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# The selective catalytic reactions for improvement of characteristics of gasolines

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The aim of the research is the development of selective catalysts for the processes improving service performance of gasolines: catalytic hydrogenation of gasoline fractions and production of octane-increasing component of fuel additives – diisopropyl ether (DIPE). The data on the content of organic compounds in the gasoline fractions after the reaction of catalytic hydrogenation show that benzene was absent, the content of aromatic compounds was reduced from 55.12% (wt.) to 32.5% (wt.). The olefins content was reduced from 0.23% (wt) to 0.11% (wt), and the paraffins content - from 12.41% (wt.) to 11.99% (wt), whereas the iso-paraffins content increased from 30.08% (wt) to 34.09% (wt). The content of naphthenes increased from 2.12% (wt.) to 10.14% (wt.). The developed catalytic method of DIPE synthesis from iso-propanol and propane under mild conditions allowed production at a yield of 30.5-68.5%. The most active and stable catalysts for synthesis of DIPE from iso-propanol are molybdenum- and nickel-containing catalysts. The maximum DIPE yield in the optimal temperature range (250-300 ºC) was 62.0-68.5%.

**Keywords:** catalysts, gasoline, hydrogenation, additives, diisopropyl ether, metal blocks

## INTRODUCTION

Today the production of gasolines is one of the major processes in the oil refining industry and largely determines not only the development of the industry, but also the strategic potential of a country [1,2].

Catalytic hydrogenation of straight-run gasoline distillates in the presence of efficient catalysts allows hydrogenation of benzene and polycyclic aromatic hydrocarbons - one of the most perspective and relevant methods of improvement of the operational properties of fuels [3-6]. The increased content of aromatic hydrocarbons, especially bicyclic ones, leads to reduction of speed and completeness of combustion of fuel, promotes carbonizing in the combustion system of the engine and worsens the ecological situation in the world. Thus, the development of highly effective catalysts for catalytic hydrogenation (hydrodearomatization) providing hydrogenation of benzene and polycyclic aromatic hydrocarbons in gasoline fractions improves the composition and ecological characteristics of gasoline - a prospective urgent task. The development of gasoline production is connected with the desire to improve the basic operational properties of the fuel – knock resistance, estimated octane number, as well as reduction of the toxic effects of gasoline, i.e. improvement of the sustainability of the used fuels. Such issues can be solved either by changing the chemical composition (conversion of gasoline compounds) or by application of fuel additives. The use of various fuel additives worldwide allows production of fuels which release minimal amount of nitrogen oxides, carbon oxides, and various organic substances into the atmosphere during combustion and exploitation. Diisopropyl ether (DIPE) is a promising substitute for MTBE due to non-toxicity, lower volatility and lower production costs [7-9]. The aim of this research was to develop catalysts for the two processes that improve the operational properties of gasoline: (1) catalytic hydrogenation of gasoline fractions (hydrodearomatization) and (2) synthesis of octane-enhancing component of additives – DIPE.

## EXPERIMENTAL

In the research two types of catalysts were used: in order to study the hydrogenation of the aromatic ring in gasoline fractions supported catalysts based on platinum group metals with additives were synthesized; whereas for DIPE synthesis research catalysts on metal blocks were prepared. Synthesis methodology for both types of catalysts was developed earlier by the authors of this article [10-17]. For the preparation of the supported hydrogenation catalysts the following carriers were used: aluminum oxide γ-$Al_2O_3$, $SiO_2$ and activated carbon. The catalysts were prepared by deposition of the respective active metal compounds on the carrier by impregnation. Two-component catalysts (based on Pd-Pt, Rh-Pt, Pd-Rh) were prepared by joint impregnation of the support with the solutions

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of the corresponding compounds. For the Pd-Pt samples 2% solution of $Na_2CO_3$ was also used. The dripping of $Na_2CO_3$ solution was performed after termination of support impregnation with the solutions of the compounds containing the active component. Before each experiment, the catalysts were reduced in a solvent medium in hydrogen for 30 min in the conditions required for the experiment.

The preparation of the catalysts on the metal blocks for the synthesis of DIPE was conducted according to the methodology comprising several successive steps: (i) preparation of metal blocks, (ii) impregnation of blocks with secondary support (based on aluminum), and (iii) application of active metal compounds on the metal blocks impregnated with a secondary carrier [10-14]. For the preparation of metal blocks a heat-resistant foil of 50 µm thickness and required length and width was used, which was corrugated by folding of the superimposed smooth foil and corrugated tape into a cylindrical block (Figure 1). For the preparation of the catalysts on the metal blocks the corresponding salts of the active metals (acetates, nitrates, etc.) were applied. Catalysts with molybdenum, tungsten, manganese, vanadium, nickel and niobium as the active phase were synthesized using the compounds of the base metals. The metal compounds were applied on the secondary carrier by impregnation of alumina and zeolites NaY, ZSM-5 with different silicate modules (30 and 80). The metal concentrations ranged from 3% to 7 %.

As a method for the synthesis of nano-sized complex-oxide catalysts the pyrolysis of polymer-salt compositions was used. This method is versatile, flexible, simple to implement, and allows production of catalysts with sufficient surface area and adhesion [11, 14, 18-20]. For introduction of the complex-oxide compounds of such metals as vanadium and tungsten, oxygen-containing ammonium salts were used, e.g. tungstic acid, ammonium metavanadate. As polymer components the nonionic water-soluble polymers polyvinyl alcohol, polyethylene glycol, which form stable aqueous solutions with the salt forms, were applied. The metal block carrier was impregnated with the polymer-salt solutions followed by heat treatment. As a result, nanosized particles of vanadium, tungsten and nickel oxides (15-20 nm size) were obtained.

For the qualitative and quantitative analyses of the starting compounds and reaction products the following methods were used: gas-liquid chromatography (GLC), iodometric titration and aniline point method. Chromatographic analysis of the starting compounds and products was carried out by GLC on different devices: “Crystal 2000M” with capillary column Zebron ZB-1 30 ml × 0.53 mm ID × 5.00 μm with 100% dimethylsiloxane liquid phase (gas-carrier – helium, detector – flame-ionization); “Crystal 4000M Lux” with capillary column Zebron ZB-1 30 ml × 0.53 mm ID × 5.00 μm with 100% dimethylsiloxane liquid phase (gas-carrier – helium, detector – flame-ionization), “Chrom-5” with a packed column with a stationary phase of 15% Carbowax-1500, and gas-liquid chromatograph 3700 with a packed column (stationary phase of 15% Carbowax-1500). GLC analysis of the gasoline fractions was conducted according to the standard GOST R 52714-2007 [21, 22]. The total time of GLC analysis was 15-20 min for the DIPE synthesis and 90-120 min for the hydrogenation of gasoline fractions. The determination of octane number was performed by motor and research methods.

## RESULTS AND DISCUSSIONS

### *Hydrogenation of gasoline fractions*

The liquid phase hydrogenation of the aromatic ring in gasoline fractions was carried out at elevated pressure of hydrogen on a high-pressure kinetic installation (HPKI) and on a pulp digester – the apparatus for the processes at elevated pressure with heating was from Amar Equipment Ltd [16, 17].

a b

**Fig.1.** The metal blocks for the laboratory samples of catalysts: a - perspective view; b - cross-sectional view

The process was carried out in compliance with the isobaric-isothermal mode. The results of experiments on the reduction of hydrocarbons and gasoline fractions were documented in the form of curves in a Cartesian coordinate system, where the horizontal axis represented the duration of the experiment in min (τ), and the vertical axis - the amount of absorbed hydrogen in $cm^3$.

In this paper the hydrogenation of two gasoline fractions was studied: the stable catalysate LG (benzene content – 0.37%) and straight-run gasoline AVT (benzene content – 3.18%), both obtained from Atyrau Oil Refinery LLP. The reactions were carried out with electrolytic hydrogen from a cylinder (99.8%), whereas, for the GLC helium (99.992%) from a cylinder was used. As the solvents iso-propanol and "reagent grade" hexane were applied.

It was found that during the first minutes of the reactions the hydrogen absorption was much higher on the Rh-Pd and Rh-Pt catalysts than on the catalysts of other composition. The results of the final samples showed that the content of benzene and other aromatics decreased (in total). The hydrogenation of gasoline fractions at various hydrogen pressures on the most active and stable catalyst Rh-Pt (9:1)/$Al_2O_3$ was studied. With an increase in hydrogen pressure in the range of 0.5-5.0 MPa the reaction time was reduced by a factor of 2. Benzene content of 0.06% was observed only at a pressure of 3.0 MPa, whereas at other hydrogen pressure levels benzene was absent in the final samples. After the hydrogenation of gasoline fractions the aromatics content in the final samples was within 32.5-34.6%. According to the bilogarithmic dependence of velocity on pressure the reaction order as per hydrogen after absorption of 1.0 mole of hydrogen was close to 1.0.

Tables 1, 2 present data on the hydrogenation of gasoline fractions on different catalysts. Data on quantitative and qualitative composition of the initial gasoline fractions and after hydrogenation are shown. Fig. 2 shows the chromatogram of the initial sample of gasoline stable catalyst LG.

The data on the group composition of organic compounds in gasolines showed (fig.3) that after the catalytic hydrogenation benzene was absent, the aromatics content decreased from 32.5 to 55.12% (wt.), the olefins content - from 0.23 to 0.1 % (wt.), and the paraffins content - from 12.41 to 11.99% (wt.), whereas the content of isoparaffins increased from 30.08 to 34.09% (wt.) and of naphthenes – from 2.12 to 10.14% (wt.).

**Table 1**. Hydrogenation of gasoline fractions of Atyrau Oil Refinery LLP on various catalysts at $P_{H2}$ = 4.0 MPa, T=25°C in hexane. $V_{gasoline\ fraction}$ =30.0 ml, $V_{solvent}$=10.0 ml.

| Catalyst | Gasoline fraction | Component content, % wt. | | | |
|---|---|---|---|---|---|
| | | Benzene | | Aromatics (in total) | |
| | | initial sample | after hydrogenation | initial sample | after hydrogenation |
| 2% Rh-Pt/ HY (80) | stable catalysate LG | 3.18 | 0.2 | 55.12 | 37.2 |
| | straight-run gasoline AVT | 0.37 | 0.1 | 9.93 | 5.25 |
| 5% Rh-Pt/$Al_2O_3$ | stable catalysate LG | 3.18 | 0.0 | 55.12 | 32.8 |
| | straight-run gasoline AVT | 0.37 | 0.0 | 9.93 | 4.8 |
| 2% Pt HZSM-5 (30) | stable catalysate LG | 3.18 | 1.2 | 55.12 | 42.0 |
| | straight-run gasoline AVT | 0.37 | 0.0 | 9.93 | 5.4 |
| 2 % Pt/HZSM-5 (80) | stable catalysate LG | 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 LG | 3.18 | 1.5 | 55.12 | 40.0 |
| | straight-run gasoline VT | 0.37 | 0.2 | 9.93 | 6.1 |
| 2% Pd-Cu/C | stable catalysate LG | 3.18 | 2.0 | 55.12 | 42.0 |
| | straight-run gasoline AVT | 0.37 | 0.3 | 9.93 | 6.4 |

**Table 2.** Group composition of hydrocarbons in the gasoline fraction stable catalysate LG before and after the hydrogenation on 0.5% Rh-Pt / $Al_2O_3$

| Gasoline fraction | Hydrocarbons content, % wt. / % vol. | | | | | |
|---|---|---|---|---|---|---|
| | Paraffins | Iso-paraffins | Olefins | Naphthenes | Aromatics (in total) | Benzene |
| Before hydrogenation | 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 |

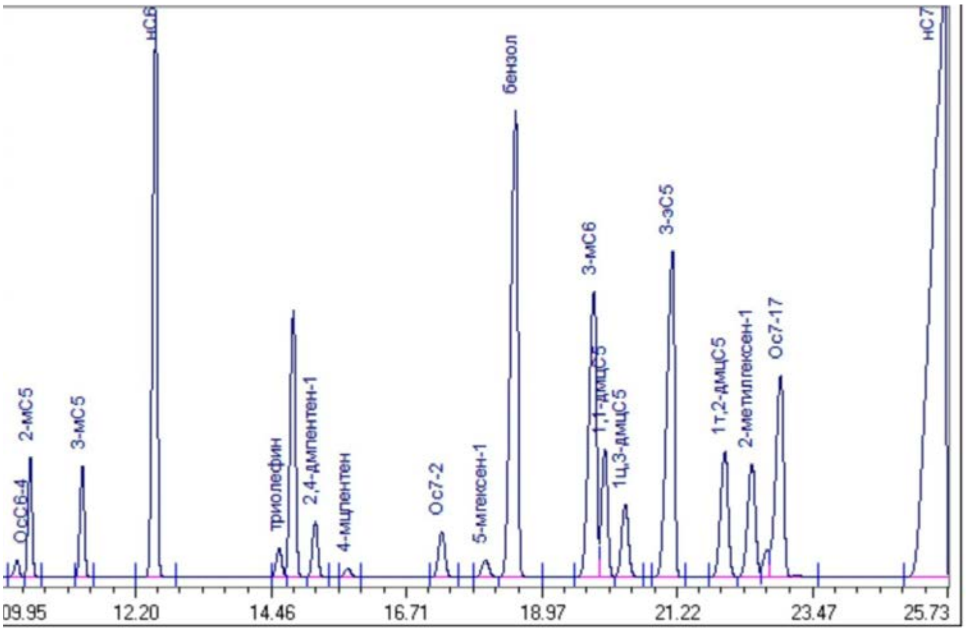


**Fig. 2.** Chromatogram of initial sample of gasoline stable catalysate LG (a peak of benzene at 18.2)

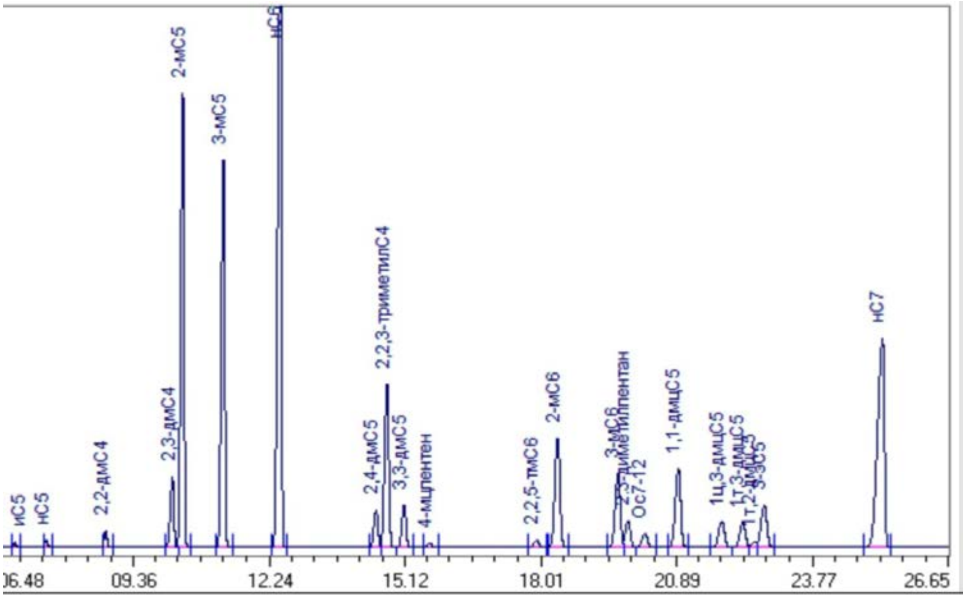


**Fig 3.** Chromatogram of a sample of gasoline stable catalysate LG after hydrogenation (no peak of benzene)

The octane numbers of the gasoline fractions before and after hydrogenation were determined by the Independent Centre of Expertise of oil products ORGANIC LLP (Almaty, Kazakhstan). The rated octane number of the stable catalysate did not change both before and after the hydrogenation and was equal to 94 units; whereas the motor octane number before the hydrogenation was 82.6 and after – 82.7. The octane number of the straight-run gasoline fraction AVT before and after the experiment was 60, whereas the motor octane number was 50. The octane number data confirmed that the process of hydrodearomatization of gasoline fractions did not reduce their octane number.

## DEVELOPMENT OF THE CATALYTIC METHOD FOR DIPE PRODUCTION

The DIPE synthesis reaction from iso-propanol or propane was carried out in a flow-through installation on a metal block catalyst which was placed in a quartz reactor. The reactor with an internal diameter of 10 mm was heated by an electric furnace (Fig. 4). The reactor temperature varied from 150 to 600°C and was measured by a chromel-alumel thermocouple.

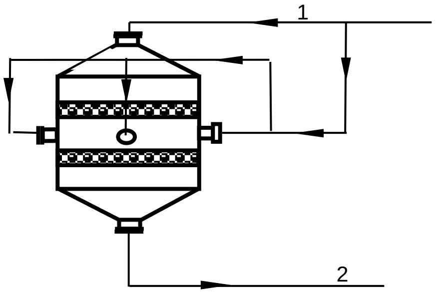


**Fig. 4.** Scheme of the catalytic reactor P2601 for DIPE synthesis. 1 - initial reagent (iso-propanol); 2 – reaction product (DIPE).

The isopropyl alcohol (or propane from a cylinder) was fed to the reactor via the plunger pump, where the catalyst was placed beforehand. The amount of the metal block catalyst was 3 ml.

The activity of the catalysts in the synthesis of DIPE was determined by iso-propanol (propane) conversion and DIPE yield.The catalytic conversion of isopropyl alcohol into DIPE was examined on various catalysts of various acidity within the temperature range of 150-300ºC (Table 3). It was found that the process should be carried out at temperatures not exceeding 300°C, as the catalyst selectivity and DIPE yield decreased because of the formation of a by-product – propylene (Fig.5).

By partial oxidation of propane on the catalyst based on vanadium and molybdenum, $WO_3$-$V_2O_5/Al_2O_3$, iso-propanol was formed with a yield of 80-82.1%, and DIPE – 2.5-2.95%. On the $WO_3/ZrO_2$ catalysts at 300-500°C propanol was formed with a yield of 59.9%-72%. When 0.1% of Pd was added to the $WO_3/ZrO_2$ catalyst the conversion of propane to DIPE increased to 76.4-80.1% at 500°C.

Physical and chemical properties of the synthesized catalysts were determined by various physical and chemical methods of analysis: BET, TPD, electron microscopy (EM), XRD. The analysis of the carriers and catalysts by XRD showed that in case of a catalyst on a metal carrier based on $V_2O_5$-$WO_3$ there were peaks at 4.38, 3.4, 2.8Å and orthorhombic lattice. In the active phase no NiO-crystal lattice was formed.

The electron microscopy of the samples was performed on EM-125K by the one-stage replicas method with extraction using microdiffraction (magnification of 160K), as well as on a focused beam microscope Jeol JSM-6610 (Japan). On the nickel-tungsten-vanadium and nickel-copper catalysts on the metal carriers accumulation of solid particles that did not coalesce into aggregates and were dispersed on the carrier surface was observed. The particle size was mainly 20-15 nm. As an example, the results of the scanning electron microscopy analysis of a carrier $Al_2O_3$ of the catalysts (Fig. 6) and some catalysts applied onto it for the hydrogenation of gasoline fractions are shown (Fig.7). The EM data obtained in this work indicated that the $Al_2O_3$ carrier structure consisted of needle-like crystalline formations of a size of 200-300Å with specific surface area S = 117.9 $m^2/g$ and pore size of 400Å.

**Table 3.** Synthesis of DIPE on 3%-catalysts of different compositions at 200ºC

| Catalyst | Conversion, % | Selectivity, % mol. DIPE |
|---|---|---|
| $Al_2O_3$ / NiO | 6.2 | 24.0 |
| $Al_2O_3$ -NaY / NiO | 26.3 | 28.2 |
| $Al_2O_3$-$SiO_2$/ NiO | 29.8 | 29.7 |
| $Al_2O_3$-$SiO_2$/ $Mo_3$ | 40.1 | 60.0 |
| $Al_2O_3$-$SiO_2$/ $Mo_3$- NiO | 56.2 | 60.8 |

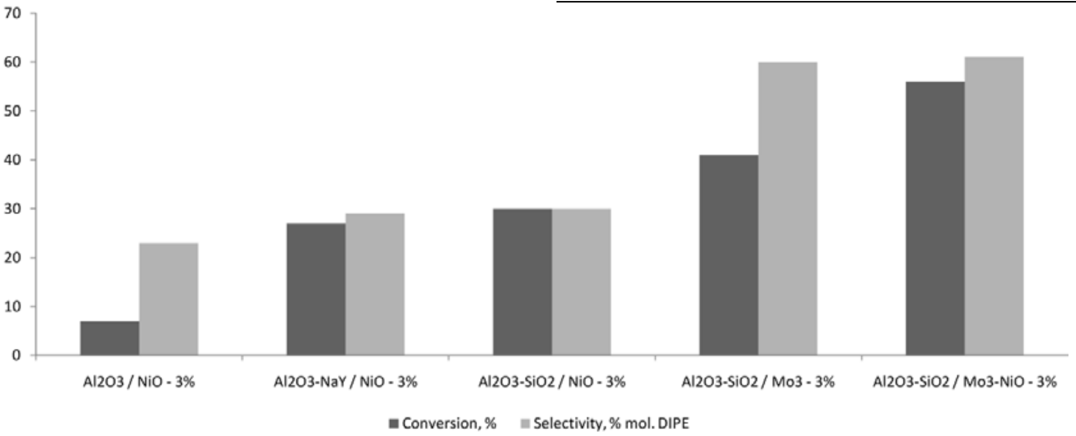
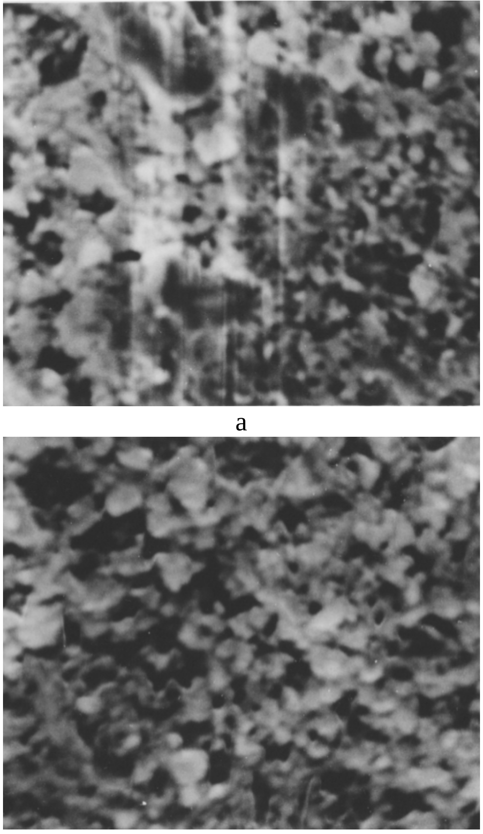


**Fig.5.** Dependence of the activity and selectivity of the catalysts on their composition in the reaction of DIPE synthesis from iso-propanol.

**Fig.6.** EM image of $\gamma$-$Al_2O_3$

The results of the analyses of the physical and chemical characteristics of the catalysts showed that the synthesized catalysts had a considerable surface area and pore volume.



a

b

**Fig.7.** EM images of different supported catalysts used for the hydrogenation of gasoline fractions**:** a - 5% Pd-Pt/$\gamma$-$Al_2O_3$, b - 2%-Pd-Cu/$\gamma$-$Al_2O_3$

The strength and concentration of acid sites of the Ni-Mo catalysts supported on the metal blocks after reaction and regeneration cycles were determined by the method of thermal desorption of ammonia. It was found that with the increase in the duration of the reaction a gradual decrease of catalyst acidity took place, presumably due to the blocking of the active sites by hydrocarbon deposits that resulted in a decrease of their catalytic activity.

## CONCLUSION

Catalyst systems for the processes for improving the quality of gasolines were synthesized: for the catalytic hydrogenation of gasoline fractions and the synthesis of octane-enhancing component of additives – diisopropyl ether (DIPE). The data on the group composition of organic compounds in gasolines showed that after the catalytic hydrogenation benzene was absent, the aromatics content decreased from 32.5 to 55.12% (wt.), the olefins content - from 0.23 to 0.1 % (wt.), the paraffins content - from 12.41 to 11.99% (wt.), whereas the content of isoparaffins increased from 30.08 to 34.09% (wt.) and that of naphthenes – from 2.12 to 10.14% (wt.). The octane number of the gasoline fractions after hydrogenation remained almost unchanged, while the benzene content decreased from 3.18 % (starting samples) to total absence in the final samples. It was found that the optimum catalyst composition for the synthesis of DIPE from iso-propanol under the experimental conditions was based on molybdenum and nickel compounds. On the catalysts of the following compositions 3% $Al_2O_3$/NiO and 3%$Al_2O_3$-NaY/NiO soot formation was observed, and the activity of the catalysts decreased. DIPE yield within the optimal temperature range (250-300$^{o}$C) was 62.0-68.5%.

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# СЕЛЕКТИВНИ КАТАЛИТИЧНИ РЕАКЦИИ ЗА ПОДОБРЯВАНЕ НА ХАРАКТЕРИСТИКИТЕ НА ГАЗОЛИНИ

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(Резюме)

Целта на изследването е да се разработят селективни катализатори за процесите, подобряващи действието на газолините: каталитично хидрогениране на газолиновите фракции и получаване на компонент, повишаващ октана в горивните добавки – диизопропилов етер (ДИПЕ). Данните за съдържанието на органични компоненти в газолиновите фракции след каталитично хидрогениране показват отсъствие на бензен, намаляване на съдържанието на ароматни съединения от 55.12% (тегл.) на 32.5% (тегл.), на олефини от 0.23% (тегл.) на 0.11% (тегл.) и на парафини – от 12.41% (тегл.) на 11.99% (тегл.), докато съдържанието на изопарафини се повишава от 30.08% (тегл.) на 34.09% (тегл.) и това на нафтени – от 2.12% (тегл.) на 10.14% (тегл.). Разработеният каталитичен метод за синтез на ДИПЕ от изопропанол или пропан при меки условия позволява получаването на добиви от 30.5-68.5%. Най-активни и стабилни катализатори за синтеза на ДИПЕ от изопропанол са молибден- и никел-съдържащите катализатори. Максималният добив в оптималния температурен интервал (250-300 °C) е 62.0-68.5%.