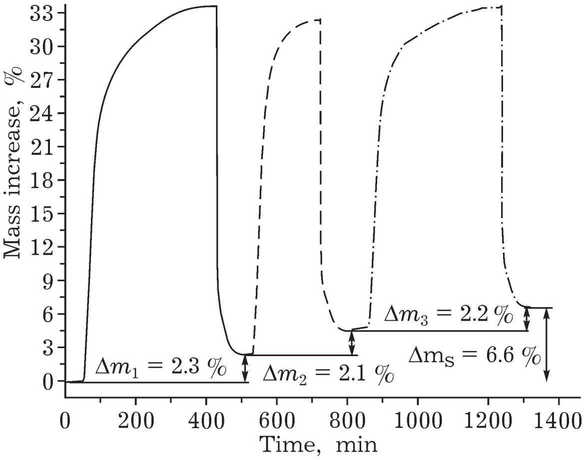

Fig. 3. Three cycles of adsorption/desorption of decane on Y type zeolite (fraction 0.5–1 mm). Adsorption temperature: 30 °C; desorption temperature: 250 °C.

nealed zeolites BEA and Y types are compared in Fig. 2. One can see that the adsorption capacity of the zeolite of Y type is 36.1 mass %, and that of Y type zeolite is 13.1 mass %. Complete saturation of Y type zeolite with decane vapour occurs within 3.5 h, the residue after desorption at 250 °C is 2.7 mass %.

Three consequent cycles of decane adsorption/desorption on Y type zeolite are shown in Fig. 3. Adsorption value in the first cycle was 33.6 mass %, then it decreased gradually (30.1 and 29.2 mass % in the second and in the third cycles, respectively). Total residue on the sample after three cycles of adsorption/desorption was 6.6 mass %.

The presence of residue after desorption is explained by partial coking of decane on the acid centres of zeolite. Decane molecules in the pores of zeolite interact with atmospheric oxygen, which leads to partial destruction of the carbon framework and to the formation of coke deposits. Thus, for more efficient removal of hydrocarbons and regeneration of the porous system of zeolite, the addition of catalytically active component is necessary. In practice, a small amount of platinum or palladium is most frequently used as oxidation activator [16].

The data on adsorption characteristics of zeolites towards decane and toluene are shown in Table 2. One can see that BEA type zeolite nearly equally captures both decane (13.1 mass %) and toluene (15.0 mass %). At the same time, for zeolite Y, the transition from decane to toluene causes a decrease in sorption capacity with respect to hydrocarbon almost by a factor of 3. So, we may conclude that about 2/3 of pores open for decane in zeolite Y are inaccessible for adsorption of toluene molecules. Adsorption value with respect to toluene is comparable for both zeolite types (see Table 2).

Analyzing the data presented in Tables 1 and 2 we may conclude that both micro- and mesopores of zeolites take part in adsorption. For both zeolite types, the value of decane and toluene residue after desorption at 30 °C is comparable and equals 10–11 mass %. The obtained result correlates with approximately equal number of micropores in BEA and Y zeolites. Additional capacity of Y type zeolite with respect to decane is provided by the high concentration of mesopores in the material (78 %). It is important to note that the morphology of pores in this zeolite that efficiently holds non-branched decane has no effect on the adsorption capacity with respect to toluene.

It follows from the data shown in Table 1 that the total pore volume for BEA type zeolite is 0.31 cm^3/g; micropores account for the larger part (0.24 cm^3/g). If we assume that decane is not adsorbed in micropores, then only 15 % of micropores in zeolite Y (0.21 of 1.40 cm^3/g) do not participate in adsorption, while the cor-

TABLE 2

Generalization of the results on adsorption/desorption of decane and toluene on BEA and Y type zeolites

Parameters	BEA		Y	
	Decane	Toluene	Decane	Toluene
Adsorption capacity at 30 °C, mass %	13.1	15.0	36.1	13.0
Residue after desorption at 30 °C, mass %	10.0	9.8	11.3	10.2
Residue after desorption at 250 °C, mass %	1.5	2.3	2.7	0.8
Specific surface, m^2/g, after desorption	350	535	615	734
Total pore volume, cm^3/g, after desorption	0.21	0.30	1.10	1.39

responding value for BEA type zeolite is 78 % (see Table 1). This fact explains the substantial difference between these zeolite types in their adsorption capacity with respect to decane.

PALLADIUM CATALYSTS IN THE OXIDATION OF CARBON OXIDE (II)

In the investigation of the catalytic properties of afterburners, the most interesting aspect is their activity in the oxidation of the most toxic component of exhaust gases – carbon monoxide. In our studies we prepared the Pd/Al_2O_3 catalyst using as support γ-Al_2O_3 (Condea, S_{BET} = 200 m^2/g, granule size 0.25–0.5 mm) calcined in the air at 700 °C. Palladium was deposited in the amount of 0.03–1 mass % by means of impregnation for moisture capacity from aqueous solutions of H_2PdCl_4 (below designated as $Pd(Cl)/Al_2O_3$) and palladium nitrate ($Pd(NO_3)/Al_2O_3$). The samples were dried at first at room temperature, then in a muffle at 100 °C for 12 h, and after that the sample were calcined in the air at a temperature of 600 °C for 10 h.

Determination of the activity of catalyst samples was carried out using a flow-type setup. A sample of catalyst with a mass of 300 mg (fraction 0.25–0.5 mm) was placed in a quartz U-shaped reactor. Temperature in the reactor was risen from 60 to 300 °C at a rate of 10 °C/min. Reaction flow rate was 300 mL/min. Each catalyst was subjected to three cycles of heating–cooling, which allowed us to evaluate the stability of catalyst functioning. A criterion for comparing the activity was $T(50)$, which is temperature of 50 % conversion of CO.

Reaction flow was a model mixture of the following composition, vol. %: H_2O 5, CO 0.15, O_2 14, NO 0.01, C_xH_y (a mixture of hydrocarbons) 0.0081; N_2 – balance. The stability of catalysts to the action of high temperature was tested by means of hydrothermal treatment of samples at 800 °C in humid air (volume concentration of H_2O: 10 %) for 14 h.

Important feature of palladium catalysts is their activity in the oxidation of CO, starting from very low concentrations of deposited metal. It is noteworthy that an increase in the oxidative activity stops sharply when palladium concentration of 0.25 mass % is achieved (Fig. 4).

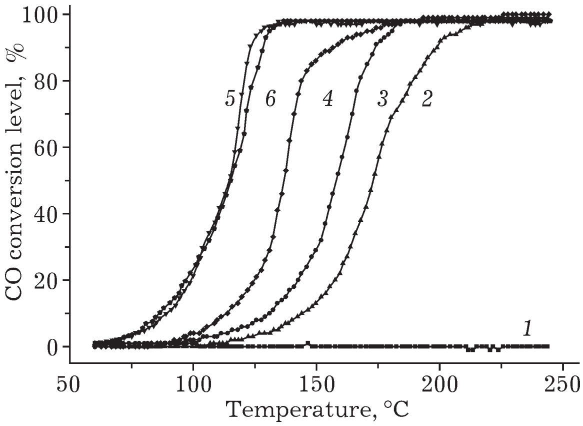

Fig. 4. Dependence of the activity of catalyst in CO oxidation on the concentration of supported palladium (Pd/Al_2O_3), mass %: Al_2O_3 (*1*), 0.03 (*2*), 0.06 (*3*), 0.125 (*4*), 0.25 (*5*), 1 (*6*). Samples of catalysts were tested after hydrothermal treatment.

Taking into account S_{sp} of aluminium oxide used (200 m^2/g), the concentration of 0.25 mass % corresponds to the degree of support surface filling with palladium ions not higher than 0.5 % of monolayer. This allows us to conclude that stabilization of the active forms of Pd is due to the presence of special centres on the surface of γ-Al_2O_3, and the concentration of these centres is insignificant.

We studied the effect of palladium deposition procedure and the nature of precursors (nitrate and chloride complexes) on the activity of Pd/Al_2O_3 catalyst in the oxidation of CO. The values of parameter $T(50)$ for these catalysts containing 0.25 mass % Pd are listed in Table 3. Attention should be paid to substantially higher activity of the catalyst prepared from palladium nitrate in comparison with the sample prepared from the chloride precursor after calcination in the air at 600 °C. One can see that hydrothermal treatment of the latter allows one to improve the activity substantially.

The activity of palladium catalysts with low platinum content was also compared with the reference sample containing 2 % platinum (see Table 3). One can see that the sample with treatment temperature 800 °C (0.25 % $Pd(Cl)/Al_2O_3$-800) in the first cycles exhibits higher activity than the reference sample, in spite of substantially lower concentration of the active metal. Nevertheless, platinum catalyst demonstrates good stability from one cycle to another, while

TABLE 3

Effect of precursor and treatment conditions on the activity of catalysts

Catalysts	Palladium precursor	Treatment conditions	$T(50)$		
			Cycle 1	Cycle 2	Cycle 3
0.25 % $Pd(NO_3)/Al_2O_3$	Nitrate	10 h, 600 °C	129	153	159
0.25 % $Pd(Cl)/Al_2O_3$	Chloride	10 h, 600 °C	235	250	242
0.25 % $Pd(Cl)/Al_2O_3$-800	Chloride	14 h, 800 °C, 10 % H_2O	115	140	145
2 % Pt/Al_2O_3 (reference sample)	–	14 h, 800 °C, 10 % H_2O	165	166	165

parameter $T(50)$ for all palladium catalysts increases monotonously. In the opinion of a number of researchers, this is connected with the oxidation of Pd to form PdO [17]. As a consequence, purely palladium catalysts still have not found commercial application yet for afterburning of exhaust gases from diesel engines.

It should be noted that temperature-programmed-reduction (TPR) procedure in hydrogen allows one to detect the presence of PdO phase in oxidized samples of Pd-containing catalysts reliably on the basis of the characteristic peak of hydrogen absorption in the region 10–20 °C [18–20]. The TPR data (Fig. 5) point to the fact that PdO is almost absent from the samples obtained from palladium chloride; however, this phase was detected in the samples obtained from palladium nitrate.

The obtained results provide evidence of higher dispersity of supported palladium in the samples prepared from the chloride precursor. Calcination of these samples in the air at 800 °C causes baking of the active component and to the appearance of PdO phase (see Fig. 5, sample T_{act} = 800 °C (Cl)). TPR results are in good agreement with EXAFS [21] and spin probe data [22] for Pd/Al_2O_3 catalysts, which confirms the presence of atomically dispersed ion clusters Pd^{2+} in chloride samples when the concentration of supported Pd is up to 0.5 mass %.

In spite of the high dispersity of palladium in chloride catalysts, its activity in CO oxidation turned out to be low in comparison with the nitrate samples. This is due to the presence of residual chloride ions in these samples. Experiments showed that its removal is possible as a result of hydrothermal treatment of catalysts at 500–550 °C. Data shown in Table 3 provide evidence that chloride samples subjected to the standard hydrothermal treatment procedure give extremely high activity exceeding the $T(50)$ parameter for nitrate samples.

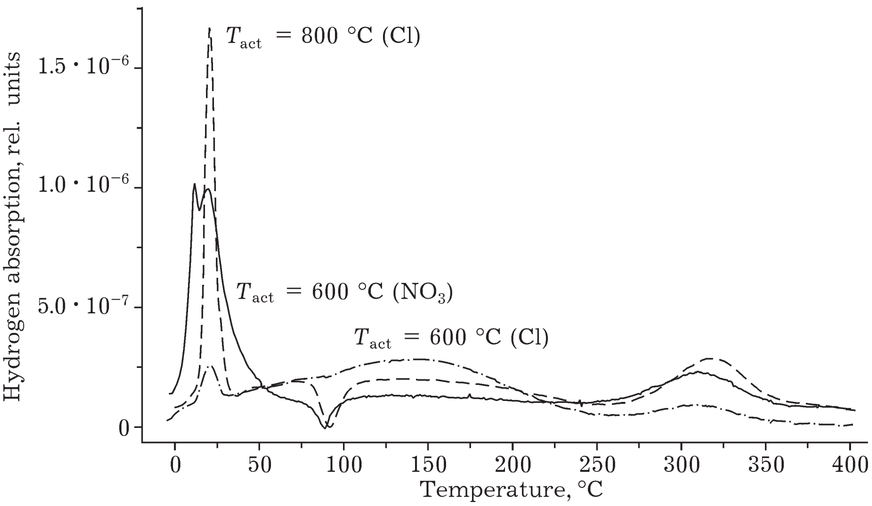

Fig. 5. TPR spectra of catalysts 0.5 % Pd/Al_2O_3 prepared from chloride and nitrate precursors after calcination in the air at different temperatures.

CONCLUSION

At present, integrated solution of the ecological problem of air pollution with exhaust gases is impossible without the application of adsorption and catalytic approaches. The use of adsorbents is due to the necessity to capture hydrocarbons in the cold cycle of engine operation, while catalysts provide complete neutralization of hazardous impurities at increased temperature.

The most evident candidates for adsorption trap are zeolite materials; however, not all of them satisfy requirements dictated by rigid conditions of neutralizer functioning. These criteria are fist of all, the adsorption capacity with respect to a broad range of hydrocarbons, as well as the ability to regenerate pores and high thermal stability. We demonstrated that zeolites of BEA and Y types having comparable toluene capturing ability exhibit substantial differences in the sorption capacity for non-branched decane. In this case, determining factor is the porous structure of zeolite. Higher adsorption capacity of BEA type zeolite towards decane is due to the presence of substantial volume of mesopores, which are almost absent in zeolite Y.

Investigation of palladium catalysts Pd/Al_2O_3 showed that it is atomically dispersed ion forms of palladium stabilized on specific centres of the support that are responsible for the high activity of samples in the oxidation of CO. The use of chloride precursor in combination with subsequent hydrothermal treatment of the catalyst allows one to conserve highly dispersed state of supported palladium thus providing the high catalytic activity.

Unfortunately, it must be stated that in spite of extremely high activity in the first cycles of tests, palladium catalysts do not exhibit stability which characterizes platinum catalysts. Gradual transformation of active Pd forms into PdO leads to permanent decrease in activity from one cycle to another in longevity tests. For this reason, the efforts of many researchers are directed at present to the development of alloyed catalysts combining high activity with acceptable stability. Replacement of even a small amount of platinum by palladium will allow one to reduce the total cost of the converter in view of more than 3-fold difference between these metals in price.

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