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E-mail: tuktin_balga@mail.ru, n-nikk@bk.ru, kadir.yeleussin@gmail.com,
a.abilmagzhanov@ifce.kz, alma130467@mail.ru**HYDROPROCESSING OF PETROLEUM FRACTIONS
OVER MODIFIED ALUMINIUM OXIDE CATALYSTS**

Abstract. The hydro processing of gasoline and diesel oil fractions over aluminum-nickel-molybdenum catalysts modified by additives HY, ZSM-5, phosphorus and rare earth elements were studied. At the hydro processing of straight-run gasoline over NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(30%)-Al₂O₃ the content of isoalkanes increases in comparison with the initial from 26.3 to 35.7- 38.3% at 320-400°C. The octane number of refined gasoline at 400°C is 83.7 (RON) and 69.7 (MON). The sulfur content decreases from 0.037% (initial gasoline) to 0.0022%.

At hydro processing of straight-run gasoline over NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ in the range of 320–400 °C the content of isoalkanes is 30.7- 44.3%. The octane number of refined gasoline at 400°C is maximum and is equal to 91.8 (RON) and 72.4 (MON). Under these conditions the sulfur content decreases from 0.0092% to 0.0028%.

The optimal conditions for the hydro processing of straight-run gasoline were revealed: T=400°C, V=2 h⁻¹, P = 4.0MPa. The catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-HY-Al₂O₃ has the highest hydro desulfurizing activity, the residual sulfur content at 400°C is 0.0012%.

The catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ has the highest hydro desulfurizing activity. At hydro processing of straight-run diesel fraction on this catalyst under optimal conditions the sulfur content decreases from 0.6400 % to 0.0740 % and during hydro processing of a straight-run diesel fraction with a higher sulfur content 0.8042% - up to 0.053%, which, apparently, is associated with the presence in the feedstock of various types of organosulfur compounds. The lowest pour point and cloud point under optimal conditions reaches minus 39.6°C and minus 30.5°C respectively.

Thus, developed modified zeolite-containing catalysts for the hydro processing of gasoline and diesel fractions carry out hydro processing, hydro isomerization and hydrogenation in one stage. The developed catalysts make possible to obtain high-octane low-sulfur gasoline and low-solidification low-sulfur diesel fuel.

Key words: catalyst, straight-run gasoline, diesel oil fraction, zeolite, hydro processing.

Introduction. Currently, most petrochemical processes are carried out using catalysts. Further intensification of production depends on the creation of new, more active and selective catalysts. The development of new generations of catalysts for the processing of hydrocarbon raw materials is necessary for the creation of new efficient technologies in this area.

To obtain high-quality motor fuels from sulfurous, paraffinic oils, catalytic hydro processing processes are used: hydro processing, hydro isomerization and hydrogenation. As a result of hydro processing, sulfur, nitrogen compounds, unsaturated hydrocarbons are removed, thermal stability is increased, the corrosiveness of fuels is reduced, the formation of deposits during storage is reduced, and the color and smell of motor fuel are improved. Currently, there is a tendency to tighten requirements for the composition of motor fuels, the insufficiently high quality of which is one of the causes of environmental pollution, therefore, the main attention of many oil refineries is focused on increasing the depth of hydro desulfurization. In this regard, for the production of high-quality motor fuels at the present stage, the catalytic processes of deep hydro processing of oil fractions are of great importance [1-10].

Recently, in connection with the involvement of high-sulfur oil in the refining and the deepening of its refining, the requirements for the catalysts for the hydro processing of gasoline and diesel fractions of oil have increased. In the global production of motor fuels, there is a constant tendency to tighten their environmental characteristics. To increase the volume of production of petroleum products, expand their range and improve quality, changes in the existing technology of oil refining using highly efficient catalysts are required. In this regard, the creation of new highly efficient catalysts for the hydro processing of low-octane gasolines and diesel fractions is very important [11 - 21].

In this paper presents the results of hydro processing of gasoline and diesel oil fractions over new aluminum-nickel-molybdenum catalysts, modified with additives ZSM-5, HY, phosphorus and rare earth elements (REE).

Experimental part. New modified zeolite-containing alumina catalysts modified by the introduction of metals with variable valence and phosphorus were developed and prepared: NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(20%)-Al₂O₃, NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(30%)-Al₂O₃, NiO-MoO₃-La₂O₃-P₂O₅-ZSM-HY-Al₂O₃ and NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃. The catalysts were prepared by impregnating a mixture of aluminum hydroxide with zeolites ZSM-5, HY and aqueous soluble salts of nickel, molybdenum, tungsten, cerium, lanthanum and phosphoric acid. After impregnation, the catalyst samples were molded and dried at 150⁰C for 5 hours, then calcined at 550⁰C for 5 hours. Using the synthesized modified zeolite-containing catalysts, a study of the hydro processing of gasoline and diesel oil fractions was carried out. The process was carried out in a high-pressure flow-through installation with a fixed catalyst layer at varying of temperature 320-400⁰C, pressure of 2.5-4.0MPa and space velocity 1.0-3.0 h⁻¹.

The hydrocarbon composition of the reaction products was analyzed on chromatographs «Chromatek-Crystal». The analysis of sulfur content in the feedstock and products was carried out in LLP «OilSert International» (Almaty). Determination of the pour point and cloud point were carried out on a «LAZ M2» device.

Results and discussion. On synthesized new modified zeolite-containing alumina catalysts the study of the hydro processing of straight-run gasoline and diesel fractions of oil was carried out.

At hydro processing of straight-run gasoline over NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(20%)-Al₂O₃ as the temperature increases to 350⁰C isoalkane content increases from 26.3 to 32.8 % (table 1). The content of naphthenic hydrocarbons in the catalysis ranges from 22.5 to 31.8 %, olefins - 3.3-4.0 %. The yield of the liquid phase with an increase in temperature from 320 to 400 ⁰C varies from 92.5 to 70.0%. The octane number of gasoline refined at 400 ⁰C is 85.6 (RON). Under these conditions the sulfur content in the final product decreases from 0.037% (initial gasoline) to 0.0120 at 350 ⁰C and up to 0.0102% at up to 400 ⁰C.

Table 1 - Influence of temperature on the conversion of gasoline over NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(20%)-Al₂O₃ at V = 2 h⁻¹, P = 4.0 MPa

Products, %	T, °C				
	Initial	320	350	380	400
Paraffins C ₅ -C ₆	33.4	31.2	25.9	25.2	25.7
Iso-alkanes	26.3	26.1	32.8	31.9	22.1
Olefins	3.7	3.6	4.0	3.4	3.3
Aromatic hydrocarbons	5.6	7.3	11.8	17.0	19.3
Naphthenic hydrocarbons	31.0	31.8	25.5	22.5	29.6
Yield of liquid phase, %	-	92.5	80.0	70.0	70.0
Sulfur content, %	0.0375	0.0230	0.0120	0.0110	0.0102
Octane number (RON)	77.7	82.2	79.2	82.0	85.6
Octane number (MON)	53.8	60.9	62.5	66.1	63.9

Table 2 shows the results obtained in the hydro processing of the gasoline fraction on the NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(30%)-Al₂O₃. At hydro processing of straight-run gasoline at 320⁰C isoalkane content increases from 26.3 to 38.3%. As the temperature increases to 400⁰C isoalkane content decreases to 35.7 %. At varying the temperature in the range 320-400⁰C the yield of aromatic hydrocarbons varies from 12.6 to 19.6 % and naphthenic hydrocarbons decreases from 26.5 to 21.8 %. The amount of olefins ranges

from 3.7 to 4.2 %. The yield of the liquid phase with an increase in temperature from 320 to 400⁰C varies from 70.0 to 50.0%. The octane number of gasoline at 400⁰ C is 83.7 (RON) and 69.7 (MON). The sulfur content in the final product decreases from 0.037% (initial gasoline) to 0.0022%.

Table 2 - Influence of temperature on the conversion of gasoline on NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(30%)-Al₂O₃ at V = 2 h⁻¹, P = 4.0 MPa

Products, %	T, °C				
	Initial	320	350	380	400
Paraffins C ₅ -C ₆	33.4	18.9	19.6	19.2	19.1
Iso-alkanes	26.3	38.3	37.8	36.7	35.7
Olefins	3.7	3.7	4.2	3.7	3.9
Aromatic hydrocarbons	5.6	12.6	12.6	18.1	19.5
Naphthenic hydrocarbons	31.0	26.5	25.8	22.3	21.8
Yield of liquid phase, %		70.0	65.0	57.5	50.0
Sulfur content, %	0.037	0.0125	0.0110	0.0091	0.0022
Octane number (RON)	77.7	79.6	81.5	82.7	83.7
Octane number (MON)	53.8	64.8	65.8	67.4	69.7

At hydro processing of straight-run gasoline at catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-HY-Al₂O₃ at 320⁰C the content of isoalkanes increases as compared with the feedstock from 32.6 to 41.9%. However, with increasing temperature from 320 to 400⁰C contents of isoalkanes and naphthenic hydrocarbons reduced from 41.9 to 34.2% and from 26.3 to 22.3% respectively. The amount of aromatic hydrocarbons increases from 7.3 to 20.9 %, the content of olefins in the catalyzate is 3.6-3.9 %. Yield of the liquid phase as the temperature increases from 320 to 400⁰ C is changed from 85.0 to 55.0%. The octane number of refined gasoline increases with temperature in the range of 320-400⁰C: from 81.9 to 87.0 (RON) and from 63.2 to 68.9 (MON), while the sulfur content decreased from 0.0375 to 0.0012%.

At hydro processing of straight-run gasoline over NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ at 320⁰C isoalkane content increased from initial of 36.8 to 44.3% (table 3). When the temperature rises to 400⁰C is reduced and isoalkanes content equal to 30.7 %. When the temperature rises in the range 320-400⁰C the yield of aromatic hydrocarbons varies from 10.4 to 28.3 %, naphthenic hydrocarbons is increased from 20.3 to 30.3 %. The amount of olefins depends little on the process temperature and is 4.3 - 5.8 %. The yield of the liquid phase with an increase in temperature from 320 to 400⁰C decreases from 74.8 to 55.4%. The octane number of gasoline at 400⁰C is maximum and is equal to 91.8 (RON) and 72.4 (MON). Under these conditions the sulfur content decreases from 0.0092% to 0.0028%.

Table 3 - Influence of temperature on the process of hydro processing of straight-run gasoline on the catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ at V = 2 h⁻¹, P = 4.0 MPa

Products, %	T, °C				
	Initial	320	350	380	400
Paraffins C ₅ -C ₆	27.3	20.7	10.0	8.5	5.0
Iso-alkanes	36.8	44.3	32.4	32.6	30.7
Olefins	4.8	4.3	5.4	5.6	5.8
Aromatic hydrocarbons	9.2	10.4	18.7	24.8	28.3
Naphthenic hydrocarbons	21.9	20.3	33.4	28.5	30.3
Yield of liquid phase		74.8	65.7	59.0	55.4
Octane number (RON)	78.9	84.3	89.8	90.0	91.8
Octane number (MON)	60.9	70.4	69.2	71.8	72.4
Mass fraction of sulfur, %	0.0092	0.0036	0.0033	0.0030	0.0028

The study of the effect of pressure on the process of hydro processing of straight-run gasoline over NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ showed that with an increase in pressure in the range of 2.5-4.0 MPa the maximum amount of isoalkanes observed at P=2.5 MPa and equal to 34.9% (table 4). With a further increase in pressure, their yield decreases to 30.7% at 4MPa, while the concentration of naphthenic hydrocarbons increases from 22.9 to 30.3%. The concentration of aromatic and olefinic hydrocarbons

depends little on pressure and ranges from 27.3-29.7% and 4.6-5.8% respectively. The octane number of gasoline refined at 4.0 MPa is 91.8 (RON) and 72.4 (MON). The sulfur content decreases from 0.0092% (initial gasoline) to 0.0028% at 4.0 MPa.

Table 4 - Influence of pressure on the process of hydro processing of straight-run gasoline on the catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ at 400°C and 2 h⁻¹

Products, %	P, MPa				
	Initial	2.5	3.0	3.5	4.0
Paraffins C ₅ -C ₆	27.3	7.9	6.0	4.0	5.0
Iso-alkanes	36.8	34.9	34.3	30.6	30.7
Olefins	4.8	4.6	5.3	5.0	5.8
Aromatic hydrocarbons	9.2	29.7	27.3	28.4	28.3
Naphthenic hydro carb.	21.9	22.9	27.1	32.0	30.3
Liquid phase yield		52.0	50.4	53.2	55.4
Octane number (RON)	78.9	89.6	88.3	88.9	91.8
Octane number (MON)	60.9	72.9	71.8	70.1	72.4
Mass fraction of sulfur,%	0.0092	0.0047	0.0035	0.0033	0.0028

At hydro processing of straight-run gasoline fraction to the catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ when changing the space velocity from 1.0 to 3,0 h⁻¹ contents isoalkanes in catalyzate equals 30.1 - 30.7% (table 5). The amount of aromatic and naphthenic hydrocarbons in the resulting product also changes little with a change in the volumetric feed rate. The yield of olefinic hydrocarbons ranges from 4.9 to 5.8%. The octane number of the resulting gasoline increases compared to the original (78.9) to 90.9-91.8 (RON), the residual sulfur content decreases compared to the feedstock from 0.0092 to 0.0036.

Table 5 - Influence of the volumetric velocity of raw material on the process of hydro processing of straight-run gasoline on the catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ at 400°C and 4.0 MPa

Products, %	V, h ⁻¹				
	Initial	1.0	1.5	2.0	3.0
Paraffins C ₅ -C ₆	28.0	5.0	4.9	5.0	4.1
Iso-alkanes	35.5	30.6	30.2	30.7	30.1
Olefins	4.8	4.9	5.4	5.8	5.2
Aromatic hydrocarbons	8.1	31.6	30.6	28.3	29.7
Naphthenic hydrocarbons	23.6	27.8	28.9	30.3	30.8
Liquid phase yield		50.1	48.0	55.4	43.0
Octane number (RON)	78.9	89.0	90.9	91.8	90.7
Octane number (MON)	60.6	71.3	70.7	72.4	72.1
Mass fraction of sulfur,%	0.0092	-	0.0019	0.0028	0.0036

Analysis of the obtained results shows that under optimal conditions during the processing of straight-run gasoline fraction, the highest octane number is characteristic of the catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃: 91.8 (RON). The catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-HY-Al₂O₃ has the highest hydro desulfurizing activity, the residual sulfur content at 400 °C is 0.0012%.

Thus, modified zeolite-containing catalysts for the hydro processing of gasoline fractions have been developed and synthesized, which carry out hydro processing, hydro isomerization and hydrogenation in one stage. The developed catalysts make it possible to obtain high-octane low-sulfur gasoline.

Tests of the catalyst NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(30%)-Al₂O₃ were carried out in the process of hydro processing of the diesel fraction of oil % (table 6). The pour point of the diesel fraction after hydro processing at 320°C and 4.0 MPa decreased from minus 18.3 to minus 35.9°C. By increasing the temperature to 400°C, pour point is reduced to minus 58.9 °C. The cloud point in these conditions falls from minus 11.3 to minus 30.7 - 57.7 °C. Yield of hydro finished diesel fuel is 90.0 -100.0 %. The sulfur content is reduced in comparison with the original diesel fraction from 0.560 0 % to 0.0536%.

Table 6 – Hydro processing of the diesel fraction over NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(30%)-Al₂O₃Al₂O₃

The main parameters of the process		Sulfur content,%	Pour point, °C	Cloud point, °C	Yield, %
Initial diesel fraction		0.560 0	-18.3	-11.3	
Process temperature, °C	320	-	-35.9	-30.7	100
	350	-	-51.3	-51.0	92.5
	380	-	-54.9	-48.1	91.0
	400	0.0536	-58.9	-57.7	90.0

During hydro processing of straight-run diesel fraction on the catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ with a sulfur content of 0.6400%, the pour point decreases from minus 13.6 to minus 39.6 °C, the cloud point temperature under these conditions varies from minus 12.4 to minus 30.5 °C. The yield of hydro finished diesel fuel is 92.0-97.5%. Under optimal conditions (400 °C, 2 h⁻¹, 4.0 MPa) the sulfur content decreases from 0.6400% in the initial fraction to 0.0740 (table 7). During the hydro processing of the diesel fraction of oil with a higher sulfur content (0.8042%) on the catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ in the range 320-400 °C, the sulfur content decreases from 0.8042% in the original fraction to 0.0530% at 400°C.

Table 7- Hydro processing of straight-run diesel oil fraction on the NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃

Process temperature, °C	Cloud point, °C	Pour point, °C	Yield, %	Mass fraction of sulfur,%
Initial diesel fraction	-12.4	-13.6		0.6400
320	-24.1	-31.2	97.5	0.1900
350	-30.5	-35.4	95.8	0.1200
380	-33.0	-33.5	94.5	0.0760
400	-30.5	-39.6	92.0	0.0740

It should be noted that with the weighting of the fractional composition of the processed raw materials the proportion of hard-to-remove sulfur compounds increases. As a result, the higher activity of catalysts in the hydro desulfurization of the gasoline fraction compared to the diesel fraction is due to the predominance of mercaptans, disulfides of the gasoline fraction of oil, while in the diesel fraction sulfur is mainly found in the form of sulfides, thiophenes and benzothiophenes. In connection with the tightening of the permissible sulfur content in diesel fuel, the main attention of many oil refineries is focused on increasing the depth of hydro desulfurization. To obtain low-sulfur, environmentally friendly diesel fuel, technologies and catalysts for deep hydro desulfurization are being developed to remove sulfur atoms contained in complex hydrocarbon molecules. When switching to the Euro-5 standard for sulfur content from 50 to 10 ppm, processing of low-reactive polyalkyldibenzothiophene is required [22-24].

Table 8 shows the results obtained in the study of the effect of pressure on the process of hydro processing of diesel oil fraction on the catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃. With an increase in pressure from 3.0 to 4.0 MPa, the pour point changes from minus 30.2 to minus 38.2°C, the cloud point - from minus 29.1 to minus 37.9°C, the sulfur content decreases compared to initial from 0.6400 to 0.0530%. With increasing pressure the yield of the target product practically does not change.

Table 8 - Influence of pressure on the process of hydro processing of a diesel fraction of oil on the catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃

Pressure, MPa	Cloud point, °C	Pour point, °C	Yield, %	Mass fraction of sulfur,%
Initial diesel fraction	-12.4	-13.6		0.6400
3.0	-29.1	-30.2	95.0	0.1300
3.5	-28.3	-28.9	97.5	0.0980
4.0	-37.9	-38.2	94.2	0.0530

By increasing the space velocity of from 1.0 to 3.0 h⁻¹ at hydro processing of diesel fraction over catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ the cloud point decreases from minus 39.3 °C to minus 28.4 °C, a pour point also decreases from minus 39.6 °C to minus 28.7 °C. The yield of hydro finished fuel ranges from 94.2 to 97.1%. With a decrease in the space velocity of the feedstock, a decrease in the amount of residual sulfur is observed (table 9).

Table 9 - Influence of the space velocity on the process of hydro processing of the diesel fraction of oil on the catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃

Space velocity, h ⁻¹	Cloud point, °C	Pour point, °C	Yield, %	Mass fraction of sulfur, %
Initial diesel fraction	-12.4	-13.6		0.6400
1.0	-39.3	-39.6	97.1	0.0510
2.0	-37.9	-38.2	94.2	0.0530
3.0	-28.4	-28.7	95.2	0.1200

Comparison of results shows that the catalyst NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ has the highest hydro desulfurizing activity. When a straight-run diesel fraction is hydro processed on this catalyst under optimal conditions (400°C, 2 h⁻¹, 4.0 MPa) the sulfur content decreases from 0.640% to 0.074%. When a straight-run diesel fraction with a higher sulfur content 0.8042% is hydro processed - up to 0.053%, which is due to the presence of various types of organosulfur compounds in the feedstock. The lowest pour point and cloud point under optimal conditions is observed during hydro processing of diesel fractions over NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ and reaches minus 39.6°C and minus 30.5°C respectively

Earlier, we found that when processing gasoline and diesel fractions on polyfunctional catalysts with dehydrogenating, hydrogenating and acidic capabilities, the *n*-alkane dehydrates first on the metal centers of the catalyst, the formed olefin on the acid center turns into a carbonium ion, which is easily isomerized [25, 26].

The results obtained when testing catalysts in the process of hydro processing of diesel oil fractions show that the greatest decrease in the pour point and cloud point occurs at a temperature of 380 - 400 °C. During the hydro processing of diesel and gasoline fractions, the lowest residual sulfur content is observed at a temperature of 400 °C. The studied catalysts make it possible to obtain winter grades of diesel fuels with a low sulfur content.

Thus, in the study of the process of hydro processing of straight-run gasoline and diesel fractions on modified alumina catalysts NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM (20,0%)-Al₂O₃, NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM (30,0%) -Al₂O₃, NiO-MoO₃-La₂O₃-P₂O₅-ZSM-HY-Al₂O₃ and NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃, it was found that the developed and synthesized catalysts have polyfunctional properties and in one stage they carry out hydro processing, hydro isomerization to obtain low-sulfur low-solidifying diesel fuel and low-sulfur high-octane gasoline.

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МОДИФИЦИРЛЕНГЕН АЛЮМООКСИДТІ КАТАЛИЗАТОРЛАРДА МҰНАЙ ФРАКЦИЯЛАРЫН ГИДРОӨНДЕУ

Аннотация. ZSM-5, фосфор және СЖЭ қоспаларымен модификацияланған алюмоникелмолибден модификацияланған катализаторларында бензинді және дизельді мұнай фракцияларын гидроөңдеу процесі зерттелді. 320-400°C температурада, 3,0–4,0 МПа қысымда және шикізатты берудің көлем жылдамдығы 1–3 сағ⁻¹ кезінде катализатордың стационарлық қабаты бар жоғары қысымды ағынды қондырғыда тура айдалған бензин мен мұнайдың дизельді фракцияларын гидроөңдеу процестері қарастырылды.

NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(20%)-Al₂O₃ катализаторында тура айдалған бензинді гидроөңдеу кезінде температураның 320-дан 400 °C-қа дейін өсуі арқылы сұйық фазаның шығымы 92,5-тен 70,0%-ға дейін өзгереді. 400°C-та жақсартылған бензиннің октан саны 85,6 (З.Ә.) құрайды. Соңғы өнімдегі күкірт мөлшері 0,037%-дан (бастапқы бензин) және 400°C-қа, 0,0102%-ға дейін төмендейді.

NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(30%)-Al₂O₃ катализаторында тура айдалған бензинді гидроөңдеу кезінде 320-400°C температурада изоалкандардың құрамы бастапқы 26,3-тен 35,7–38,3%-ға дейін артады. Температураның 320-дан 400°C-қа дейін өсуі барысында сұйық фазаның шығымы 70,0-ден 50,0%-ға дейін өзгереді. 400°C жақсартылған бензиннің октан саны 83,7 (З.Ә.) және 69,7 (М.Ә.) құрайды. Осы жағдайларда бензин

фракциясын гидроөңдеу кезінде соңғы өнімдегі күкірт мөлшері 0,037%-дан (бастапқы бензин) 0,0022%-ға дейін төмендейді.

NiO-MoO₃-La₂O₃-P₂O₅-ZSM-HY-Al₂O₃ катализаторында тура айдалған бензинді гидроөңдеуде 320^oC температурада алынған катализаттағы изоалкандардың мөлшері бастапқы шикізатпен салыстырғанда 32,6-дан 41,9%-ға дейін өседі. 400^oC кезінде изоалкандардың құрамы 34,2%-ға дейін төмендейді. Температураның 320-дан 400^oC-қа дейін өсуі негізінде сұйық фазаның шығуы 85,0-ден 55,0%-ға дейін өзгереді. Тазартылған бензиннің октандық саны 320–400^oC аралығында артады: зерттеу әдісі бойынша 81,9-дан 87,0-ге дейін және мотор әдісі бойынша 63,2-ден 68,9-ға дейін, күкірттің құрамы 0,0375-тен 0,0012%-ға дейін төмендеді.

NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ катализаторында тура айдалған бензинді гидроөңдеу кезінде 320–400^oC интервалында изоалкан мөлшері 30,7–44,3% құрайды. Температураның 400^oC-қа дейін өсуі арқылы изоалкан мөлшері төмендейді және 30,7%-ға тең болады. Температураның 320-дан 400^oC-қа дейін өсуі арқылы сұйық фазаның шығуы 74,8-ден 55,4% -ға дейін азаяды. 400^oC бензиннің октан саны максималды 91,8 (З.Ә.) және 72,4 (М.Ә.). Бұл жағдайда алынған бензиндегі күкірт мөлшері 0,0092%-дан 0,0028%-ға дейін төмендейді.

NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ катализаторы негізінде тура айдалған бензинді гидроөңдеу процесіне шикізат берудің қысымы мен көлемдік жылдамдығының әсері зерттелді. Тура айдалған бензин фракциясын гидроөңдеу үшін келесі оңтайлы жағдайлар анықталды: 400^oC, V=2 сағ⁻¹, P=4,0 МПа. Ең жоғары октандық сан NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ катализаторына тән екендігі анықталды: 91,8(З.Ә.). NiO-MoO₃-La₂O₃-P₂O₅-ZSM-HY-Al₂O₃ катализаторы жоғары гидродесульфуризациялы белсенді болып келеді, 400^oC күкірттің қалдық мөлшері 0,0012% құрайды.

NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ және NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(30%)-Al₂O₃ катализаторларын күкірттің әртүрлі мөлшері бар мұнайдың дизельді фракцияларын гидроөңдеу процесінде сынау жұмыстары жүргізілді.

Нәтижелерді салыстыру жұмыстары көрсеткендей, NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ катализаторы ең жоғары гидродесульфуризациялы белсенді. Оңтайлы жағдайларда (400^oC, 2 сағ⁻¹, 4,0 МПа) осы катализаторда тура айдалған дизель фракциясын гидроөңдеу кезінде күкірт мөлшері 0,6400%-дан 0,0740%-ға дейін төмендейді, ал күкірт мөлшері жоғары тура айдалған дизель фракциясын гидроөңдеу кезінде 0,8042%-дан 0,053%-ға дейін төмендейді, шамасы, бұл бастапқы шикізатта күкіртті органикалық қосылыстардың алуан түрлеріне байланысты болуы мүмкін. Оңтайлы жағдайларда қату және лайланудың ең төменгі температурасы NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ катализаторында дизель фракцияларының гидрожақ-сарғаны байқалады және сәйкесінше минус 39,6^oC және минус 30,5^oC жетеді.

Осылайша бір уақытта гидротазарту, гидроизомеризация және гидроизомерлеу жүргізетін бензин мен дизель фракцияларын гидроөңдейтін модифицирлен цеолитті катализаторлары жасалды. Дайындалған катализаторлар жоғары октанды, аз күкіртті бензин және төмен температурада кататтын аз күкіртті дизель отынын алуға мүмкіндік береді.

Түйін сөздер: катализатор, тура айдалған бензин, дизельді мұнай фракциясы, цеолит, гидроөңдеу.

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ГИДРОПЕРЕРАБОТКА НЕФТЯНЫХ ФРАКЦИЙ НА МОДИФИЦИРОВАННЫХ АЛЮМООКСИДНЫХ КАТАЛИЗАТОРАХ

Аннотация. Изучен процесс гидропереработки бензиновой и дизельных фракций нефти на модифицированных алюмоникельмолибденовых катализаторах, модифицированных добавками ZSM-5, фосфора и PЗЭ. Исследование процессов гидропереработки прямогонного бензина и дизельной фракций нефти проводилось в проточной установке высокого давления со стационарным слоем катализатора при температурах 320–400^oC, давлении 3,0–4,0 МПа и объемной скорости подачи сырья 1–3ч⁻¹.

При гидропереработке прямогонного бензина на катализаторе NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(20%)-Al₂O₃ выход жидкой фазы с ростом температуры от 320 до 400^oC меняется от 92,5 до 70,0%. Октановое число обогороженного при 400^oC бензина составляет 85,6 (И.М.), содержание серы в конечном продукте снижается с 0,037% (исходный бензин) до 0,0102% при 400^oC.

При гидропереработке прямогонного бензина на катализаторе NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(30%)-Al₂O₃ при температуре 320–400^oC содержание изоалканов повышается по сравнению с исходным от 26,3 до 35,7–38,3%. Выход жидкой фазы с ростом температуры от 320 до 400^oC меняется от 70,0 до 50,0%. Октановое число обогороженного при 400^oC бензина составляет 83,7 (И.М.) и 69,7 (М.М.). При гидропереработке

бензиновой фракции в этих условиях содержание серы в конечном продукте снижается с 0,037% (исходный бензин) до 0,0022%.

При гидропереработке прямогонного бензина на катализаторе NiO-MoO₃-La₂O₃-P₂O₅-ZSM-HY-Al₂O₃ при температуре 320°C содержание изоалканов в получаемом катализате растет по сравнению с исходным сырьем от 32,6 до 41,9%. При 400°C содержание изоалканов снижается до 34,2%. Выход жидкой фазы с ростом температуры с 320 до 400 °C меняется от 85,0 до 55,0%. Октановое число облагороженного бензина увеличивается в интервале 320–400°C: по исследовательскому методу от 81,9 до 87,0 и моторному методу от 63,2 до 68,9, при этом содержание серы снизилось 0,0375 до 0,0012%.

При гидропереработке прямогонного бензина на катализаторе NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ в интервале 320-400°C содержание изоалканов составляет 30,7–44,3%. При росте температуры до 400°C содержание изоалканов понижается и равно 30,7%. Выход жидкой фазы с ростом температуры от 320 до 400°C уменьшается от 74,8 до 55,4%. Октановое число облагороженного при 400°C бензина максимально и равно 91,8 (И.М.) и 72,4 (М.М.). В этих условиях содержание серы в получаемом бензине снижается с 0,0092% до 0,0028 %.

Изучено влияние давления и объемной скорости подачи сырья на процесс гидропереработки прямогонного бензина на примере катализатора NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃.

Выявлены оптимальные условия гидропереработки прямогонной бензиновой фракции: 400°C, V=2 ч⁻¹, P=4,0МПа. Установлено, что наиболее высокое октановое число 91,8 (И.М) характерно для катализатора NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃. Катализатор NiO-MoO₃-La₂O₃-P₂O₅-ZSM-HY-Al₂O₃ обладает наиболее высокой гидрообессеривающей активностью, остаточное содержание серы при 400°C составляет 0,0012%.

Проведены испытания катализаторов NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ и NiO-MoO₃-Ce₂O₃-P₂O₅-ZSM(30%)-Al₂O₃ в процессе гидропереработки дизельных фракций нефти с различным содержанием серы. Сравнение полученных результатов показывает, что наибольшей гидрообессеривающей активностью обладает катализатор NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃. При гидропереработке прямогонной дизельной фракции на этом катализаторе в оптимальных условиях (400°C, 2 ч⁻¹, 4,0 МПа) содержание серы снижается с 0,6400% до 0,0740%, а при гидропереработке прямогонной дизельной фракции с более высоким содержанием серы 0,8042% – до 0,053%, что, по-видимому, связано с присутствием в исходном сырье различных видов сероорганических соединений. Наиболее низкая температура застывания и помутнения в оптимальных условиях наблюдается при гидрооблагораживании дизельных фракций на катализаторе NiO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ и достигает минус 39,6°C и минус 30,5°C соответственно.

Таким образом, разработаны и синтезированы модифицированные цеолитсодержащие катализаторы гидропереработки бензиновых и дизельных фракций, которые в одну стадию проводят гидроочистку, гидроизомеризацию и гидрирование. Разработанные катализаторы позволяют получать высокооктановый малосернистый бензин и низкозастывающее малосернистое дизельное топливо.

Ключевые слова: катализатор, прямогонный бензин, дизельная фракция нефти, цеолит, гидропереработка.

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