SYNTHESIS OF CATALYSTS ON THE METAL BLOCK CARRIERS AND TESTING THEIR EFFECTIVENESS IN THE REAL CONDITIONS OF OPERATION

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ABSTRACT

The aim of the work is the preparation of full-size catalysts with honeycomb channel structure on metal block carriers and their use in pilot industrial scale tests during cleaning of exhaust gases of motor transport and industrial harmful emissions. The synthesized catalysts on metal carriers were used for pilot industrial scale tests with JSC “Embamunaigas” (Kazakhstan) on exhaust gases from oil heating furnaces in order to reduce toxic emissions. The effectiveness of neutralization of toxic emissions on the oilfield “S.Balgimbaev” was as follows: CO - 99.6 %, NO - 20.4 % and NOₓ - 19.6 %.

The reduction of toxic emissions on the oilfield “Southwest Kamyshitovoye” in the furnace PT-16/150 after the catalysts was as follows: CO - 100 %, NO - 7.7 %, NOₓ - 7.7 % and SO₂ - 57.1 %.

Keywords: ecology, oil refining, motor transport, toxic gases, catalysts, metal blocks.

INTRODUCTION

To date human impact on the environmental situation of the world has become globalized. Since the mid 80s of the last century, measures for protection of the ozone layer have been undertaken [1 - 3]. Constantly increasing number of cars is one of the reasons for the degradation of the ecological situation in the cities and towns. With the growth of motor transport which use in national economics and modern engineering rises, air pollution with exhaust gas increases. In the absence of appropriate treatment methods many industrial plants pollute atmosphere with combustible or odorous compounds as well. The cost of gas cleaning catalysts produced in the world is more than 2.2 billion dollars per year, oil refining catalysts ~ 2.0 billion dollars per year, and catalysts for the chemical industry - 3.9 billion dollars per year. Most of the platinum produced worldwide (100 t/y) is used for gas cleaning catalysts [4 - 6]. The problem of cleaning motor transport and industrial exhaust gases is one of the urgent problems of the mankind, which has attracted the attention of public and scientists of leading countries of the world. Protection of the environment from industrial and traffic pollution is constantly increasing demands on improvement of methods of catalysts synthesis for cleaning and neutralization of gas emissions and toxic contaminants [7 - 9]. Current environmental problems of the Republic of Kazakhstan are complex, diverse and geographically differentiated. According to the volume of pollutants emissions from stationary sources into the atmosphere the country is in the top three among CIS countries, after Russia and Ukraine. In Kazakhstan about 3 million tons of harmful substances such as carbon and nitrogen oxides, hydrocarbons, etc., are emitted daily. The level of air pollution in many industrial cities of the Republic of Kazakhstan exceeds current regulatory limitations by more than 6 - 10 times because of emissions from motor transport, boilers and industrial plants. In Kazakhstan, at the national level, the share of total emissions of
pollutants into the atmosphere by all anthropogenic sources reaches 60 % in average [1, 6, 8]. The degree of neutralization of toxic substances in the industry is traditionally on the middle level, and as a result, the regions of its deployment are sources of the most toxic emissions. Since 1994, cars in Europe and midsize utility trucks in the US, which are run on diesel fuel, have been fitted with catalysts intended to reduce the level of particulates of liquid hydrocarbons or soluble fractions of gaseous hydrocarbons, and carbon monoxide in the exhaust gases. Since October 2001, 3 EURO European standard, regulating the emission of gaseous pollutants and particulates of automobile engines, was entered into force on.

Among the well-known methods of recycling and neutralization of harmful emissions from industry and motor transport the deep catalytic oxidation of organic compounds down to carbon dioxide and water is the most effective one [9 - 12].

The aim of the work is preparation of full-size catalysts with honeycomb channel structure on metal block carriers and their use in pilot industrial scale tests during cleaning of exhaust gases of motor transport and industrial harmful emissions.

EXPERIMENTAL

The full-size block metallic catalysts on carriers with a honeycomb structure of channels were produced and tested in real conditions of transport and industrial objects. The primary carrier is made of heat-resistant foil of 50 µ thick. A washcoat is a suspension of aluminum salts. Catalyst preparation is carried out by the method developed by the authors [13 - 15]. To prepare the active catalyst component solutions were employed the active compositions based on metals of the platinum group and oxides of Mn, Ni, Co, Fe, Ce, obtained from the corresponding salts (formates, acetates and nitrates). In the case of catalysts based on platinum metals, platinum metals were transferred into the colloidal state: as active ingredients of catalysts are used acetates of Pt and Pd and their π-complexes. For some catalyst samples in the step of preparing of the active phase was also used polyethylene glycol (PEG). The solutions of palladium prepared by dissolving Pd in acetic acid containing 3 % HNO₃. Nitric acid is removed in the process of evaporation to a complete cessation of evolution of nitrogen oxides.

π-complexes of Pd and Pt were obtained by reacting allyl alcohol with the salts of these metals.

The synthesized catalysts (Fig. 1) had high thermal and mechanical stability, developed surface area, which contributes to the low pressure drop, and easiness with orientation in the reactor. Block catalysts were cylindrical in shape and easy to place at the source of toxic emissions. The developed catalysts on metal carriers for cleaning motor transport and industrial exhaust gases met the standard EURO-3. Three types of catalysts (on the basis of 0.2 % Pd, and 0.1 % Pt) promoted with manganese and nickel oxides were tested in the reaction of oxidation of CO and CH₄ before and after prolonged exploitation. The degree of CO oxidation on all catalysts before and after long-term tests did not change significantly. Based on the results obtained the catalysts were recommended for industrial tests [14, 15].

On the pilot and experimental basis of JSC “D.V.Sokolsky IFCE” the full-size block catalysts on metal carriers with honeycomb channel structure were prepared. The samples made for oil heating furnaces were applied for pilot industrial-scale tests of the catalysts with JSC “Embamunaigas” (Kazakhstan) with real exhaust gases on oil heating furnaces in order to reduce toxic emissions. The catalysts were prepared from the heat-resistant foil by winding the smooth and corrugated foil in the metal block of cylindrical shape, followed by the application of active agents (based on metal compounds of Groups 7 - 8). Then the prepared full-size catalysts were forwarded to assembly, where
cylinders were made. There were pins for the catalysts in the cylinders.

The diameter of the block filter for the furnace PTB-10/64 was 410 mm, height – 400 mm. For PT-furnace 16/150 the diameter of the catalytic filter 500 mm, height 400 mm, and the dimensions of the catalyst for 3.5-PT oven were 900 mm by 400 mm. The catalytic filters were installed directly on exhaust gas pipes of oil heating furnaces after before-the-catalyst samples were taken (Fig. 2) In order to reduce heat transfer the catalysts were wrapped with insulating mineral wool with reflective foil.

During the operation of furnaces the gas temperature was measured before and after the catalysts with a mercury thermometer and a temperature sensor analyzer. The concentration of toxic gases before and after the catalytic filters was measured with a gas analyzer MCI-150 “Boshi”.

The catalytic filters were also set in the furnace with forced air supply PTB-10/64 on the oilfield “S.Balgimbaevo” (Kazakhstan). The temperature of exhaust gases before the catalyst was 350°C, the concentration of toxic gases before the catalyst was 1,280 ppm for carbon monoxide (CO), 49 ppm for nitrogen oxide (NO), and 51 ppm for total nitrogen oxides (NOx). Another batch of the catalytic filters was installed in the furnaces for heating oil and water on the oilfield “Southwestern Kamyshitovoye” (Kazakhstan): in the oven PT-3.5 with forced air supply and in 4 PT-16/150 furnaces with own air draft.

Physical and chemical analysis of the catalysts based on basic metals was X-ray analysis with X-ray diffractometer DRON-4-0.7 with a copper anode. The samples for the X-ray analysis were prepared by mechanical destruction of the catalysts applied on the metal block. The crumbled catalysts were pulverized in an agate mortar to 100 mµ and used for the analysis.

RESULTS AND DISCUSSION

On the oilfield “S.Balgimbaevo” (Kazakhstan) the concentration of toxic gases before the catalyst was 1,280 ppm of carbon monoxide (CO), 49 ppm of nitrogen oxide (NO), and 51 ppm of total nitrogen oxides (NOx); after the catalyst there was 5 ppm of CO, 39 ppm for
NO, and 41 ppm for NO\textsubscript{x}. Thus efficiency of the neutralization of toxic emissions was as follows CO - 99.6 %, NO - 20.4 %, NO\textsubscript{x} - 19.6 %. During the pilot tests it was revealed that the catalytic filters worked effectively. They reduce the content of toxic gases from 7.7 % of nitrogen oxides and up to 100 % of carbon monoxide.

On the oilfield “Southwestern Kamyshitovoye” (Kazakhstan) efficiency of neutralization of toxic emissions in PT-3,5 furnace with the catalytic filter was as follows CO - 66.8 %, NO - 20.6 %, NO\textsubscript{x} - 20 % and SO\textsubscript{2} - 100 %. The reduction of toxic emissions in the furnaces PT-16/150 after the catalyst was 100 % for CO, 7.7 % for NO, 7.7% for NO\textsubscript{x}, and 57.1 % for SO\textsubscript{2}. According to the electron microscopy and XPS analysis data the noble metals in the initial monodisperse catalysts were in an oxidized state with a uniform distribution of metal particles on the carrier and characterized by high thermal stability. X-ray analysis of Pd and Pt showed scattering spectrum which indicates the high dispersion of the metals.

The synthesized catalysts were analyzed with a complex of physical and chemical methods. It was found that the oxide catalysts resembled spinels with a cubic lattice of NiMnO\textsubscript{4} with peaks 2Å, 52Å, 148Å, 203Å. There were also low-intensity peaks of CeO\textsubscript{2} (308 Å) and aluminum oxide (160 Å, 256 Å). According to the XRD analysis of Pd and Pt showed scattering spectrum which indicates the high dispersion of the metals.

At a diffractogram of catalysts on the basis of a cobalt there are diffraction peaks which correspond to cobalt oxide of a structure of a spinel Co\textsubscript{3}O\textsubscript{4} (CoCo\textsubscript{2}O\textsubscript{4}): 2θ = 31.35; 36.90; 44.90; 59.40; 55.90 (Fig. 3a). For the catalysts based on Pd supported on different washcoats the (111) peak of Pd (40 2θ) and peaks of Pd 46.5 (plane 200), 68.2 (plane 220) were found (Fig. 3b). Results of XRD showed that there were clear particles of Pd [13]. In Fig. 4 comparative diagrams for catalysts with various concentrations of the acid centers of different force are shown. Catalysts on basis Pt/Ni-Mn/Al\textsubscript{2}O\textsubscript{3} are characterized by the greatest concentration of the strong acid centers.

![Fig. 3a. XRD-patterns of different catalysts samples on the base of Co: 1- Co/Al\textsubscript{2}O\textsubscript{3}, 2- Co\textsubscript{3}O\textsubscript{4}.](image)

![Fig. 3b. XRD images of Pd-based catalysts on CeO\textsubscript{2}.](image)

![Fig. 4. Influence of chemical composition of the converters on the distribution of acid centers.](image)
acid centers (280 µmol/g), at Pd/Ni-Mn/Al₂O₃ catalyst the greatest concentration of the weak acid centers was 250 µmol/g.

In Table 1 the characteristics of catalysts on the base of Pt and Pd received with the use of method TPD NH₃ are presented. The data show that a total (summarized) concentration of acid centers Pt- and Pd-catalysts with the additives of nickel and manganese oxides, above, than in initial Al-platinum and Pd-catalysts. Thus, Pt- and Pd-containing catalysts at close values of the total concentration of the acid centers 660 - 620 µmol/g have a different ratio of the centers of unlike force, that possibly determines distinctions in their catalytic properties.

It was found out that the organometallic complexes of Pd and Pt at a magnification of 33,000 times had translucent areas of clusters of polymers which were filled with dispersed particles of 3 nm. At higher magnification (at 62,000 times) small rare clusters of denser particles of 5 nm (Fig. 5) were observed.

The EM analysis revealed that manganese catalysts formed fine, uniformly distributed particles on the surface of the carrier, which was also confirmed by XRD analysis [13, 14].

When changing to the acetate-based catalysts, and in particular, to the catalysts based on manganese nitrate, the particles coarsening was observed, which was apparently the reason for reduction of the manganese catalyst in the reaction of CO and hydrocarbons oxidation.

**CONCLUSIONS**

The used catalyst technology was environmentally friendly due to the replacement of nitrates and chlorides of metals with organic compounds, and highly profitable due to the lower content of noble metals in the catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Characteristics of the porous structure</th>
<th>Total concentration of the acid centers by results of NH₃ adsorption, µmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Specific surface, m²/g</td>
<td>Pores volume, cm³/g</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>200</td>
<td>0.348</td>
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<tr>
<td>Pd/Al₂O₃</td>
<td>205</td>
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<tr>
<td>Pd/Ni-Mn/Al₂O₃</td>
<td>350</td>
<td>0.274</td>
</tr>
<tr>
<td>Pt/ Ni-Mn/Al₂O₃</td>
<td>370</td>
<td>0.290</td>
</tr>
</tbody>
</table>

Table 1. Characteristics of the Pt and Pd catalysts.

Fig. 5. EM - images of clusters: a) detail of Pd cluster with 5 nm size, b) denser Pd clusters with 5 nm particle size.
The developed catalysts on metal carriers for cleaning motor transport and industrial exhaust gases met the standard EURO-3. On the pilot and experimental basis of JSC “D.V. Sokolsky IFCE” the full-size block catalysts on metal carriers with honeycomb channel structure were prepared. The samples made for oil heating furnaces were applied for pilot industrial-scale tests of the catalysts with JSC “Embamunaigas” (Kazakhstan) with real exhaust gases on oil heating furnaces in order to reduce toxic emissions. During the pilot tests it was revealed that the catalytic filters worked effectively and reduced the toxic gases content from 7.7% for nitrogen oxides and up to 100% for carbon monoxide.

The synthesized catalysts were analyzed with a complex of physical and chemical methods. X-ray analysis showed Pd and Pt scattering spectrum, which indicated a high dispersion of the metals. EM method disclosed that manganese catalysts formed fine and uniformly distributed on the surface of the carrier particles, which was also confirmed by XRD analysis.

REFERENCES