



Catalytic Hydrogenation of Gasoline Fractions under Elevated Pressure

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ABSTRACT

The objective of this study was the development of catalysts for catalytic liquid-phase hydrogenation of gasoline fractions of Atyrau Refinery LLP at elevated hydrogen pressure. The selective efficient catalysts on the basis of the platinum metals applied on various carriers are synthesized. The hydrogenation of two gasoline fractions Stable catalysate LH (0.37% benzene), straight-run gasoline AVT (3.18% benzene) was studied. After the catalytic hydrogenation the benzene is absent, the content of aromatic compounds is reduced from 55.12% to 32.5 (wt.). The content of olefins is reduced from 0.23 to 0.11% (wt.) and paraffins content is decreased from 12.41 to 11.99% (wt.), but the amount of isoparaffins increased from 30.08 to 34.09% (wt), naphthene content increased from 2.12 to 10.14% (wt). Octane numbers of petrol fractions after hydrogenation were practically unchanged, while the benzene content decreased from 3.18% (initial sample) to the total absence in the samples.

Keywords: hydrogenation, aromatic ring, gasoline, catalysts

1. INTRODUCTION

The gasolines-one of the main types of fuel for the modern technique therefore the success in development of this branch to a large extent indicates the strategic capacity of any country [1-3]. Environmental standards on quality of gasolines, and in particular, to the content of aromatic hydrocarbons in automobile gasolines, from year to year become tougher [4-7]. As a result, the catalytic hydrogenation of straight-run gasoline fractions improve the performance of petroleum fuels, oils and raw materials for the petrochemical processing

[8-13]. Thus, development of the high performance catalysts and research of catalytic hydrogenation providing the hydrogenation of benzene and polycyclic aromatic hydrocarbons in petrol fractions improving structure and ecological properties of gasolines is a perspective and actual task.

The objective of this study was to develop a catalyst for a process improving the performance of gasoline: catalytic liquid-phase hydrogenation of gasoline fractions of Atyrau Refinery LLP at elevated hydrogen pressure.

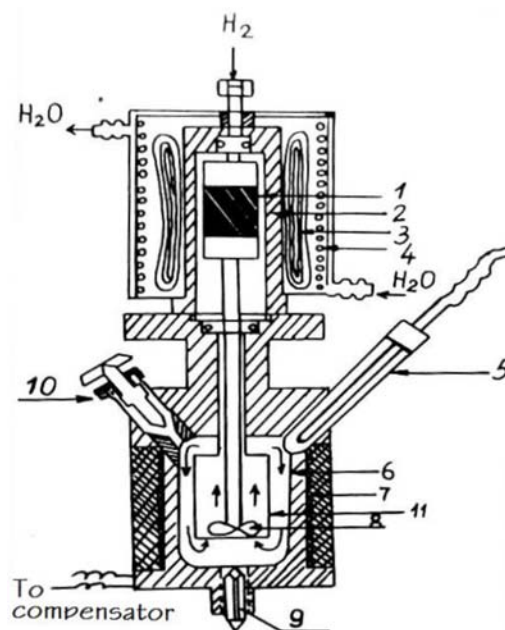
2. MATERIALS AND METHODS

2.1 Equipment and Method of Hydrogenation

The hydrogenation of petrol fractions at elevated hydrogen pressure was studied on kinetic installation of high pressure and in the autoclave-the device for carrying out processes at elevated pressure with heating of firm "Amar Equipment Ltd" (India). The main part of KIHP-the advanced autoclave of Vishnevsky (Figure 1) from a titanium of VT-3 (total amount-60.0 ml) with the hermetic electric drive, turbine stirrer (rotation speed-2800 rev/min, stirring intensity-40,000 Re). The experiments were carried out in the isobaric-isothermal mode on previously developed technique [14-18]. The start of stirring of the reaction medium is accepted to the beginning of reaction. Process of hydrogenation was fixed by quantity of hydrogen absorbed per unit of time (60 sec.). During the reaction, the samples were taken for chromatographic analysis. In the autoclave Amar Equipments Pvt.Ltd is carried out hydrogenation both the small, and enlarged batches of raw materials. For placement of reagents in this autoclave it was necessary to turn off and remove a device upper with the engine.

The hydrogenation of two gasoline fractions Stable catalysate LH (0.37% benzene), straight-run gasoline AVT (3.18% benzene) of Atyrau Refinery LLP was studied. Reactions were carried out with the electrolytic hydrogen from the balloon (99.8%), for the gas liquid chromatography (GLC) was used helium (99.992%) from a cylinder. The alcohols and hexane of mark "chemically pure" were used as solvents. Experimental conditions: amount of gasoline -5.0 or 30.0 ml, amount of catalyst within 0.5-3.0 g; 2.0-4.0 MPa hydrogen pressure, the reaction temperature-293-373 K. The results of experiments on reduction of

gasoline fractions made out in the form of curves on rectangular coordinate system, where the horizontal axis represents experience duration in min. (τ), on the y-axis of the volume of hydrogen per cm^3 .



1- rotor, 2- a shielding sleeve, 3-stator, 4- cooling of the stator, 5- thermocouple, 6- reactor vessel, 7-electrical heating, 8- spiral mixer, 9- lower cone valve 10- unit for enter the catalyst, the solvent and hydrogenated compounds, 11-guiding glass.

Figure 1. Scheme of the improved autoclave Vishnevsky with hermetic electric drive.

2.2 Analysis of the Initial Compounds, Reaction Products and Catalysts

For qualitative and quantitative analysis of the initial compounds and reaction products the methods of gas-liquid chromatography (GLC), iodometric titration and method of aniline point were used. For carrying out GLC were used the gas-liquid Chromatograph Crystal M 4000 (Yoshkar-Ola, Russia) with a capillary column Zebron ZB-1 (30 mlx 0.53 mmIDx 5.00 μm , a liquid phase - 100% dimethylsiloxane, gas-carrier-helium, the

detector - flame and ionization; the gas-liquid Chromatograph "3700": a packed column with a stationary phase of 15% Carbowax - 1500. GLC analysis of the gasoline fractions was carried out according to the method in [19-21]. The total analysis time is equal to 90-120 min. A sample of the hydrocarbon of gasoline was injected into the chromatograph, each obtained peak was identified by comparing its retention index by the table index, or visually by comparison with standard chromatograms. This method allows to carry out determination of the individual hydrocarbon composition at a concentration of at least 0.05% by wt. Hydrocarbon components eluting after C_{13+} , are defined as one group. The use of low-temperature thermostating allows to define the components of motor gasoline, including oxygenates. The mass concentration of each hydrocarbon component was determined by normalized area and coefficients of sensitivity. The peaks which are shown later n-nonane were summarized and recorded as C_{10} . Manual sample selection of gasoline fractions was carried out according to the instruction [22]. After sampling a container was stoppered. The sample was cooled to about 277 K and maintained at that temperature immediately prior to analysis. An aliquot of the cooled sample was transferred into a precooled vial with gasket and was sealed. The test specimen was collected by syringe directly from a hermetically sealed closed vial, using the manual entry of samples. Gasoline sample was stored in a refrigerator. Determination of octane number was performed by motor and research methods.

In the work were also used physical and chemical research techniques of catalysts: X-ray diffraction, infrared spectroscopic analysis method on "Specord JR-75" and "UR-20." Samples of the synthesized catalysts

were investigated by techniques a electron microscopy (scanning and penetration), BET, porosimetry, BET (by nitrogen adsorption on the apparatus "Accusorb"), porosimetry.

2.3 Preparation of Catalysts

The catalysts for the hydrogenation of gasoline fractions were synthesized by impregnating a carrier (alumina γ - Al_2O_3 , silica- SiO_2 , activated carbon, zeolites-HY, HZSM-5, modules 30 and 80) with aqueous solutions of the active metal salts - $PdCl_2$, $RhCl_3 \times 3H_2O$, $H_2PtCl_6 \times 6H_2O$, $RuOHCl_3$, $CuSO_4 \times 5H_2O$. Samples of catalysts were prepared with various atomic ratio of metals - from 9:1 to 1:9. For carrying out a stage of impregnation was prepared aqueous 1.0% solution with the compound containing the active component. A solution of the active ingredient was added dropwise at a predetermined rate in a certain temperature regime under vigorous stirring. Two-component catalysts (based on Pd-Pt, Rh-Pt, Pd-Rh) were prepared by joint impregnation of the carrier solutions of the corresponding compounds. When preparing the Pd-Pt composition of the samples was used also 2.0% solution of Na_2CO_3 . Soda solution was added dropwise to the carrier after the impregnation step of a carrier with solutions of the compounds containing the active component. Calculation of an amount of water for preparation of 2.0% Na_2CO_3 solution was carried out taking into account presence of water in hydrate. The prepared soda solution is was dripped into a glass with the carrier and the solution of the active ingredient to achieve the environmental $pH_{\text{solution}} = 8$. The catalyst mass was washed with distilled water from chlorine ions. For this purpose the water jet pump, Bunsen's flask and a Buchner filter were used. Some samples of catalysts were reduced in hydrogen current at 473 K in the quartz

furnace. The prepared catalysts were cooled to room temperature and stored in sealed containers in desiccators. Before each experiment, the catalysts in the conditions required for the experiment, was reduced in hydrogen for 30 minutes in a solvent medium.

3. RESULTS AND DISCUSSIONS

On the bimetallic catalysts of composition Rh-Pd and Rh-Pt in the first minutes of the process is much greater absorption of hydrogen than on the catalysts of another composition took place. In the final samples the content of both benzene, and aromatic compounds is decreased (in total). On different catalysts effect of hydrogen pressure on parameters hydrogenation of gasoline fractions was investigated. Thus as an example on Rh-Pt(9:1)/Al₂O₃ catalyst with increase in

pressure of hydrogen in the range of 0.5-5.0 MPa duration of process was decreased twice. Benzene with the content of 0.06% was found only at pressure of 3.0 MPa, at other pressure of hydrogen benzene in the final test was absent. As a result of gasoline fractions hydrogenation aromatics content in the final tests was within 32.5-34.6%. Order of reaction on hydrogen according to bilogarithmical dependence of speed on pressure by the time of absorption of 1 mole of hydrogen is close to 1. Figure 2 shows a typical chromatogram of a sample of the initial gasoline Stable catalysate LH. In Table 1, 2 data on hydrogenation of gasoline fractions on various catalysts are given. Data on the quantitative and qualitative compositions of initial gasoline fractions and after hydrogenation are presented.

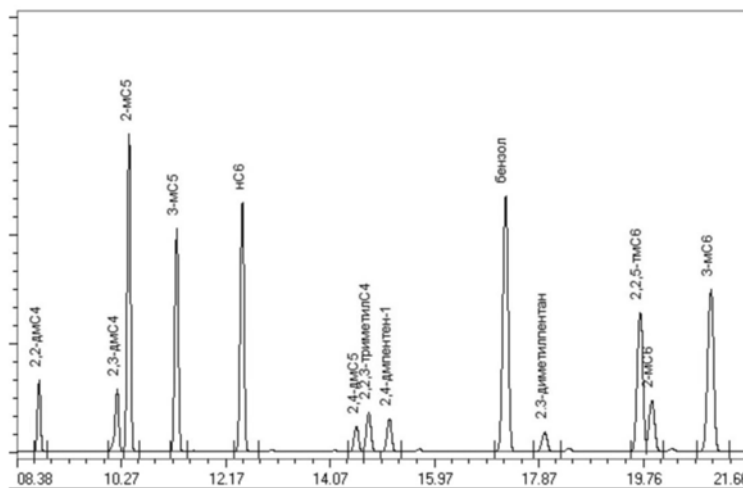


Figure 2. The chromatogram of the initial sample of gasoline stable catalysate LH (benzene peak - 17.2).

It should be noted that among carriers, except for coal, reaction rate correlates with decrease of acidity of the carrier.

On the chromatogram of the sample

after the hydrogenation of gasoline in the final sample benzene was absent - the chromatogram was without benzene peak (Figure 3).

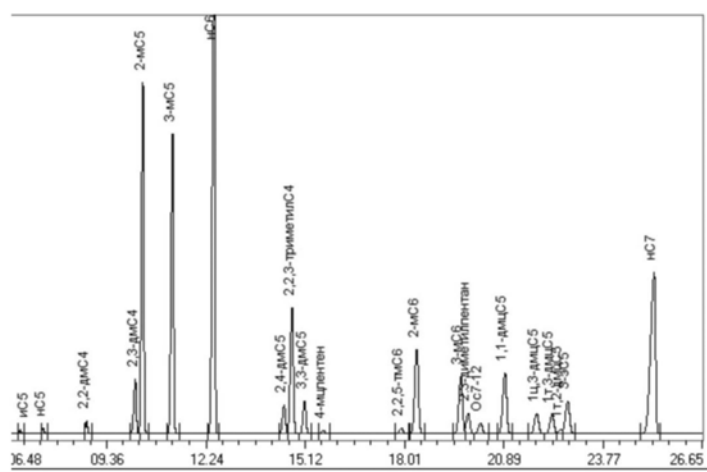


Figure 3. The chromatogram of the initial sample of gasoline stable catalysate LH after hydrogenation.

Table 1. Hydrogenation of gasoline fractions on various catalysts in hexane at $P_{H_2} = 4.0$ MPa, $T = 298$ K, $V_{\text{gasoline}} = 30.0$ ml, $V_{\text{solvent}} = 10.0$ ml, $q_{\text{cat}} = 1.0$ g, total duration - 45 min.

Catalyst	Gasoline fraction	The components content, wt.%			
		benzene		aromatics (total)	
		initial sample	after hydrogenation	initial sample	after hydrogenation
2%Rh-Pt/HY	Stable catalysate LH	3.18	0.2	55.12	37.2
	Straight-run gasoline AVT	0.37	0.1	9.93	5.25
0.5%Rh-Pt/ Al_2O_3	Stable catalysate LH	3.18	0.0	55.12	32.8
	Straight-run gasoline AVT	0.37	0.0	9.93	4.8
2%Pt/HZSM-5 (module 30)	Stable catalysate LH	3.18	1.2	55.12	42.0
	Straight-run gasoline AVT	0.37	0.0	9.93	5.4
2% Pt/HZSM-5 (module 80)	Stable catalysate LH	3.18	1.0	55.12	40.9
	Straight-run gasoline AVT	0.37	0.05	9.93	5.1
0.5%Rh-Pd/ Al_2O_3	Stable catalysate LH	3.18	1.5	55.12	40.0
	Straight-run gasoline AVT	0.37	0.2	9.93	6.1
2% Pd-Cu/C	Stable catalysate LH	3.18	2.0	55.12	42.0
	Straight-run gasoline AVT	0.37	0.3	9.93	6.4

Table 2. The group composition of hydrocarbons before and after hydrogenation, in the gasoline fraction stable catalysate LH on 0.5% Rh-Pt/Al₂O₃, $q_{cat} = 1.0$ g, total duration -45 min.

Gasoline fraction	Hydrocarbons content, % wt./ % vol.					
	paraffins	iso-paraffins	olefins	naphthenes	aromatic compounds (in total)	benzene
Initial	12.41/14.78	30.08/34.09	0.23/0.25	2.12/2.30	55.12/56.76	3.18/2.78
After hydrogenation	11.99/10.55	34.09/37.45	0.11/0.12	10.14/8.21	32.51/33.47	0/0

So, data on the composition of the group of organic substances in gasolines showed that after the catalytic hydrogenation of benzene was absent, the content of aromatic compounds was reduced from 55.12 to 32.5 % (wt.). Olefin content was reduced from 0.23 to 0.11% (wt.) and a paraffin content was reduced from 12.41 to 11.99% (wt.) and the amount of isoparaffins was increased from 34.09 to 30.08% (wt.). Naphthene content was increased from 2.12 to 10.14% (wt.).

The experimental results show that, irrespective of the amount of hydrogenated gasoline after the hydrogenation is significantly reduced content of aromatics; and more catalyst (2.0 and 0.5 g catalyst) - the less the content of both aromatics (total), and of benzene. The greatest activity in the hydrogenation of gasoline showed bimetallic Pt-Rh-catalysts on various carriers.

In the LLP “Independent Centre of Expertise of oil products ORGANIC” (Almaty, Kazakhstan) were determined octane numbers of gasoline fractions before hydrogenation and after hydrogenation. Octane number on the research method Stable catalysate both before and after the hydrogenation has not changed (94.0); the octane number by the motor method prior to the reaction - 82.6, after the reaction - 82.7. For straight-run gasoline fraction AVT octane

number on the research method before and after the experiment was equal to 60.0, by the motor method -50.0. Thus the carrying out hydrogenation in the gasoline fractions did not reduce octane number of gasolines.

By the method of scanning electron microscopy the surface of the catalyst was researched. An interesting object was one of the most active in the hydrogenation of benzene catalyst with the composition 0.5% Pt-Pd/Al₂O₃. On Figure 4, a-c are presented EM images of this catalyst at various magnifications (1-100 μm), in Figure 4d is seen the homogeneous uniform distribution of catalyst particles on the carrier surface. Metal particles of 30-80 nm in size are distributed on the surface of alumina and represent the mixed bimetallic Pt-Pd agglomerates together with Pd particles. It was revealed that in case of mixed Pt-Pd catalys nanoparticles had different diameters according to its composition (ratio between Pt and Pd). At higher amount of Pd (in % wt.), nanoparticles have larger diameters. Figure 5 shows the results of studies by scanning electron microscopy of some catalyst supports: Al₂O₃ (a) and HZSM-5 (b). Structure of Al₂O₃ carrier consists of acicular crystalline structures with the size 200-300Å, specific surface area $S = 117.9$ m²/g and pore size - 400Å. The initial sample of HZSM-5

is presented by predominantly extensive congestions of dispersible particles, which are located on the support surface. A general view shows a sample at low magnification in Figure 5, b. The results of analysis and determination of physico-chemical characteristics of catalysts show that the synthesized catalysts have a considerable surface area and pore volume. It was found that catalysts on the base of Pd-Cu supported on a surface area C is almost 2 times greater than the surface of catalysts supported on γ -Al₂O₃. Pores of catalysts with γ -Al₂O₃ carrier have the shape of cylinders, which radius are within the range 20-22 Å. According to XPS, palladium on C is fully reduced to the zero-valent state, whereas γ -Al₂O₃, palladium is not fully reduced. Electron binding energy Pd° 3d_{5/2} Pd/C is 336.5 eV, corresponding to Pd²⁺. Modification of the catalyst with copper ions does not change the binding energy of the electron Pd 3d_{5/2}.

By XRP-method it was revealed that in the copper-modified catalysts based on Pd (Pd-Cu) - Pd is in the zero valence state, and the state of copper Cu is characterized by the binding energy of 2p_{3/2} electrons, equals to 932.7 eV, corresponding to Cu⁺, so it's possible to suggest that Cu catalysts are in the form of Cu₂O. In addition to the zero valent Pd, there is also oxidized form of palladium (PdO₂) on the surface. Figure 6 shows EM image of 2%-Pd-Cu/g-Al₂O₃. 0.5%Rh-Pd (9:1)/Al₂O₃ catalyst is presented (Figure 7) by a congestion of particles to 400Å, the microdiffraction patterns of which is in view of the rings, and the separate reflexes which are located by hexagonal motive and correspond to RhO₂ (ASTM 21-1315 reflex), sometimes mixed with PdO (reflex 2.77). The electron diffraction pattern with diffuse rings Rh and Pd, pointing to small particle size - a particle size up to 30 Å is revealed.

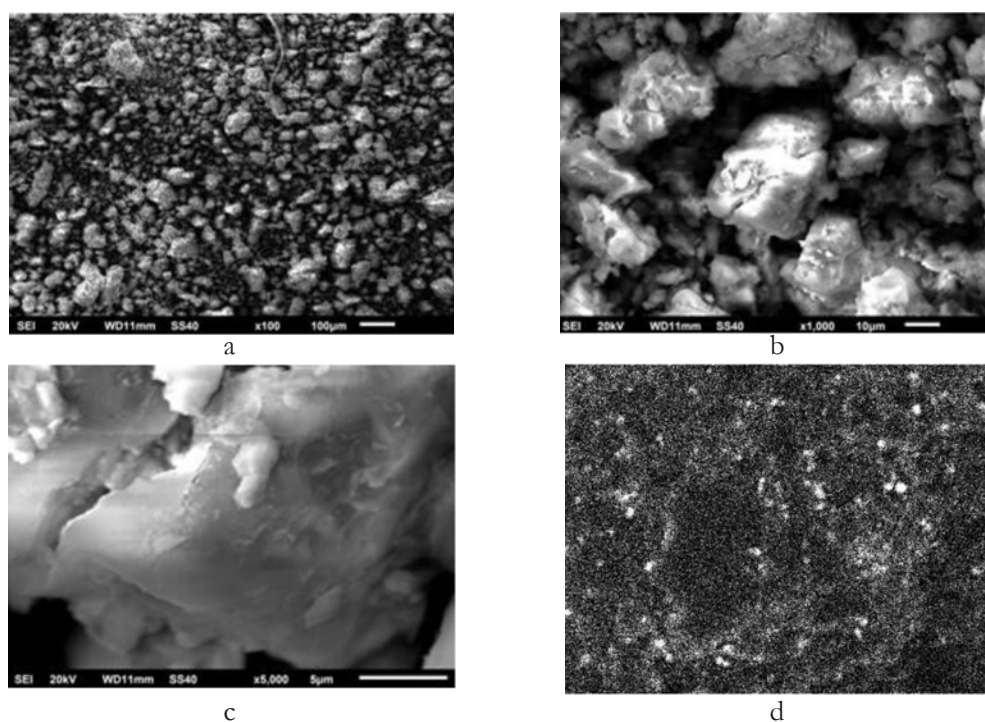


Figure 4. EM pictures-of 0.5%Pt-Pd(9:1)/Al₂O₃ catalyst at the different magnifications. a- 100, b- 1,000, c- 5,000, d- uniform distribution of catalyst particles

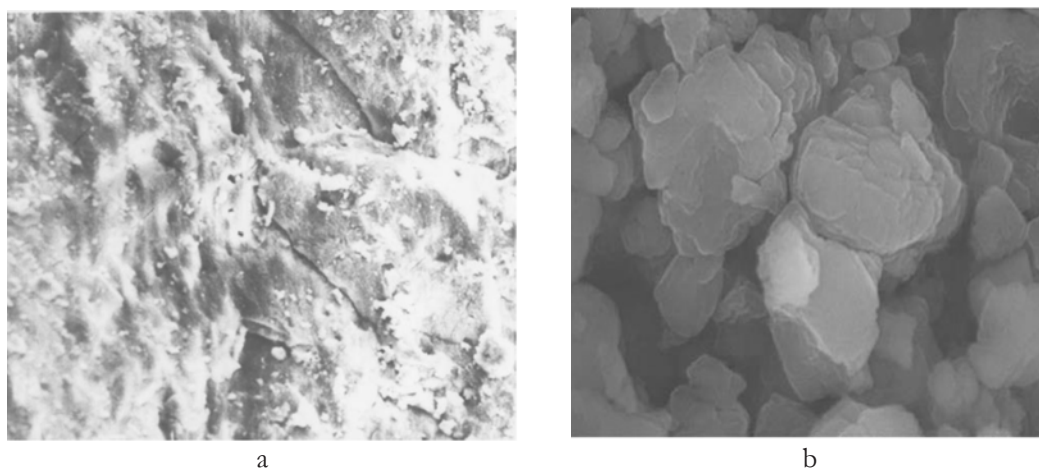


Figure 5. EM-pictures of carriers : a) γ - Al_2O_3 , b) HZSM-5.

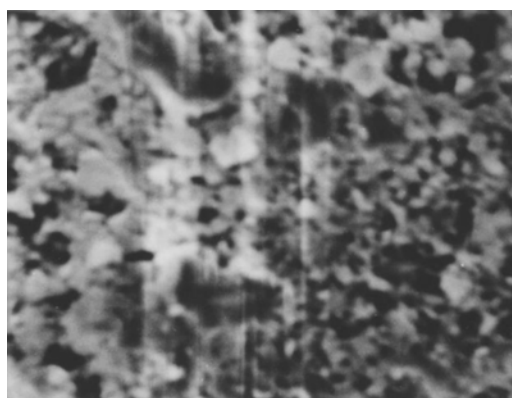


Figure 6. EM image of 2%-Pd-Cu/g- Al_2O_3 .

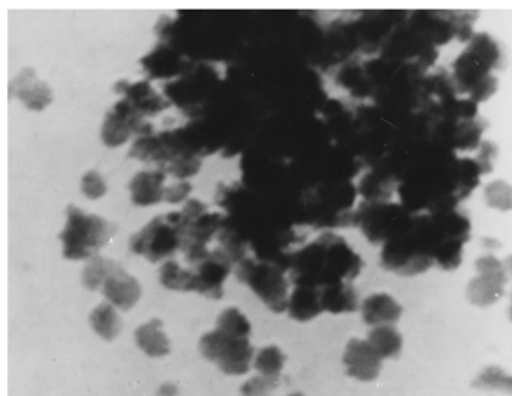
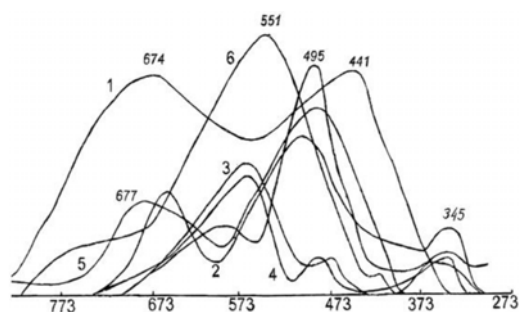


Figure 7. EM-images 0.5% Rh-Pd (9:1)/ Al_2O_3 (120.000 magnification).

Results testing of catalyst by method hydrogen TPD show that for supported bimetallic catalysts number of forms of the sorbed hydrogen, characteristic for each of the components remains constant, while the ratio between the hydrogen forms vary considerably with the change of the catalyst composition (Figure 8). Hydrogen from Pd-Pt-catalysts put on γ - Al_2O_3 is desorbed in the form of dissolved and strongly adsorbed. If use addition of Pd and Pt in composition of the Rh-catalyst there is a shift of position of peaks of a desorption of hydrogen and change in a ratio of a share of this or that form of hydrogen. Probably, the high selectivity of 0.5% Rh-Pt (9:1)/ Al_2O_3 is associated with the presence of a large share of hydrogen with an average energy bond with the surface. A mixed Pt-Pd catalyst has a higher adsorption capacity to hydrogen than platinum and palladium separately.

The results of the physico-chemical studies of the synthesized catalysts are consistent with the literature data [8-10, 23-25].



1-0.5% Rh/ Al_2O_3 ; 2 - 2%Pd/ Al_2O_3 ; 3 -0.5% Rh-Pd(1:1)/ Al_2O_3 ; 4-0.5%Rh-Pt(1:1)/ Al_2O_3 ; 5-0.5%Rh-Pd(9:1)/ Al_2O_3 ; 6-0.5%Rh-Pt(9:1)/ Al_2O_3

Figure 8. Thermal desorption of the catalysts with different compositions in condition of linear programmed increase of temperature of the catalysts from 293 to 1023 K.

4. CONCLUSIONS

Thus, the effective selective catalysts on the basis of the platinum metals applied on various carriers were developed. The hydrogenation of two gasoline fractions Stable catalysate LH (0.37% benzene), straight-run gasoline AVT (3.18% benzene) was investigated. Data on group composition of organic compounds in gasolines showed that after the catalytic hydrogenation the benzene was absent, the content of aromatic compounds was decreased from 55.12% to 32.5 (wt.). Octane numbers of gasolines after hydrogenation were unchanged and the benzene content decreased from 3.18% (initial sample) to the total absence in the samples.

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