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CREATION OF HIGH EFFECTIVE NANOSTRUCTURED CATALYSTS ON BASE OF Pt, Pd FOR NEUTRALIZATION OF MOTOR TRANSPORT EXHAUST

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ABSTRACT

The purpose of the research work is studying of the reactions of oxidation of hydrocarbons and reduction of nitrogen oxides with use of block catalysts. The methods of obtaining of Pt and Pd colloids on the block catalysts were developed. The conditions of stabilization of the colloid particles of Pt and Pd were selected. It was shown, that introduction of the promoting metal to a palladium containing colloid in the ratio 1:0.3 raised activity and stability of the catalyst.

Key words: Catalyst, Ecology, Nanostructured materials, Sol-gel processes.

INTRODUCTION

One of the vital problems of humanity, which has attracted the attention of the public and the scientists of the leading countries of the world is the problem of pollution from the motor transport and industrial wastes[1]. Air pollution leads to a slowing of growth, deterioration in the quality of forests and reduce of crop yields, disease of humans and animals, insects and plants, contributes to the acceleration of nitrogen processes of decomposition of building materials and metal corrosion. With constant increase in number of cars the degree of pollution of an atmosphere exhaust gases grows. The cars evolve up to two hundred substances from which the most part harmful to a human body and an environment[2,3]. The standards of emissions of toxic components for engines of internal combustion become tougher from year to year. The problem of protecting of environment from the harmful effects of industrial emissions and motor transport requires an immediate

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solution. One of the perspective ways of cleaning of exhaust gases in the near future is the catalytic neutralization of toxic substances, which leads to considerable lowering of the toxic compounds content in atmosphere and the same is successively using in the leading countries of the world. The majority of catalysts preparing with the using of the classical methods of active phase deposition to carrier are the polydispersive with the wide particles distribution by their sizes. In this field, the perspective direction is the using of the metalorganic compounds and colloid solutions of Pt metals as the catalysts precursors. Recently, interest to nanostructured particles production and studying has considerably grown[4,5]. It is connected by that new perspective opportunities of nanomaterials use in many branches of a science and technical equipment including catalysis have appeared. The catalysts synthesized from the metal organic compounds differ by narrow distribution of particles in the sizes in comparison with the deposited metal catalysts received by a method of impregnation[6-8]. Decrease in the contents of metal of platinum group in effective catalysts of deep oxidation of CO and hydrocarbons and in reduction of oxides in exhaust gases of engines of internal combustion is a large practical task. Synthesis of the low-percentage deposited catalysts on a basis of colloid metals with the adjustable homogeneous size of particles allows to create such catalysts.

EXPERIMENTAL

Catalysts creation on base of the metal blocks was carried out by the developed in the laboratory methods[9]. For preparation of the block carrier the heat resisting foil by thickness 50 microns of settlement length and width was cut (Fig. 1). Then a foil was subjected to corrugating, on a smooth foil the corrugated tape then were winded to the cylindrical block (Fig. 2).

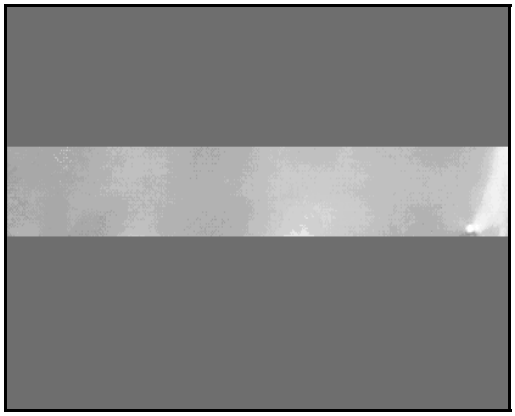

Fig. 1: Foil smooth (50 microns)

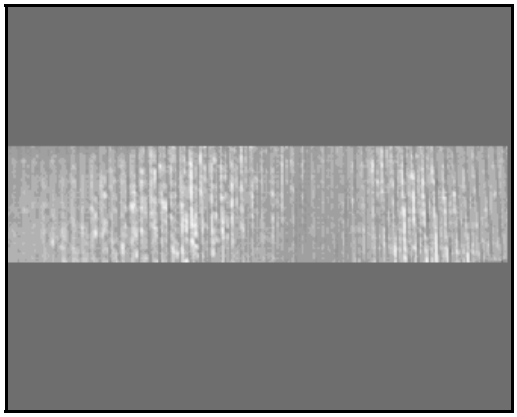

Fig. 2: The foil corrugated

As the surface of cold rolled out foil was polluted with lubricant oils and for their elimination degreasing by pure gasoline was carried out, then the carrier was washed out by ethanol and distilled water. For removal of the stayed water from channels of the block, promoting to hydroxides iron formation on a surface of a foil, the blocks were established in vertical position in a drying case and were dried within 2 hrs at temperature 473 K. Appearance of the blocks should be equal dark grey matte color, without scales and break of the initial forms. On the prepared block metal carriers with the honey comb structure of channels the secondary carrier was deposited. In this work, platinum metals were translated to colloid condition with the purpose of increase of their activity in reactions of oxidation of CO, hydrocarbons and nitrogen oxides reduction. It has allowed to create catalysts with the advanced surface adjustable by porosity, high activity and high stability. Taking into account that platinum and palladium in the nanostructured condition are very perspective materials for catalysis, possessing high activity and selectivity the nanostructured particles of platinum by hydrogen reduction of a water solution of hydrogen hexachloroplatinate (chloroplatinatinic acid) and citric acid were synthesized. Iso-propanol was used as the stabilizer of the colloid particles of platinum. The colloid platinum was obtained by such methods and was deposited on the block metal carriers with the honey comb structure of channels (Fig. 3).

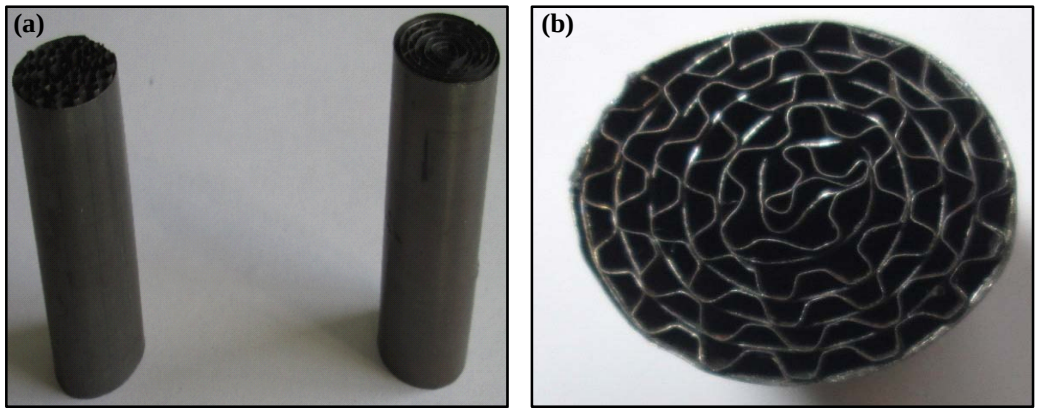

Fig. 3: The ready metal blocks (laboratory samples) -block metal supports (a) General view in front, (b) In a cross-section

For the secondary carrier deposition the metal block was immersed to suspension, under action of vibration filling all channels was provided. Surplus of suspension from channels was removed with stirring, and blocks were placed to cartridges of a centrifuge where a removal of surplus of suspension from channels of the block and its uniform

distribution on a surface took place. The metal sols put on the block carriers were dried in a drying case within 4 hrs at temperature 423 K. Catalysts were calcinated in a muffle furnace at temperature 773 K within 2 hrs. Catalysts were tested in flowing catalytic installation with a tubular reactor of integrated type with the optimized parameters of a layer of the catalyst. The contents of hydrocarbon in a mix made 0.5% by weight. The chromatographic analysis of the initial compounds and products of their transformation was spent on the chromatograph Crystal 2000 M with capillary column Zebron ZB-1 30 mL x 0,53 mm ID x 5,00 μm, a liquid phase - 100% dimethylsiloxane (gas-carrier-helium, flame ionization detector).

The total time of the analysis was 15-20 min. A gas mix was also analyzed on Chromatograph 3700, and on a gas analyzer "OPTOGAS-500.3" before and after reactor. For testing a probe of colloid catalyst on the metal carrier in volume of 2.0 cm^3 was used. Diameter of the researched block catalyst was 10 mm, length -30 mm. Catalysts were tested in reaction of reduction of nitrogen oxide by propylene at the presence of 3 % of oxygen, and at volumetric speed of a stream of a gas mix 24000 and 36000 hr^{-1}. Research of catalysts was carried out at temperature 323-773 K with an interval 50 K. The composition of researched gases included hydrocarbons (propylene, propane-butane, methane), carbon oxide, nitrogen oxide, oxygen of air, nitrogen.

On the electron microscopic researches data, the investigated catalysts differ by high dispersiveness, uniform distribution of particles of metal on the carrier[10]. The platinum received by reduction in a solution, had the sizes about 14-16 nanometers, at the same time platinum colloid, received by reduction by a citric acid, had practically mono dispersive distribution, which average size of particles made 8 nanometers.

In Table 1, the results of studying of activity of the catalysts synthesized by different methods of introduction of colloids of active metal to an alumina-oxide matrix by various methods were submitted. It was found, that Pt-containing catalysts were more active, than Pd (at the same complex former). Influence of complex former structure on activity of the catalyst was visible evidently on samples Pd: at temperature 523 K the degree of transformation of gases differed in 2 times. It was shown that at comparison of activity of Pt-containing catalysts, that the degree of transformation of gases depended as from the contents of platinum as from a complex former kind. At an identical method of introduction of platinum in the secondary carrier of the block metal catalyst activity grown with increase in the contents of platinum from 0.05% up to 0.2%. The variation of methods of introduction and dispersiveness of the colloid metal also influenced activity of catalysts.

Table 1: Test of activity of catalysts in reaction of oxidation of hydrocarbons and reduction of nitrogen oxide at the different concentrations

Samples of the catalysts	Catalyst	The active metal concentration (%)	Degree of gases transformation (CH_x/NO_x, %)			
			Temperature of research of catalysts (K)			
			773	623	523	423
1	Pt	0.05	100	76.9	17.9	0
2	Pt	0.1	100	100	89.3	10.7
3	Pt	0.1	100	88.0	40.0	0
4	Pt	0.1	100	87.3	11.5	0
5	Pd	0.1	92	82.1	6.0	0
6	Pd	0.1	100	94.2	11.6	0

Studying of the catalytic activity of the mentioned particles deposited on block metal carriers, has shown, that catalysts with the deposited platinum from citrates colloid solution possessed higher activity in comparison with the platinum received by reduction by hydrogen. So the nitrogen oxide was reduced by propylene at the presence of oxygen already at temperature 473 K (12%), reaching 60% at 623 K. The catalysts prepared by reduction of platinum from a water solution by hydrogen, showed activity on transformation NO to N_2 only at 573 K. Activity of the catalyst on total oxidation by propylene in both cases was high -92.0-95.0% at 573 K. Most likely, activity of nanostructured particles of platinum on transformation NO in N_2 by propylene at the presence of oxygen is connected not only to the size platinum colloid, but also substantially from a method of their producing.

In Table 2, the data showing activity of catalysts on a basis of a palladium colloid of various concentration, deposited on alumina were submitted. The degree of transformation of hydrocarbons at concentration Pd equal 0.2% at decreasing of temperature from 773 up to 623 K was reduced insignificantly- from 100 (773 K) up to 97.4 (623 K), at concentration Pd 0.1 and 0.05 decrease in a degree of transformation was sharper: from 100 up to 59.5 (for concentration Pd 0.1) and 57.6 (0.05). The same trend was revealed for the nitrogen oxides transformation degrees.

For increase of thermal stability of catalysts rare earth metals in a various ratio as promotors were entered. The results of study show increase of the catalytic activity of Pd/Al_2O_3-catalysts at a weight ratio of components Pd:Me = 1:0.1. At increase in quantity of

the promotor from 1:0.1 up to 1:0.3 activity of the catalyst changed insignificantly, at temperature 523 K the tendency to decreasing of a degree of transformation of hydrocarbons was visible. The further increase in quantity of the promotor from 0.3 up to 0.5 decreased activity of the catalyst. At an optimum ratio a palladium: the promotor the investigated catalysts carried out deep oxidation of hydrocarbons.

Table 2: Oxidation of hydrocarbons and reduction of nitrogen oxide on Al-palladium catalysts at the different Pd concentrations

No.	Catalyst	Pd concent-ration, by weight (%)	Degree of gases transformation CH_x/NO_x (%)				
			Temperature of research of catalysts (K)				
			773	623	523	473	423
1	Pd	0.2	100/40.8	97.4/42.6	31.5/30.4	18/15.6	0
2	Pd	0.1	100/38	59.5/23	21.6/18.3	13/9.2	0
3	Pd	0.05	100/24.8	57.6/21	19.2/16.8	8/9.4	0

CONCLUSION

Thus, methods of production of Pt and Pd colloids on block catalysts were developed. The conditions of stabilization of the colloid particles of Pt and Pd were selected. It was shown, that catalysts on base of Pt and Pd colloids had high activity in reaction of oxidation of hydrocarbons (100% at 773-573 K) and reduction of nitrogen oxides- 68%. Introduction of promoting metal into the palladium containing colloid in the ratio 1:0.3 raised activity and stability of the catalyst.

REFERENCES

1. A. G. Akhatov, Ecology and International Law, M., AST-PRESS, 512 (1996) (in Russ.).
2. E. A. Vystrobets, International Cooperation in the Field of Environment and Natural Resources, M., MNEPU, 112 (2000) (in Russ.).
3. FCCC/CP/2001/20, Guidelines for National Systems under Article 5, Paragraph 1, of the Kyoto Protocol. UNFCC Conference of the Parties, Seventh Session, 10 November (2001).
4. New EPA Rules to Cut Diesel Fuel Pollution, Will Cover off-road Machinery, USA Today, May 11, 4A (2004).

5. M. Yashimaa, L. Falkc, A. Palmqvist and K. Holmberga, Structure and Catalytic Properties of Nanosized Alumina Supported Platinum and Palladium Particles Synthesized by Reaction in Microemulsion, J. Coll. Interface Sci., **268**, 348-356 (2003).

6. O. P. Yadava, A. Palmqvist, N. Cruiseb and K. Holmberg, Synthesis of Platinum Nanoparticles in Microemulsions and their Catalytic Activity for the Oxidation of Carbon Monoxide, Coll. & Surfaces A: Physicochem. Engg. Aspects, **221**, 131-134 (2003).

7. T. Liese, E. Löffler and W. Grünert, Selective Catalytic Reduction of NO by Methane over CeO_2–Zeolite Catalysts-Active Sites and Reaction Steps, J. Catal., **197**, 123-130 (2001).

8. L. R. Sassykova and A. T. Massenova, The High Effectıve Catalysts for Neutralization of the Exhaust Gases of Motor Transport, ISCS2012, Interrn. Symposium on Catalysis and Speciality Chemicals, 23-26 Sept. 2012, Tlemcen, Algeria, 121 (2012).

9. L. R. Sassykova, A. T. Massenova, Sh. Gil'mundinov, M. M. Tel'baeva, V. N. Bunin and L. V. Komashko, Development of the Block Catalysts of New Generation for Cleaning of Exhaust Gases of Motor Transport, 15th International Congress on Catalysis ICC15, Germany, Munich, 7-17 July 2012 (2012).

10. L. R. Sassykova, A. T. Massenova, Sh. A. Gilmundinov, V. N. Bunin and K. S. Rakhmetova, The Effective Catalytic Systems on the Base of Colloid Platinum Metals for Oxidation of CO, Methane and Decomposition of Nitrogen Oxides, Selective Oxidation and Functionalization: Classical and Alternative Routes and Sources, Berlin, Germany, Preprints of the Conference (2014) pp. 181-187.

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