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Catalysts for neutralization of waste gases of the vehicles and industry

Abstract: The article is about synthesis of catalysts on block metal carriers for neutralization of waste gases of the vehicles and the industry. Alumina or alumina with the addition of a zeolite or Ce^{4+} , Ti^{4+} , Zr^{4+} , La^{3+} , Fe^{3+} were used for preparation of the washcoats. The compounds of Mn, Ni, Co, Fe and the platinum group metals were applied as the active phase. The synthesized catalysts were tested in the process of complete oxidation of NO_x , CO, C_3H_8 and $NO_x + C_3H_6 + O_2$ reaction. It was revealed that activity of Pd-Mo of catalysts increased at addition in composition of the carrier of cations Ce^{4+} и Zr^{4+} . The activity of palladium catalyst in oxidation reactions CO was equal to 90-100% and was independent of the concentration of metal, in complete oxidation of C_3H_8 at 473-623 K it was 78-90%, for Pt -containing catalyst – 95-100%. It was revealed that in case of the catalysts with base metals introducing of Ti^{4+} significantly increased the degree of reduction of nitrogen oxides with propylene.

Key words: catalyst, neutralization, waste gases, ecology

Introduction

The problem of cleaning of motor transport exhaust gases and the industrial wastes-one of the most urgent issue of the modern world. The exhaust gases of motor transport contain in their composition the hydrocarbons, carbon monoxide, nitrogen oxides, carcinogenic substances which are toxic substances and represent a considerable threat for health of the population [1-4]. Increase in number of means of motor transport – one of the reasons of deterioration in a condition of ecology in the cities and large settlements. Today decrease in harmful emissions of motor transport and the industry to the international standards is possible only by catalytic methods [5-7]. As the catalysts of CO and hydrocarbons oxidation and decomposition of nitrogen oxides are used mainly noble metals on carriers having a high catalytic activity and heat resistance to poisons. Creation of effective and stable catalysts of neutralization of waste gases of the industry and exhaust gases of motor transport and research of physical and chemical bases of improvement of the catalytic systems – an actual issue in the field of an ecological catalysis. One of the promising directions in this area – the partial replacement of noble metal on the oxide component [8, 9]. The work purpose – synthesis of catalysts on block metal carriers and research of their effectiveness in the reactions of purification of toxic industrial and vehicle emissions.

Experimental

For preparation of the block carrier the heat-resistant foil 50 μ thick exposed to goffering is used, on a strip of a smooth foil the strip of a corrugated foil is imposed, then both strips of a foil are displaced in the cylindrical block and are fixed by welding. The following stage in preparation of catalysts – the washcoat (a secondary carrier) is applied on the prepared block metal carriers with the honey comb structure of channels. In Figure 1 the laboratory samples of neutralizers are shown.



Figure 1 – the laboratory samples of neutralizers on metal blocks

As a washcoat with the addition of zeolite or alumina modified by additives Ce^{4+} , Ti^{4+} , Zr^{4+} , La^{3+} , Fe^{3+} were used. For the preparation of solutions of the active components of the catalysts oxides of Mn, Ni, Co, Fe, prepared from acetates and formates were applied. The previously weighed blocks were immersed in the required solution, then were shaken slightly from the excess solution between channels of the blocks, then were dried at 423 K for 2 hours in an oven, after which they were calcined in an electric furnace at 873 K for 2 h. The metal salts are decomposed to form metal oxides on the surface of the carrier the block. The blocks were weighed again and by a difference of masses before and after deposition the concentration of the deposited metal was determined. In case of use of catalysts on the basis of platinum metals in the reactions of oxidation of CO, hydrocarbons and nitrogen oxides decomposition platinum metals were transferred to a colloidal state. It was carried out by impregnation of catalysts by previously prepared solutions of polymers with the added solutions of active metals with the subsequent thermal decomposition. In the work platinum nano-sized particles were prepared by reduction with hydrogen in an aqueous solution containing chloroplatinic acid and citric acid. As the stabilizer of colloid platinum particles isopropyl alcohol is used. The obtained colloidal platinum metal by such methods was coated on carrier block. The metal sols supported on the block carriers were dried in an oven for 4 h at the temperature of 423 K. The catalysts were heated in a muffle furnace at 773 K for 2 h. Also in the synthesis of catalysts acetates of Pt and Pd and their π -complexes as active components of catalysts are used. Solutions of acetate of palladium were prepared by dissolution of Pd in the acetic acid containing 3% of HNO_3 . Nitric acid was removed in the course of evaporation before complete finishing of release of nitrogen oxides. Π -complexes of Pd and Pt were pre-

pared by reacting of allyl alcohol with the salts of these metals with subsequent drying of the catalysts at 423 K and calcination at $T = 773$ K for 2 h. For increase of thermal stability catalysts were modified with additives of the second metal and oxides of refractory metals. For test of catalysts the flowing catalytic installation with the tubular reactor of integrated type was used and the reactions were investigated accordingly early developed method [10-13].

The gas mixture was prepared by feeding of hydrocarbons from container and the compressed air from the line into the mixer. The hydrocarbon content of the mixture was about 0.5 %. The oxygen concentration was varied from 2.0 to 10.0 vol.%. The gas mixture was analyzed by GLC and OPTOGAZ gas analyzer before and after the reaction. Crystal 2000M and Chrom 3700 chromatographs with the flame ionization detector are used. Analysis duration – 20-30 min. The activity of the catalysts was determined at temperatures of 423-773 K.

Characteristic of activity of the catalyst was the degree of conversion (α) of initial reagent (hydrocarbon, carbon monoxide, nitric oxide), defined by the formula:

$$\alpha = \frac{C_{init} - C_{fin}}{C_{init}} \cdot 100 \%,$$

where C_{init} and C_{fin} – are the initial and final concentrations of a reagent in volume of a test.

Results and discussions

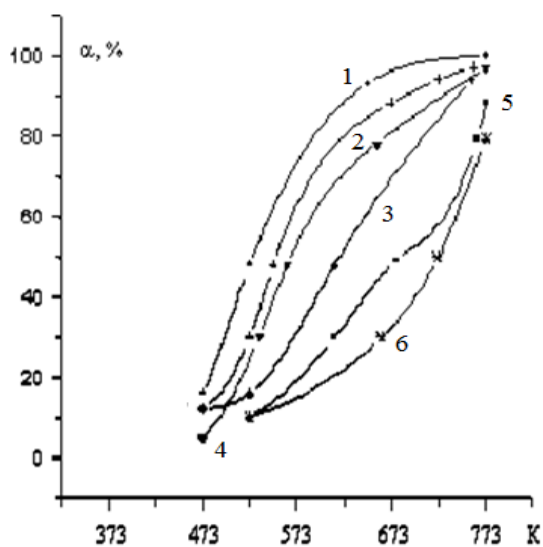
As an example, the results on studying of influence of concentration of Pt and Pd in π -allelic complexes on activity of block catalysts in reaction of oxidation of CO, C_3H_8 and reduction of NO_x at a volume speed of a stream of gases – 35,000 h⁻¹ are given in the Table.

Table – Influence of concentration of π - allylic complexes of Pt and Pd on a degree of conversion of CO, C_3H_8 , NO_x

| Catalyst | The active metal concentration, % | Conversion degree, % at the different temperatures of research of catalysts, K | | | | | | | | | | | |
|-----------------|-----------------------------------|---|-----|-----|-----|----------|------|-----|-----|--------|------|------|-----|
| | | CO | | | | C_3H_8 | | | | NO_x | | | |
| | | 773 | 623 | 523 | 473 | 773 | 623 | 523 | 473 | 773 | 623 | 523 | 473 |
| Pt π -allyl | 0.01 | 100 | 100 | 89 | 16 | 95 | 85.0 | 50 | 0 | 20 | 20.7 | 13.9 | 0 |
| Pt π -allyl | 0.05 | 100 | 100 | 92 | 50 | 98 | 94.0 | 73 | 0 | 20.7 | 21.1 | 14.4 | 0 |
| Pt π -allyl | 0.1 | 100 | 100 | 100 | 87 | 100 | 99.0 | 73 | 17 | 34.2 | 36.7 | 17.1 | 1.2 |
| Pd π -allyl | 0.1 | 100 | 100 | 100 | 83 | 53 | 22.0 | 5.0 | 0 | 18.4 | 16.8 | 8.0 | 0 |
| Pd π -allyl | 0.15 | 100 | 100 | 100 | 90 | 59 | 32.0 | 18 | 0 | 24.0 | 26.6 | 16 | 0.5 |

Data of the Table show that activity of palladium-containing catalyst in reaction of oxidation of CO doesn't significantly depend on concentration of metal and reaches 90-100% in the studied interval of temperatures. By the way the efficiency of Pd-catalyst in reaction of complete oxidation of C_3H_8 at low temperatures (623-473 K) was much lower, than that of the Pt-catalyst, and was 78-90%. The higher activity of the Pt-catalyst in reaction of NO reduction in comparison with Pd the catalyst was observed at contents of Pt equal to 0.1 % and $T=773$ K.

Research of Pt and Pd catalysts on thermo stability was carried out by maintaining of the catalyst with an interval of 5 h at $T=773$ K in a reactionary gas mixture with the contents of 0.5 % of propane-butane with the subsequent analysis of products of reaction. The total duration of researches was 100 h. The most stable appeared the catalysts obtained from acetates Pt, less stable – on basis Pd.



1-0.1% Pt-initial Pt, 2- 0.1% Pt-50 h. of testing, 3-0.1% Pt- 100 h., 4- 0.2% Pd-initial Pd, 5- 0.2% Pd-50 h. of testing , 6- 0.2% Pd-100 h. of testing

Figure 2 – Dependence of stability of catalysts in reaction of 0.5 % of propane-butane in air oxidation

It's known that by **supporting of the secondary oxide** covering on metal blocks of honey comb structure, as a rule, the carriers with the developed specific surface and porous structure are produced [14-16], and high thermal stability of the secondary oxide covering is provided with introduction to it of the modifying additives. There are the works about inclusion of cerium, zirconium, lanthanum cations into the secondary alumina coating, which stabilize

γ - Al_2O_3 phase and provide resistance to poisons or sintering of Pt, Pd, Rh-active components of the catalysts [17, 18].

In this work Pd-Mo-catalysts on Al_2O_3 carrier modified by additives of Ce^{4+} , Ti^{4+} , Zr^{4+} , La^{3+} , Fe^{3+} were prepared and investigated in reaction of $NO_x + C_3H_6 + O_2$. Activity of Pd-Mo of catalysts increased when modifying the carrier with cations of Ce^{4+} , Zr^{4+} .

Activity of Pt-Cu catalysts on the zeolite-containing carriers NaY, ZSM-5 and their hydrogen forms was studied. High activity of the catalyst is noticed when supporting of the active phase on the carrier in H^+ -form. A number of oxidic catalysts with the differing compositions of the **secondary carrier** (γ - Al_2O_3 , γ - $Al_2O_3 + TiO_2$) and of the active agent (Co+Mn, Fe+Mn) promoted and not promoted by platinum is studied. Introduction of titanium dioxide into the secondary carrier considerably increases extent of reduction of nitrogen oxides by means of propylene on both compositions of oxidic catalysts in all interval of the studied temperatures (423-773 K) and was equal to 34% at 523 K on the Co-Mn-catalyst, to 29% -on Fe-Mn, and at 773 K-33% and 55%, respectively. Promotion with platinum improves the reduction ability of cobalt-manganese catalyst on Al_2O_3 only at temperatures higher than 673 K. On the titanium-containing sample in the presence of platinum degree of NO conversion is decreased.

The samples of catalysts based on platinum group metals were investigated by electron microscope EM-125K with single stage replica method. In a sample with Pt the small congestions of dense particles which don't grow together in units and are dispersed on a carrier surface are observed. The particles sizes are predominantly 10.0 nm, 5.0 nm and less 9.0 nm (fig.3, a). In the sample with Pd there are some isolated dense particles in size 12.0 nm-15.0 nm (fig.3, b). The platinum obtained by reduction in solution has the sizes about 15.0-18.0 nanometers, at the same time, the platinum colloid obtained by reduction with lemon acid had almost monodisperse distribution, the average size of particles was equal to 8.0 nanometers. It is found that the organometallic complexes of Pd and Pt at magnification of 33,000 times represent translucent areas of the clots of polymer filled with dispersed particles of 3.0 nm. At higher magnification (in the 62,000 times) also small rare congestions of more dense particles of 5.0 nm in size are observed.

Investigation of Pt and Pd-containing catalyst by means of XPA showed X-ray scattering, which confirmed the high dispersion of catalysts obtained

by thermal decomposition of organometallic complexes.

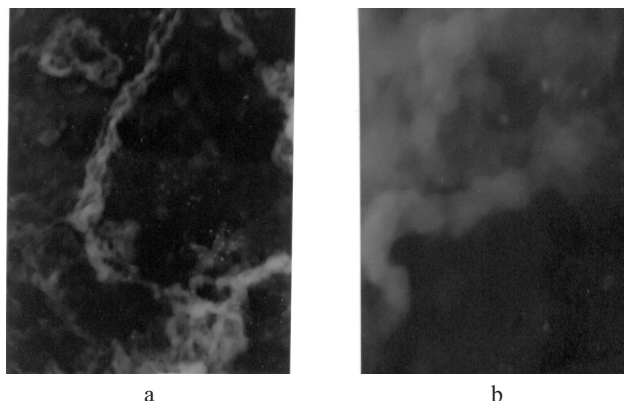


Figure 3 – EM – pictures of distribution of noble metals: Pt (a), Pd (b) on the metal carrier

Physical and chemical researches of catalysts on the basis of base metals were carried out by XRD method on x-ray diffractometer DRON-4.0.7 with the copper anode. Samples for research were prepared by mechanical destruction of the catalyst put on a block metal framework. The fallen part of the catalyst was crushed in an agate mortar up to 100 μ and was used for research by method XPA. It was found, that the oxide catalysts represented spinel with cubic lattice NiMnO₄ with peaks 2 \AA , 52 \AA , 148 \AA , 203 \AA . Also there were small intensive peaks of CeO₂ (308 \AA) and alumina (160 \AA , 256 \AA). The conducted research of supports and catalysts by means of XPA showed the formation TiO₂ – anatase structure, peaks 3.52; 1.89; 2,38 \AA . The carrier based on V₂O₅-WO₃ – peaks 4.38, 3,4, 2,8 \AA , it has an orthorhombic lattice. In the active phase NiO-crystal lattice is not formed. Catalysts based on base metals have been investigated with an electron microscope EM-on device 125M single by stage replica method. On a nickel-vanadium-tungsten sample the congestions of dense particles which don't grow together in units and are dispersed on a carrier surface are observed. The sizes of particles were mainly 15.0-20.0 nanometers.

For samples of Pd-Mo catalysts (fig.4) there are found Al₂O₃ peaks (25.5, 35.0, 37.8, 43.4, 52.9). It was found that a position of a peak of PdO (it should be at approx. 33.9-34.1) is insignificantly moved to the left, it is apparently due to slight interaction between Mo and Pd. Data XRD not don't confirm formation of solid solution or alloy of Pd-Mo.

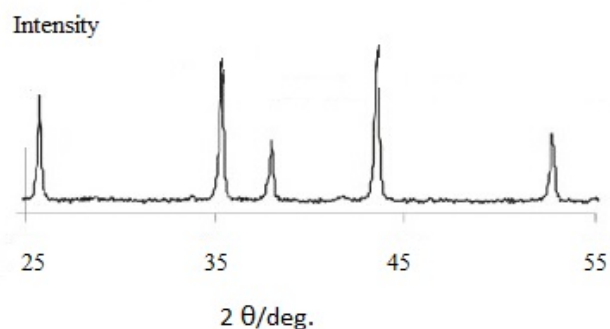


Figure 4 – XRD image of Pd-Mo/Al₂O₃ catalyst (after calcination)

Conclusions

Catalysts for neutralization of toxic gases of the industry and motor transport on metal carriers with the honey comb structure of channels are prepared. For preparation of the secondary carrier were used either aluminum oxide or aluminum oxide with the addition of a zeolite or Ce⁴⁺, Ti⁴⁺, Zr⁴⁺, La³⁺, Fe³⁺. For preparation of solutions of the active components of catalysts are applied oxides of Mn, Ni, Co, Fe, obtained from acetates and formiates. Also were synthesized the samples of catalysts based on metals of the platinum group converted into colloidal state. The activity of Pd-Mo catalysts carrier is increased by modifying with cations Ce⁴⁺, Zr⁴⁺. The activity of the palladium catalyst does not depend on the metal concentration in the CO oxidation reaction and is about 90-100%. However, the effectiveness of the Pd-catalyst in the C₃H₈ complete oxidation reaction at low temperatures (623-473 K) is significantly lower than of Pt-catalyst, and is 78-90%. For catalysts based on base metals introducing into the secondary carrier of Ti⁴⁺ significantly increases the degree of reduction of nitrogen oxides with propylene, at 523 K on a Co-Mn-catalyst – 34%, on Fe-Mn – 29%, at 773 K – 33% and 55%, respectively.

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