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Д.В. Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
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NEWS

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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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**B.T. Tuktin, L.B. Shapovalova, A.A. Tenizbayeva,
A.Z. Abilmagzhanov, R.I. Egizbaeva**

JSC "Institute of Fuel, Catalysis and Electrochemistry named after D.V. Sokolsky", Almaty, Kazakhstan.

E-mail: tuktin_balga@mail.ru, n-nikk@bk.ru, aliya.85@mail.ru,
a.abilmagzhanov@ifce.kz, e_raikul@mail.ru

HYDROTREATING AND HYDROISOMERIZATION OF OIL FRACTIONS ON MODIFIED ALUMINUM-COBALT- MOLYBDENUM CATALYSTS

Abstract. In this work we are given results and research of hydro refining of gasoline and diesel oil fractions on alumina catalysts $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-Ce}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-HY-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-AAC-ZSM-Al}_2\text{O}_3$. The catalysts were prepared by impregnating a mixture of aluminum hydroxide and zeolites ZSM-5, HY with aqueous solutions of salts Co, Mo, La and phosphoric acid. Large-scale laboratory tests of the synthesized catalysts were carried out in the process of hydro processing of various types of gasoline and diesel fractions.

At hydro treating of straight-run gasoline over $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ shows that in the temperature range 320 - 350°C the maximum amount of isoalkanes is formed 33.4-40.4%. The octane number of refined gasoline increases in comparison with the initial one from 78.9 to 89.3 (RON) and from 60.9 to 73.4 (MON). The sulfur content of catalysate with increasing temperature up to 400°C decreased to 0.0012 %.

At hydro processing of catalytic cracking gasoline on $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ the octane number of refined gasoline is slightly reduced. The sulfur content of catalysate with increasing temperature up to 400°C decreased from initial with from 0.0134 to 0.0014 %.

It was found that the lowest pour point and cloud point of hydro-refined diesel fuel is observed on the catalyst $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$. After hydro treating on this catalyst the pour point and cloud point are equal to minus 52.7°C and minus 40.8°C accordingly. This same catalyst has the highest hydro desulfurization activity: the sulfur content decreases from 0.5600% to 0.104%.

Thus, the developed modified zeolite-containing catalysts $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-Ce}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-HY-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-AAC-ZSM-Al}_2\text{O}_3$, exhibiting high activity at hydro treating of gasoline and diesel fractions and is able in one stage deep hydro treating, hydro isomerization and hydrocracking which allows to obtain low-sulfur, high-octane gasoline and low-sulfur and low solidifying diesel fuel which is important for operation of vehicles in winter conditions.

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

Introduction. Recently, due to the necessity of deep processing heavy sour crude oil significantly increased requirements for the process of hydrotreating petroleum oil fractions. The efficiency of hydrotreating processes is mainly determined by the properties of the catalysts used. To carry out deep hydrotreating of petroleum fractions, it is necessary to use new efficient catalysts and technologies. According to international standards, a significant limitation of the content of sulfur, benzene, aromatic and olefinic hydrocarbons in motor fuels is required. At present, environmental requirements for the quality of motor fuels are being tightened, which requires their deep hydrotreating and refining. In many countries, catalysts are being searched to increase the depth of removal of sulfur-containing compounds and the technology for the production of motor fuels is being improved. Existing catalysts for the hydroprocessing of petroleum fractions in Kazakhstan and the CIS countries do not always meet the increased requirements for the quality of motor fuels. To improve the quality of motor

fuels, to reduce the cost of their production, an urgent and priority task is the creation of highly effective polyfunctional catalysts for processing petroleum fractions. In this case great importance is the development of catalysts for hydrotreatment of a certain type of oil [1-20].

This paper presents results and research hydrorefining gasoline and diesel oil fractions on new aluminum-cobalt-molybdenum catalysts, modified with additives of zeolite ZSM-5 and HY, lanthanum and phosphorus.

Experimental part. Enlarged batches of catalysts $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-Ce}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-HY-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-AAC-ZSM-Al}_2\text{O}_3$ were prepared. The catalysts were prepared by impregnating a mixture of aluminum hydroxide and zeolites ZSM-5, HY, with aqueous solutions of cobalt, molybdenum, lanthanum, and phosphoric acid salts. Then granulation and shaping were carried out. Thereafter, the catalysts pellets were dried at 150°C and calcined at 550°C. Enlarged laboratory tests of the synthesized catalysts were carried out in the process of hydroprocessing of various types of gasoline and diesel fractions. Tests performed in high-pressure flow installation with a stationary catalyst layer at 320-400°C, pressure 2.5 - 4.0 MPa and the space velocity 1.0 - 3.0 h⁻¹.

The hydrocarbon composition of the reaction products was analyzed on chromatographs «Chromatek-Crystal». The analysis of the sulfur content was carried out in «Oilsert International» LLP (Almaty) and the laboratory of physicochemical methods of ITKE. The determination of the pour point and cloud point was carried out on a «LAZ M2» device.

The physicochemical characteristics of the synthesized catalysts were investigated by electron microscopy «EM-125K» transmission electron microscope using microdiffraction [21]. To determine the number of acid sites, the method of temperature-programmed desorption of ammonia was used [22].

Results and its discussion. During the hydroprocessing of straight-run gasoline on the catalyst $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ in the temperature range 320-350°C (table 1) the maximum amount of isoalkanes is formed 33.4-40.4%. At higher temperatures the yield of isoalkanes is reduced to 32.2% at 400°C. The content of aromatic hydrocarbons in the catalyzate under these conditions increases from 14.9 to 20.1 %. The octane number of refined gasoline increases in comparison with the initial one from 78.9 to 89.3 (RON) and from 60.9 to 73.4 (MON). The sulfur content of catalyzate with increasing temperature up to 400°C decreased to 0.0012 %.

Table 1 - Influence of temperature on the hydroprocessing of straight-run gasoline on the catalyst $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ at $V = 2 \text{ h}^{-1}$, $P = 4.0 \text{ MPa}$

Products, %	T, °C				
	Initial	320	350	380	400
Paraffins C ₅ -C ₆	27.3	14.5	7.1	4,3	14.7
Iso-alkanes	36.8	39.3	40.4	33.4	32.2
Olefins	4.8	6.8	7.0	7.4	4.0
Aromatic hydrocarbons	9.2	14.9	17.8	23.1	20.1
Naphthenic hydrocarbons	21.9	24.5	27.7	31.8	23.0
Yield of the liquid phase		77.0	49.0	44.5	55.0
Octane number (RON)	78.9	81.4	84.9	88.3	89.3
Octane number (MON)	60.9	66.3	69.4	69.2	73.4
Weight fraction of sulfur, %	0.0092	0.0072	0.0062	0.0056	0.0012

The influence of pressure on the process of hydro-processing of straight-run gasoline on the catalyst $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ was studied. It can be seen that the yield of the liquid phase with an increase in pressure from 2.5 to 4.0 MPa decreases from 95.0 to 55.0% (table 2). The content of isoalkanes changes little with increasing pressure and ranges from 30.8 to 36.2%. The amount of aromatic hydrocarbons increases from 14.3 to 20.1%, the yield of olefins slightly increases in comparison with the original from 4.8 to 6.3%. The octane number of refined gasoline increases in comparison with the initial one from 78.9 to 89.3 (RON) and from 60.9 to 73.4 (MON). With increasing pressure the sulfur content decreased in comparison with the initial from 0.0092 to 0.0012 %.

Table 2 - Effect of pressure on the process of hydrorefining of straight-run gasoline over a catalyst CoO-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	22.1	20.1	20.8	16.7
Iso-alkanes	36.8	34.4	36.1	30.8	36.2
Olefins	4.8	6.2	4.6	6.3	4.0
Aromatic hydrocarbons	9.2	14.3	13.2	15.9	20.1
Naphthenic hydrocarbons	21.9	20.8	25.9	26.1	23.0
Yield of the liquid phase		95.0	91.7	88.0	55.0
Octane number (RON)	78.9	81.4	81.4	82.7	89.3
Octane number (MON)	60.9	64.5	63.2	63.5	73.4
Weight fraction of sulfur, %	0.0092	0.0025	0.0020	0.0013	0.0012

The hydroprocessing of catalytic cracking gasoline on the catalyst CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ has been investigated. Yield of the liquid phase as the temperature increases from 320 to 400 °C decreases from 95.0 to 90.0%. In the temperature range 320 - 400 °C maximal content of isoalkanes observed at 320 °C and is equal to 44.5 %. The amount of isoalkanes in the range of 350 - 400 °C ranges from 37.2 to 42.7%. The amount of aromatic hydrocarbons is increased from 28.7 to 37.4% with increasing process temperature to 400 °C. Yield olefins falls significantly compared to initial (31.2%), decreasing from 13.3 to 3.9% with increasing temperature from 320 to 400 °C. The amount of naphthenic hydrocarbons in the resulting catalysis ranges from 6.9-8.3%. The octane number of refined gasoline changes in comparison with the original from 88.7 to 85.8 (RON) and from 80.1 to 79.5 (MON). The sulfur content with increasing temperature up to 400 °C decreased from initial from 0.0134 to 0.0014 %.

The effect of pressure on the process of hydroprocessing of catalytic cracking gasoline on the catalyst CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ was studied (table 3). When the pressure is varied from 2.5 to 4.0 MPa, the amount of isoalkanes in the resulting product is 38.9-41.3%. The concentration of naphthenic hydrocarbons decreases with increasing pressure in the range of 2.5-4.0 MPa from 10.3% to 8.0%. The amount of aromatic hydrocarbons is 35.8-37.4%. The yield of the liquid phase ranges from 90.0-97.0%. The octane number of gasoline refined at 4.0 MPa is 85.8 (RON) and 79.5 (MON). The sulfur content in the final product is reduced from 0.0134% (initial gasoline) to 0.0014% at 4.0MPa.

Table 3 - Influence of pressure on the process of hydroprocessing of catalytic cracking gasoline on the catalyst CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃

Products, %	P, MPa				
	Initial	2,5	3.0	3,5	4.0
Paraffins C ₅ -C ₆	6.3	8.9	9.3	10.1	9,4
Iso-alkanes	25,4	40.9	38.9	39.5	41.3
Olefins	31.2	4.0	4.2	4.9	3.9
Aromatic hydrocarbons	30.1	35.8	37.1	36.6	37.4
Naphthenic hydrocarbons	7.0	10.3	10,4	9.0	8.0
Yield of the liquid phase		97.0	95.5	93.0	90.0
Octane number (RON)	88.7	85.6	86.0	84.8	85.8
Octane number (MON)	80.1	78.9	79.7	78.9	79.5
Weight fraction of sulfur, %	0.0134	0.0019	0.0018	0.0015	0.0014

In hydroprocessing of catalytic cracking gasoline using catalyst CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ when changing the feed space velocity of from 1.0 to 3.0 h⁻¹ the content of isoalkanes changes little - 41.3 - 41.5%, the concentration of aromatic hydrocarbons is 36.1 - 38.2%, the yield of naphthenic hydrocarbons ranges from 7.2 to 8.9%. The yield of olefinic hydrocarbons is significantly reduced compared to the original (31.2%) and at a feed space velocity of 3.0 h⁻¹ is 3.0%. The octane number of the

resulting gasoline is 85.0-85.8 (RON) and 79.0 -79.5 (MON). Gasoline with the lowest sulfur content – 0.0006% was obtained at a feed rate of 1.0 h⁻¹.

In testing the catalyst CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ in the process of hydrotreating of diesel oil found that with increasing temperature from 320 to 400 °C pour point and cloud point of the diesel fraction is reduced by 36.7 and 37.1°C, respectively. The yield of diesel fuel is 92.0-100%. The sulfur content after the hydrotreating of diesel fraction at 380- 400°C decreases from 0.560 to 0.104% (table 4).

Table 4 - Influence of temperature on the hydroprocessing of the diesel fraction on the catalyst CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ at V = 2 h⁻¹, P = 4.0 MPa

Process temperature, °C	Cloud point, °C	Pour point, °C	Weight fraction of sulfur, %	Yield, %
Initial diesel fraction	-11.3	-18.3	0.560	-
320	-42.8	-47.5	0.448	100
350	-48.4	-49.0	0.323	96.0
380	-44.7	-50.0	0.296	94.0
400	-40.8	-52.7	0.104	92.0

At P=4.0 MPa, V = 2.0 h⁻¹ the hydroprocessing of straight-run gasoline fraction on the catalyst CoO-MoO₃-Ce₂O₃-P₂O₅-ZSM-HY-Al₂O₃ was investigated (table 5). Yield of the liquid phase as the temperature increases from 320 to 400 °C decreases from 77.0 to 60.0%. In the temperature range 320-400 °C maximal content isoalkanes observed at 320°C and is equal to 41.3 % . At higher temperatures, their number is 36.9-41.3%. The content of aromatic hydrocarbons increases from 12.9 to 19.7% with an increase in the process temperature up to 400 °C. The amount of olefins and naphthenic hydrocarbons ranges from 5.6 to 6.3% and 20.1-25.3%, respectively. The octane number of refined gasoline increases in comparison with the initial one from 79.2 to 87.3 (RON) and from 61.1 to 72.7 (MON). The sulfur content with increasing temperature up to 400°C decreased from initial with from 0.0080 to 0.0016 %.

Table 5 - Influence of temperature on the hydroprocessing of straight-run gasoline catalyst CoO-MoO₃-Ce₂O₃-P₂O₅-ZSM-HY-Al₂O₃ at V = 2 h⁻¹ and P = 4.0 MPa

Products, %	T, °C				
	Initial gasoline	320	350	380	400
Paraffins C ₅ -C ₆	27.5	17.0	12.7	12.8	14.2
Iso-alkanes	39.8	41.3	40.0	36.9	39.8
Olefins	5.8	5.6	6.3	5.6	6.2
Aromatic hydrocarbons	8.7	12.9	15.7	22.8	19.7
Naphthenic hydrocarbons	18.2	23.2	25.3	21.9	20.1
Yield of the liquid phase		77.0	67.0	65.0	60.0
Octane number (RON)	79.2	84.0	86.4	85.2	87.3
Octane number (MON)	61.1	68.7	71.0	70.8	72.7
Weight fraction of sulfur, %	0.0080	0.0036	0.0027	0.0023	0.0016

In hydroprocessing gasoline of catalytic cracking on CoO-MoO₃-Ce₂O₃-P₂O₅-ZSM-HY-Al₂O₃ with increasing temperature up to 320-350 °C content of isoalkanes increases from 25.4 to 47.5 % (table 6) . With a further increase in temperature, there is a decrease in the amount of formed isoalkanes to 40.3% (400 °C). Under these conditions, the amount of aromatic hydrocarbons in the produced gasoline increases from 25.5 to 35.0 % . The content of naphthenic hydrocarbons in the catalysis is low and ranges from 6.1 to 8.3 % . The concentration of olefins in the catalyzate decreases from 31.2 % to 8.0 % . Yield of the liquid phase with increasing temperature in the range 320-400 °C varies between 95.0-100%. The octane number of ennobled at 400 °C catalytic cracking gasoline is 86.1 (RON) and 79.6 (MON). The sulfur content in the final product is reduced from 0.0134% (original gasoline) to 0.0029%.

Table 6 - Influence of temperature on the hydroprocessing of catalytic cracking gasoline on the catalyst CoO-MoO₃-Ce₂O₃-P₂O₅-ZSM-HY-Al₂O₃ at V = 2 h⁻¹, P = 4.0 MPa

Products, %	T, °C				
	Initial gasoline	320	350	380	400
Paraffins C ₅ -C ₆	6.3	8.8	9.2	10.6	8.1
Iso-alkanes	25.4	47.5	47.3	43.0	40.3
Olefins	31.2	12.1	7.6	5.0	8.0
Aromatic hydrocarbons	30.1	25.5	29.4	32.6	35.0
Naphthenic hydrocarbons	7.0	6.1	6.6	8.1	8.3
Yield of the liquid phase		100	97.5	95.5	95
Octane number (RON)	88.7	86.2	85.2	85.4	86.1
Octane number (MON)	80.1	81.0	79.0	78.0	79.6
Weight fraction of sulfur, %	0.0134	0.0048	0.0047	0.0035	0.0029

The hydroprocessing of straight-run gasoline on the catalyst CoO-MoO₃-La₂O₃-P₂O₅-AAC-ZSM-Al₂O₃ has been investigated. When hydroprocessing the gasoline fraction in the temperature range of 320-400 °C, the content of isoalkanes ranges from 30.9-37.1 %. Under these conditions, the amount of aromatic hydrocarbons decreases from 33.2 to 8.7 %. The yield of naphthenic hydrocarbons is growing from 13.6 to 26.9 %. Yield of the liquid phase as the temperature increases from 320 to 400 °C decreases from 91.3 to 70.2%. The octane number of gasoline after hydroprocessing increases from 83.7 (IM) and 58.9 (MM) in the initial to 79.1 (RON) and 78.9 (MON) at 400 °C. The sulfur content of catalysate with increasing temperature decreases from 0.0088 to 0.0001 % with 400 °C.

In testing the catalyst CoO-MoO₃-La₂O₃-P₂O₅-AAC-ZSM-Al₂O₃ in the hydrorefining of straight-run diesel fractions shown that the process temperature is raised from 320 to 400 °C pour point decreases from minus 28.5 to minus 40.0 °C. The cloud point under these conditions varies from minus 28.2 °C to 39.7 °C. The yield of hydrorefined diesel fuel is 80.0-87.5%. Sulfur content with increasing temperature up to 400 °C decreases from 0.6400 to 0.0671% (table 7).

Table 7 - Hydroprocessing of straight-run diesel oil fraction on the catalyst CoO-MoO₃-La₂O₃-P₂O₅-AAC-ZSM-Al₂O₃ at V = 2 h⁻¹, P = 4.0 MPa

Temperature, °C	Cloud point, °C	Pour point, °C	Yield, %	Weight fraction of sulfur, %
Initial	-16.1	-16.4	-	0.6400
320	-28.2	-28.5	80.0	0.0659
350	-32.4	-32.7	83.5	0.0553
380	-33.1	-33.4	87.5	0.0888
400	-39.7	-40.0	80.0	0.0671

Comparison of the results obtained in the study of the hydroprocessing of straight-run gasoline shows that the catalysts CoO-MoO₃-Ce₂O₃-P₂O₅-ZSM-HY-Al₂O₃, CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ and CoO-MoO₃-La₂O₃-P₂O₅-AAC-ZSM-Al₂O₃ have high hydrodesulfurizing activity. Under optimum conditions (P=4,0MPa, V = 2h⁻¹ and 400°C) the hydrodesulfurization degree of CoO-MoO₃-La₂O₃-P₂O₅-AAC-ZSM-Al₂O₃ is 98.86%, on CoO-MoO₃-Ce₂O₃-P₂O₅-ZSM-HY-Al₂O₃ - 80.0% and on CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ - 86.9% (residual sulfur content is 0.0001%, 0.0016 and 0.0012% respectively).

In the hydroprocessing of straight-run gasoline on catalysts CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃, CoO-MoO₃-Ce₂O₃-P₂O₅-ZSM-HY-Al₂O₃ and CoO-MoO₃-La₂O₃-P₂O₅-AAC-ZSM-Al₂O₃ there is an increase in the octane number compared to the original from 78.9 to 89.3, from 79.2 to 87.3 and from 79.1 to 88.4, respectively. This is mainly due to an increase in the content of isoalkanes and aromatic hydrocarbons in hydro-refined gasoline.

In gasoline hydroprocessing catalytic cracking was shown that under optimal conditions (p = 4,0MPa, V = 2h⁻¹ and 400 °C) the degree of hydrodesulfurization catalyst CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ is 89.5%, on CoO-MoO₃-Ce₂O₃-P₂O₅-ZSM-HY-Al₂O₃ - 78.4%, the residual sulfur content is 0.0014 and 0.0029% respectively. The initial sulfur content in catalytic cracked gasoline is 0.0134%.

It has been established that among the developed catalysts the lowest pour point and cloud point of hydro-refined diesel fuel is observed on the catalyst CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃. After

hydroprocessing at this catalyst pour point and cloud point are minus 52.7 °C and minus 40.8°C respectively. The same catalyst has the highest hydrodesulfurization activity: the sulfur content decreases from 0.5600% to 0.104% (the degree of hydrodesulfurization is 81.4%).

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 hydrodesulfurization of the gasoline fraction in comparison with 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 [6, 9, 23]

The activity of catalysts is related to the surface structure, composition and state of active sites. The physicochemical characteristics of the catalysts have been studied using various methods (EM, BET). The BET method has shown that the developed catalysts are characterized by pores with $d \approx 1.5\text{--}2.5$ nm.

Using temperature-programmed ammonia desorption, the acid-base characteristics of the catalysts were determined. On the surface of the catalyst $\text{CoO-MoO}_3\text{-Ce}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-HY-Al}_2\text{O}_3$ the acid sites with $T_{\text{des}} = 250$ °C prevail, their number is $8.57 \cdot 10^{-4}$; mol/g catalyst. The temperature of desorption of ammonia from the surface of the catalyst $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ shifts to the region of lower temperatures up to 230 °C, its amount is $8.05 \cdot 10^{-4}$ mol/g catalyst. Number more weakly acid sites at desorbed 150 °C on the catalysts $\text{CoO-MoO}_3\text{-Ce}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-HY-Al}_2\text{O}_3$ and $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ is small and amounts to 1.88 and $2.33 \cdot 10^{-4}$ mol/g of catalyst, respectively. The total amount of ammonia desorbed from the surface of the catalysts $\text{CoO-MoO}_3\text{-Ce}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-HY-Al}_2\text{O}_3$ and $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ practically the same: 10.45 and $10.38 \cdot 10^{-4}$ mol/g of catalyst.

Electron microscopic studies of the dispersion, structure and state of active centers allowed to establish that on the surface of the catalyst $\text{CoO-MoO}_3\text{-Ce}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-HY-Al}_2\text{O}_3$ there are clusters with $d \approx 4.0\text{--}5.0$ nm composed of smaller particles, identifying x as the Ce_2O_3 . There are structures with $d \leq 10.0$ nm, which include Ce_6O_{11} , CoMoP , $\text{Ce}(\text{MoO}_4)$, CoAlO_4 , $\text{Ce}_8\text{Mo}_{12}\text{O}_{49}$, $\text{Al}_5\text{Co}_2\text{Ce}_4$, CoSi , $\text{Ce}_2\text{Mo}_3\text{O}_{12}$ и $\text{Ce}_4(\text{P}_2\text{O}_7)_3$. In addition, single dense particles were found, consisting of $\text{Co}(\text{H}_2\text{PO}_3)_2 \cdot 6\text{H}_2\text{O}$, AIP and MoPO_4 with $d \leq 10.0$ nm.

The catalyst $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ is characterized by extensive accumulations of small particles with $d \approx 3.0\text{--}5.0$ nm, corresponding to a mixture of phases MoOPO_4 , La_2O_3 , MoO_5 , and La_2MoO_3 . Also, small accumulations of highly dispersed particles with a size of $\approx 8.0\text{--}10.0$ nm were found, which can be attributed to $\text{La}_4(\text{P}_2\text{O}_7)_3$. There are small transparent aggregates with $d \leq 20.0$ nm related to LaAlO_3 in a $\gamma\text{-La}^0$ mixture. The appearance of $\gamma\text{-La}^0$ can be associated with redox processes occurring between the components of the active phase.

It should be noted that the detected structures AlMo_3 , CoSi , LaAlO_3 and MoSi_2 indicate the incorporation of metals-components of the active phase into the structure of the zeolite with the formation of new centers that can function as Lewis acid centers [24].

The studied catalysts are characterized by the presence of both metal and acid-base centers. The acid sites can include metals in various oxidation states, fixed both inside the zeolite cavities and on their outer side [24 - 26]. Electron microscopy studies made it possible to establish that on the surface of the studied catalysts there are several types of surface structures that differ significantly both in size and in the chemical state of the components. The catalysts are highly dispersed, the metal components of the active phase are predominantly in an oxidized state, forming associate clusters on the surface, the dispersion, structure and state of which is determined by the nature of the catalyst components.

Thus, modified zeolite-containing catalysts $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-Ce}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-HY-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-AAC-ZSM-Al}_2\text{O}_3$ exhibiting high activity in the hydrorefining of gasoline and diesel fractions, capable of one-stage deep hydrotreating, hydroisomerization and hydrocracking [23, 27], which makes it possible to obtain low-sulfur, high-octane gasoline and low-sulfur and low-solidifying diesel fuel, which is important for the operation of vehicles in winter conditions.

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**Б.Т. Туктин, Л.Б. Шаповалова, А.А. Тенизбаева,
А.З. Абилямгажанов, Р.И. Егизбаева**

«Д.В. Сокольский атындағы Жанармай, катализ
және электрохимия институты» АҚ, Алматы, Қазақстан

МОДИФИЦИРОВАННЫЕ АЛЮМОКОБАЛЬТМОЛИБДЕННЫЕ КАТАЛИЗАТОРЫ МУНАЙ ФРАКЦИЙ НА ГИДРОТАЗАЛАУ ЖӘНЕ ГИДРОИЗОМЕРЛЕУ

Аннотация. Жұмыста мұнайдың бензин және дизель фракцияларын алюмооксидті катализаторларда $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-Ce}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-HY-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-AAC-ZSM-Al}_2\text{O}_3$ гидроөңдеуді зерттеу нәтижелері келтірілген.

Катализаторлар алюминий гидроксиді мен ZSM-5 цеолит қоспасын, кобальт, молибден, лантан және фосфор қышқылы тұздарының НУ су ерітінділерімен сіндіріп дайындады. Түйіршіктеу мен қалыптаудан кейін катализаторларды 150°C -та кептіріп, 550°C -та қыздырды.

Әртүрлі бензин және дизель фракцияларды гидроөңдеу процесінде синтезделген катализаторлардың ірілендірілген зертханалық сынақтар жүргізілді. Сынақтар $320\text{-}400^\circ\text{C}$ температурада, $2,5\text{-}4,0$ МПа қысымда және шикізат берудің көлем жылдамдығы $1,0\text{-}3,0$ сағ⁻¹ кезінде катализатордың стационарлық қабаты бар жоғары қысымды ағынды қондырғыда жүзеге асырылды.

Реакция өнімдерінің көмірсутегі құрамы «Хроматэк-Кристалл» хроматографында талданды. Күкірт құрамын «Oilser International» ЖШС-да (Алматы қ.) талдау жүргізілді. Қату және лайлану температурасын анықтау Лаз М2 аспабында жүзеге асырылды.

$\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ катализаторында тура айдалған бензинді гидроөңдеу кезінде $320\text{-}350^\circ\text{C}$ температура аралығында изоалкалардың көп саны $33,4\text{-}40,4\%$ пайда болатынын көрсетеді. Жоғары температурада изоалкалар шығыны 400°C кезінде $32,2\%$ -ға дейін төмендейді. Катализаттағы ароматты көмірсутек құрамы $14,9\text{-}20,1\%$ -ға дейін артады, нафтендік көмірсутектердің шығуы $24,5\text{-}23,0\%$ шегінде ауытқиды. Бензиннің октан саны бастапқы көрсеткішпен салыстырғанда $78,9\text{-}89,3$ -ке (З.Ә) және $60,9\text{-}73,4$ -ке (М.Ә.) дейін артады. Температураны 400°C -қа дейін арттырғанда катализаттағы күкірт мөлшері $0,0012\%$ -ға дейін төмендеді.

$\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ катализаторында каталитикалық крекинг бензинін гидроөңдеу кезінде жақсартылған бензиннің октандық саны шамалы төмендейді. Температураның 400°C -қа дейін өсуі арқылы катализаттағы күкірттің құрамы бастапқы көрсеткішпен салыстырғанда $0,0134$ -тен $0,0014\%$ -ға дейін төмендеді. $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ катализаторында каталитикалық крекинг бензинін гидроөңдеу кезінде шикізатты көлемдік беру жылдамдығы $1,0$ -ден $3,0$ сағ⁻¹-ға дейін өзгергенде катализаттағы изоалкалар құрамы шамалы өзгереді: $41,3\text{-}41,5\%$, ароматты көмірсутек концентрациясы $36,1\text{-}38,2\%$ құрайды, нафтенді көмірсутектер шығымы $7,2\text{-}8,9\%$ құрайды. Олефинді көмірсутектердің шығымы бастапқы ($31,2\%$) және шикізат көлем беру жылдамдығы $3,0$ сағ⁻¹ тең болғанда $3,0\%$ -ды көрсетті. Құрамында $0,0006\%$ күкірті ең аз бензин көлем беру жылдамдығы $1,0$ сағ⁻¹ тең болғанда алынған.

Гидрожақсартылған дизель отынының қату және лайланудың ең төмен температурасы $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ катализаторында байқалады. Гидроөңдеуден кейін осы катализаторда қату және лайлану температурасы тиісінше минус $52,7^\circ\text{C}$ және минус $40,8^\circ\text{C}$ -қа тең. Бұл катализатор ең жоғары гидрокүкіртсіздендіру активтілігін көрсетті: күкірт мөлшері $0,5600\%$ -дан $0,104\%$ -ға дейін төмендейді. Дайындалған модифицирленген цеолитті катализаторлар $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-Ce}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-HY-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-AAC-ZSM-Al}_2\text{O}_3$ бензин мен дизель фракцияларын гидроөңдеу кезінде жоғарғы белсенді болып келеді, бір сатыда терең гидротазалауға, гидроизомеризациялауға және гидрокрекингке қабілетті, бұл қыста көлік құралдарының жұмысына маңызды болып саналатын төмен күкірт, жоғары октанды бензин мен аз күкіртті және төмен температурада қататын дизель отынын алуға мүмкіндік береді.

Мұндай зерттеулер $\text{CoO-MoO}_3\text{-Ce}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-HY-Al}_2\text{O}_3$ және $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-AAC-ZSM-Al}_2\text{O}_3$ катализаторларында жүргізілді.

Түйін сөздер: тура айдалған бензин, мұнайдың дизель фракциясы, цеолит, катализатор, гидротазалау.

Б.Т. Туктин, Л.Б. Шаповалова, А.А. Тенизбаева, А.З. Абилямгажанов, Р.И. Егизбаева

АО "Институт топлива, катализа и электрохимии им. Д.В. Сокольского", Алматы, Казахстан

ГИДРООЧИСТКА И ГИДРОИЗОМЕРИЗАЦИЯ НЕФТЯНЫХ ФРАКЦИЙ НА МОДИФИЦИРОВАННЫХ АЛЮМОКОБАЛЬТМОЛИБДЕНОВЫХ КАТАЛИЗАТОРАХ

Аннотация. В данной работе приведены результаты исследования гидропереработки бензиновых и дизельных фракций нефти на алюмооксидных катализаторах $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-Ce}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-HY-Al}_2\text{O}_3$, $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-AAC-ZSM-Al}_2\text{O}_3$.

Катализаторы готовили пропиткой смеси гидрооксида алюминия и цеолитов ZSM-5, HY водными растворами солей кобальта, молибдена, лантана и фосфорной кислоты. После гранулирования и формования катализаторы сушили при 150°C и прокаливали при 550°C .

Были проведены укрупненные лабораторные испытания синтезированных катализаторов в процессе гидропереработки различных видов бензиновых и дизельных фракций. Испытания осуществляли в проточной установке высокого давления со стационарным слоем катализатора при температурах 320-400°C, давлении 2,5-4,0 МПа и объемной скорости подачи сырья 1,0-3,0 ч⁻¹.

Углеродородный состав продуктов реакции анализировали на хроматографах «Хроматэк-Кристалл». Анализ содержания серы проводился в ТОО «Oilser International» (г. Алматы). Определение температуры застывания и помутнения проводились на приборе ЛАЗ М2.

При гидропереработке прямогонного бензина на катализаторе CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ показано, что в интервале температур 320 - 350°C образуется максимальное количество изоалканов 33,4-40,4%. При более высоких температурах выход изоалканов снижается до 32,2% при 400°C. Содержание ароматических углеводородов в катализате возрастает от 14,9 до 20,1%, выход нафтеновых углеводородов колеблется в пределах 24,5-23,0%. Октановое число облагороженного бензина повышается по сравнению с исходным от 78,9 до 89,3 (И.М.) и от 60,9 до 73,4 (М.М.). Содержание серы в катализате с ростом температуры до 400°C снизилось до 0,0012%.

При гидропереработке бензина каталитического крекинга на катализаторе CoO -MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ октановое число облагороженного бензина незначительно снижается. Содержание серы в катализате с ростом температуры до 400°C снизилось по сравнению с исходным с 0,0134 до 0,0014%.

При изменении объемной скорости подачи сырья от 1,0 до 3,0 ч⁻¹ содержание изоалканов в катализате мало меняется – 41,3-41,5%, концентрация ароматических углеводородов составляет 36,1-38,2%, выход нафтеновых углеводородов колеблется в пределах от 7,2 до 8,9%. Выход олефиновых углеводородов значительно снижается по сравнению с исходным (31,2%) и при объемной скорости подачи сырья, равной 3,0 ч⁻¹, составляет 3,0%. Бензин с наиболее низким содержанием серы –0,0006% получен при скорости подачи сырья, равной 1,0 ч⁻¹.

При испытании катализатора CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃ в процессе гидропереработки дизельной фракции нефти установлено, что наиболее низкая температура застывания и помутнения гидрооблагороженного дизельного топлива наблюдается на катализаторе CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃. После гидропереработки на этом катализаторе температура застывания и помутнения равны минус 52,7°C и минус 40,8°C соответственно. Этот же катализатор обладает наиболее высокой гидрообессеривающей активностью: содержание серы понижается с 0,5600% до 0,104%.

Таким образом, разработаны модифицированные цеолитсодержащие катализаторы CoO-MoO₃-La₂O₃-P₂O₅-ZSM-Al₂O₃, CoO-MoO₃-Ce₂O₃-P₂O₅-ZSM-HY-Al₂O₃, CoO-MoO₃-La₂O₃-P₂O₅-AAC-ZSM-Al₂O₃, проявляющие высокую активность при гидропереработке бензиновых и дизельных фракций, способные в одну стадию проводить глубокую гидроочистку, гидроизомеризацию и гидрокрекинг, что позволяет получать малосернистый, высокооктановый бензин и малосернистое низкокзастывающее дизельное топливо, что важно для работы автотранспорта в зимних условиях.

Аналогичные исследования были проведены на катализаторах CoO-MoO₃-Ce₂O₃-P₂O₅-ZSM-HY-Al₂O₃ и CoO-MoO₃-La₂O₃-P₂O₅- AAC-ZSM -Al₂O₃.

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

Information about the authors:

*Tuktin B.T., Head of the sector of motor fuels, Doctor of Chemical Sciences, JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan, <https://orcid.org/0000-0003-3670-4010>, tuktin_balga@mail.ru;

Shapovalova L.B., Chief Researcher, Motor Fuels Sector, Doctor of Chemical Sciences, JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan, <https://orcid.org/0000-0002-3682-5878>, n-nikk@bk.ru;

Tenizbayeva A.A., Lead engineer of the sector of motor fuels JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan, <https://orcid.org/0000-0001-9801-0757>, aliya.85@mail.ru;

Abilmagzhanov A.Z., First Deputy Director, Ph.D in Chemistry, JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan, <https://orcid.org/0000-0001-8355-8031>, a.abilmagzhanov@ifce.kz;

Egizbaeva R.I., Senior Researcher, Motor Fuels Sector, candidate of chemical sciences, JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan, <https://orcid.org/0000-0002-4630-4021>, e_raikul@mail.ru

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