N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2018. 2518-1491.2**
Volume 5, Number 431 (2018), 13 – 19

УДК 541.128.665

B.T.Tuktin, A.S.Tenizbaeva, N.N.Nurgaliyev, L.B.Shapovalova, V.I. Yaskevich

"D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry", Almaty, Kazakhstan
E-mail: tuktin_balga@mail.ru

STUDY OF HYDRO PURIFICATION ANDHYDROIZOMERIZATIONSTRAIGHT-RUN GASOLINE FRACTION OVER MODIFIED Ni (Co)-Mo- Al_2O_3- CATALYSTS

Abstract. The article presents the results of studies of hydropurificationand hydroisomerization of a straight-run gasoline fraction on new zeolite-containing alumonickel (cobalt) molybdenum catalysts modified with phosphorus and (rare earth element) REE: $CoO-MoO_3-Ce_2O_3-P_2O_5-Al_2O_3$-ZSM (KGO-18) and $NiO-MoO_3.Ce_2O_3-P_2O_5-Al_2O_3$-ZSM (KGO-3). The effect of temperature, pressure and the volume flow rate of the feedstock was studied. Investigation of the processes of hydroprocessing of straight-run gasoline was carried out in a high-pressure flow system with a stationary catalyst bed at temperatures of 320-400^{0}C, a pressure of 3.0 -4.0 MPa and a feed rate of 0.5-3.0hr^{-1}.

At hydroprocessing of straight-run gasoline with high hydrodesulfurizing activity the catalyst KGO-18 possesses. The sulfur content of the catalyst decreased from 0.0080 (reference gasoline) to 0.0015% with an increase in temperature to 400°C. After hydroprocessing the straight-run gasoline fraction on the KGO-3 catalyst at 400°C, the octane number of the hydro-upgraded gasoline rises from 79.0 (reference gasoline) to 92.4 research method (RM) and from 62.4 to 77.0 motor method (MM). Under these conditions, the octane number of hydrotreated gasoline on the catalyst KGO-18 is increased in comparison with the initial from 78.9 to 90.7 (RM) and by the motor method from 60.9 to 71.7.

Electron microscopic studies have shown that the modified Ni (Co)-Mo-Al_2O_3 catalysts are highly disperse, the metal components of the active phase are predominantly in the oxidized state, forming cluster-associates on the surface whose dispersion and structure and state are determined by the nature of the catalyst components.

Key words: zeolite, straight run gasoline, catalyst, hydrotreatment.

Introduction

In the oil refining industry, hydropurification and hydroisomerization processes are widely used to produce high-quality motor fuels, which are one of the main processes widely used in the oil refining industry.

In connection with the deepening of the processing of high-sulfur oil, there is a growing need to improve the existing catalysts for the hydrotreating of oil fractions. In accordance with modern requirements, a significant limitation of the sulfur, benzene, aromatic and olefinic hydrocarbons in motor fuels is necessary. The known industrial catalysts do not provide the required degree of hydrotreating. In many countries, catalysts are being searched for increasing the depth of removal of sulfur-containing compounds and improving the technology for the production of motor fuels.

The problem of choosing the most effective catalyst is complex and requires in each case an individual approach. Recently, specific catalytic systems for the hydroprocessing of a specific type of raw material have been purposefully developed [1-19].

In this paper, the results of hydropurification and hydroisomerization studies of a straight-run gasoline fraction on new zeolite-containing alumonickel (cobalt) molybdenum catalysts modified with phosphorus and REE: $CoO-MoO_3-Ce_2O_3-P_2O_5-Al_2O_3$-ZSM (KGO-18) and $NiO-MoO_3-Ce_2O_3$- $P_2O_5-Al_2O_3$-ZSM (KGO-3).

Experimental part

New modified zeolite-containing catalysts of CGO were developed. The catalysts were prepared by impregnating a mixture of aluminum hydroxide and zeolite ZSM with aqueous solutions of nickel (cobalt) nitrate, ammonium paramolybdate and the introduction of modifying additives. After molding, the catalyst was dried at 150°C and calcined at 550°C for 5 hours.

New zeolite-containing modified catalysts were synthesized for the process of hydrotreating gasoline fractions of oil:CoO-MoO$_3$- Ce$_2$O$_3$-P$_2$O$_5$-Al$_2$O$_3$-ZSM (KGO-18);NiO-MoO$_3$- Ce$_2$O$_3$-P$_2$O$_5$ - Al$_2$O$_3$-ZSM (KGO-3).

Investigation of the processes of hydroprocessing straight-run gasoline in a high-pressure flow system with a stationary catalyst bed at temperatures of 320-400^{0}C, a pressure of 3.0-4.0 MPa and a volumetric feed rate of 2hr^{-1}. The hydrocarbon composition of the reaction products was analyzed on chromatographs "Chromatec-Crystal" and "Chromium-5". Analysis of sulfur content in feedstock and products was carried out in «Oilsert International» LLP (Almaty).

To study the structure and state of the catalyst surface, the electron microscopy method was used [20, 21].

Results and discussion

When hydrolyzing the gasoline fraction on the catalyst KGO-3 at 320^{0}C at V = 2.0hr^{-1} and P = 4.0MPa, the content of isoalkanes increases from 40.3% (initial fraction) to 44.0%, with an increase in temperature to 400^{0}C, their amount slightly reduced to 37.5% (Table 1). Under these conditions, the proportion of aromatic hydrocarbons in the resulting catalyst varies from 14.7 to 29.4%. The content of naphthenic hydrocarbons in the catalyst is 19.4-22.5%, olefinic hydrocarbons - 4.2 - 6.1%. The yield of the liquid phase with increasing temperature from 320 to 400^{0}C decreases from 80.0 to 75.0%.The octane number of hydrotreated gasoline in these conditions rises from 79.0 (reference gasoline) to 92.4 (RM) and from 60.9 to 77.0 (MM). After processing the gasoline fraction with an initial sulfur content of 0.0080% on the catalyst KGO -3, the mass fraction of sulfur in the catalyst decreased to 0.0039% with an increase in temperature to 400 ° C.

Table 1 - Effect of temperature on the process of hydroprocessing of the gasoline fraction on the catalyst KGO-3

Products,%	T˚C				
	Initialgasoline	320	350	380	400
Paraffins C$_5$-C$_6$	25,7	14,5	8,5	5,1	6,9
Iso-alkanes	40,3	44,0	42,2	46,2	37,5
Olefins	5,1	4,3	6,1	4,2	4,4
Aromatichydrocarbons	8,9	14,7	23,2	25,1	29,4
Naphthenichydrocarbons	20,0	22,5	20,0	19,4	21,8
Yield of the liquid phase	-	80,0	78,5	78,6	75,0
Octane number by research method	79,0	85,6	87,9	89,1	92,4
Octane number by motor method	60,9	71,9	73,4	74,2	77,0
Massfractionofsulfur,%	0,0080	0,0064	0,0060	0, 0057	0,0039
Note: P=4,0MPa, V=2,0ч$^{-1}$					

The influence of pressure on the process of hydroprocessing of the gasoline fraction on the catalyst KGO-3 at V = 2.0 hr^{-1} and T = 400^{0}C was studied (Table 2). With an increase in pressure in the interval 2.5-4.0 MPa, the amount of isoalkanes is 37.2-38.9%, the concentration of naphthenic hydrocarbons decreases from 17.0% to 21.9%.The concentration of aromatic hydrocarbons in the resulting catalyst ranges from 29.4-30.9%, olefins - 3.4-9.0%. The yield of the liquid phase is 70.0-75.0%. The octane number of gasoline enriched at 4.0 MPa is 92.4 (RM) and 77.0 (MM). When hydrolyzing the gasoline fraction, the sulfur content of the final product decreases from 0.0080% (reference gasoline) to 0.0039% at 4.0 MPa.

Table 2 - Influence of pressure on the process of hydroprocessing of the gasoline fraction on the catalyst KGO-3

Products,%	Pressure, MPa				
	Initial gasoline	2,5	3,0	3,5	4,0
Paraffins C_5-C_6	25,7	8,5	4,2	8,7	6,9
Iso-alkanes	40,3	37,8	38,9	37,2	37,5
Olefins	5,1	3,4	9,0	6,3	4,4
Aromatichydrocarbons	8,9	30,9	30,9	30,8	29,4
Naphthenichydrocarbons	20,0	19,8	17,0	17,0	21,8
Yield of the liquid phase	-	70,0	70,0	72,0	75,0
Octane number by research method	79,0	90,0	91,0	91,5	92,4
Octane number by motor method	60,9	75,4	74,9	76,5	77,0
Massfractionofsulfur,%	0,0080	0,0061	0,0057	0,0049	0,0039
Note: P=4,0MPa, V=2,0hr^{-1}: V=2,0hr^{-1}andT= 400^{0}C.					

During the hydroprocessing of the gasoline fraction on the catalyst KGO-3 (P = 4.0 MPa and 400°C), when the volumetric feed rate of the feed varies from 1.0 to 2.5 hr^{-1}, the content of isoalkanes in the catalyst varies from 31.4 to 37.5% the concentration of aromatic hydrocarbons is 29.0-30.7%, of naphthenic hydrocarbons is from 15.4 to 21.8%. The amount of olefinic hydrocarbons varies between 2.7-4.4%. The octane number of the gasoline produced increases with hydrotreating on the catalyst KGO-compared to the initial (79.0) to 92.4-93.7 (RM). The yield of the liquid phase is 75.0-78.0%. When hydrolyzing the gasoline fraction on the catalyst KGO-3, the sulfur content in the final product decreases from 0.0080% (reference gasoline) to 0.0039% at 4.0 MPa (Table 3)

Table 3 - Influence of the space velocity on the process of hydroprocessing of the gasoline fraction on the catalyst KGO-3.

Products,%	Volumetricspeed, h^{-1}			
	Initial gasoline	1.0	1.5	2.0
Paraffins C_5-C_6	25,7	20,2	17,4	6,9
Iso-alkanes	40,3	31,4	33,8	37,5
Olefins	5,1	2,7	2,7	4,4
Aromatichydrocarbons	8,9	29,0	30,7	29,4
Naphthenichydrocarbons	20,0	16,6	15,4	21,8
Yield of the liquid phase	-	78,0	77,0	75,0
Octane number by research method	79,0	93,7	93,5	92,4
Octane number by motor method	60,9	77,4	77,6	77,0
Massfractionofsulfur,%	0,0080	0,0037	0,0039	0,0039
Note: P= 4.0MPa, 400˚C				

When studying the influence of temperature on the process of hydroprocessing of straight-run gasoline on the catalyst KGO-18, it was shown that in the temperature range 320-350^{0}C the maximum amount of isoalkanes is 39.7-38.2% (Table 4). At higher temperatures, the yield of isoalkanes decreases to 34.4% at 400 ^{0}C. The content of aromatic hydrocarbons in the catalyst under these conditions increases from 15.2 to 24.8%, the yield of naphthenic hydrocarbons decreases from 26.1 to 24.0%. The amount of olefinic hydrocarbons varies within the range of 4.6-7.6%. The yield of hydro-upgraded gasoline decreases from 70.7 to 60.5% with increasing temperature from 320 to 400^{0}C.The octane number of hydrotreated gasoline is increased compared with the original from 79.0 to 90.7 (MI) and by the motor method from 60.9 to 71.7. The sulfur content of the catalyst decreased from 0.0080 (reference gasoline) to 0.0015% with an increase in temperature to 400°C.

Table 4 - Effect of temperature on the process of hydroprocessing straight-run gasoline on catalyst KGO-18

Products,%	T°C				
	Initialgasoline	320	350	380	400
Paraffins C_5-C_6	27,3	11,4	15,1	12,5	12,2
Iso-alkanes	36,8	39,7	38,2	34,0	34,4
Olefins	4,8	7,6	5,6	5,4	4,6
Aromatichydrocarbons	9,2	15,2	18,7	20,9	24,8
Naphthenichydrocarbons	21,9	26,1	22,3	27,2	24,0
Yield of the liquid phase	-	70,7	68,3	65,0	60,5
Octane number by research method	79,0	82,6	84,9	88,1	90,7
Octane number by motor method	60,9	67,8	67,7	68,5	71,7
Massfractionofsulfur,%	0,0080	0,0049	0,0026	0,0030	0,0015
Note: P=4,0MPa, V=2,0hr^{-1}					

Table 5 shows the results obtained in a study of the effect of pressure on the process of hydroprocessing straight-run gasoline on the catalyst KGO-18. Studies have shown that in the pressure range 2.5-4.0 MPa, the content of isoalkanes in the catalyst increases from 31.2 to 38.8%. The amount of aromatic hydrocarbons in this pressure range increases from 25.8% to 32.8%, while a decrease in the yield of naphthenic hydrocarbons from 30.1% to 22.9%. The content of olefinic hydrocarbons is 5.3-6.2%.The yield of hydro-upgraded gasoline increases with increasing pressure from 58.0 to 90.0%. The octane number of hydro-upgraded gasoline is increased compared to the initial from 79.0 to 90.7 by the research method and by the motor method from 60.9 to 71.7. The sulfur content of the catalyst decreased from 0.0080 to 0.0015% as the temperature increased to 400^{0}C.

Table 5 - Influence of pressure on the process of hydroprocessing
of straight-run gasoline on the catalyst KGO-18 at T = 400°C, V = 2.0 h^{-1}

Products,%	P, MPa				
	Initialgasoline	2,5	3,0	3,5	4,0
Paraffins C_5-C_6	27,3	7,6	12,6	7,6	7,2
Iso-alkanes	36,8	31,2	32,0	37,8	38,8
Olefins	4,8	5,3	5,5	3,0	6,2
Aromatichydrocarbons	9,2	25,8	26,9	31,3	32,8
Naphthenichydrocarbons	21,9	30,1	22,9	20,3	22,9
Yield of the liquid phase		58,0	70,0	75,0	90,0
Octane number by research method	79,0	87,7	91,5	88,2	90,7
Octane number by motor method	60,9	70,3	72,3	72,5	71,7
Massfractionofsulfur,%	0,0080	0,0013	0,0013	0,0012	0,0015
Note: V=2,0hr^{-1}andT= 400^{0}C.					

When hydrolyzing the gasoline fraction on the catalyst KGO-18 (P = 4.0 MPa and 400°C) with an increase in the feed rate of feed from 0.5 to 3.0 hr^{-1}, the content of isoalkanes in the catalyst increases from 31.3 to 35.0 %, the amount of aromatic hydrocarbons is 25.7-32.8%, the yield of naphthenic hydrocarbons is 26.3-34.9%, of olefinic hydrocarbons varies between 5.8-6.3% (Table 6). The octane number of the produced gasoline increases with hydrotreating on the catalyst KGO-18 in comparison with the initial (79.0) to 89.2-90.7 (RM).The yield of the liquid phase fluctuates within the limits of 80.4-94.6%. During hydroprocessing of the gasoline fraction on the catalyst KGO-18 at P = 4.0 MPa and 400^{0}C and sulfur feed rates of 0.5 hr^{-1} sulfur-containing compounds in the final product were not detected. With an increase in feed rate, the residual sulfur content fluctuates between 0.0012 and 0.0026% (Table 6).

Table 6- Influence of the volumetric feed rate on the process
of hydroprocessing of straight-run gasoline on the catalyst KGO-18

Products,%	V, ч$^{-1}$					
		0,5	1,0	2,0	2,5	3,0
Paraffins C_5-C_6	27,3	3,5	8,2	3,2	7,9	6,5
Iso-alkanes	36,8	31,3	30,0	22,8	34,3	35,0
Olefins	4,8	6,3	6,2	6,2	5,8	5,7
Aromatichydrocarbons	9,2	25,8	27,7	32,8	25,7	26,2
Naphthenichydrocarbons	21,9	33,1	27,9	34,9	26,3	26,6
Yield of the liquid phase	-	94,6	93,8	90,0	86,4	80,4
Octane number by research method	79,0	89,7	89,2	90,7	90,7	92,1
Octane number by motor method	60,9	71,5	68,9	71,7	72,1	71,5
Massfractionofsulfur,%	0,0080	-	0,0012	0,0015	0,0024	0,0026
Note: P=4,0MPaand400˚C						

The conducted studies of the process of hydroprocessing of the straight-run gasoline fraction allowed to establish that the catalyst KGO-18 possesses higher hydrodesulfurizing activity in comparison with the catalyst KGO-3: the residual sulfur content at 400°C is 0.0015 and 0.0039%, respectively. Under these conditions, the octane number of gasoline hydroprocessed on the catalyst KGO-18 is 90.7 (RM), and the gasoline produced on the catalyst KGO-3 has an octane number of 92.4 (RM). The observed increase in the octane number is mainly due to the enhancement of the process of hydroisomerization of n-alkanes and the increase in the content of aromatic hydrocarbons.

The activity of the catalysts is related to the surface structure, composition and state of the active sites. An electron-microscopic study was made of the structure and state of the active sites of catalysts KGO-3 and KGO-18.

According to the electron microscopy data, the catalysts are highly disperse, the metal components of the active phase are predominantly in the oxidized state, forming cluster-associates on the surface, the dispersion, structure and state of which is determined by the nature of the catalyst components.

The KGO-3 catalyst is characterized by the presence of clusters with d = 3.0 - 4.0 nm, which are formed by finely dispersed particles with d <0.05 nm, which include NiSi2 and Ni2O3. In addition, there are single particles with signs of hexagonal faceting with d ≈ 15.0-30.0 nm, consisting of the compounds $AlNi_2Si$, AlNi, Ge_2O_3, MoO (OH) $_2$, $AlMo_3$, $MoSi_2$, Al_3Ce and $CeAlO_3$ (Figure 1).

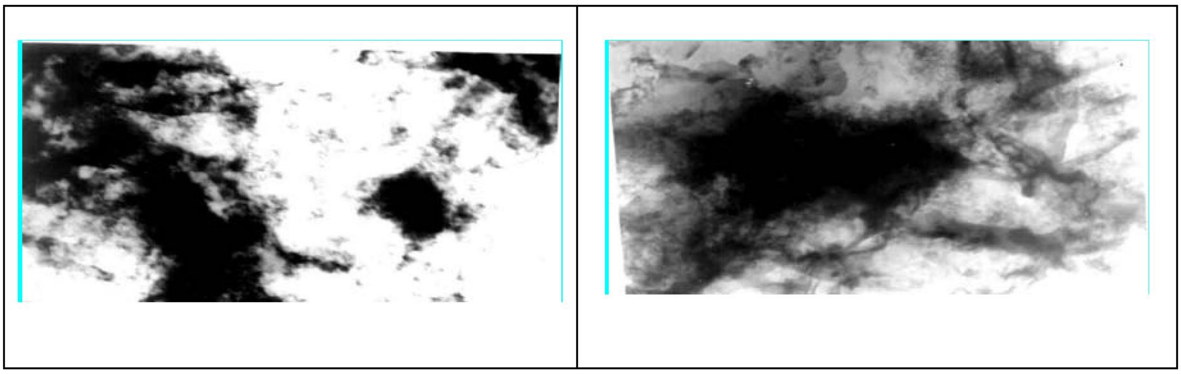

Figure 1 - Electron microscopic RMages of the catalyst KGO-3

Clusters of highly dispersed particles of various shapes with d = 50-200 nm, consisting of $Co_2Mo_3O_8$, CeP_2O_7, $AlPO_4$, CoOOH, $MoOPO_4$, α-Co (P_2O_7), Ce (MoO_4) $_2$, are found on the surface of the catalyst KGO-18 (Fig. 2). In addition, there are 4-5 nm particles formed by Ge4 (P2O7) 3, CoSi, MoP, $MoSi_2$, $Ge_6O_{11}$and $CoMoP_2$.

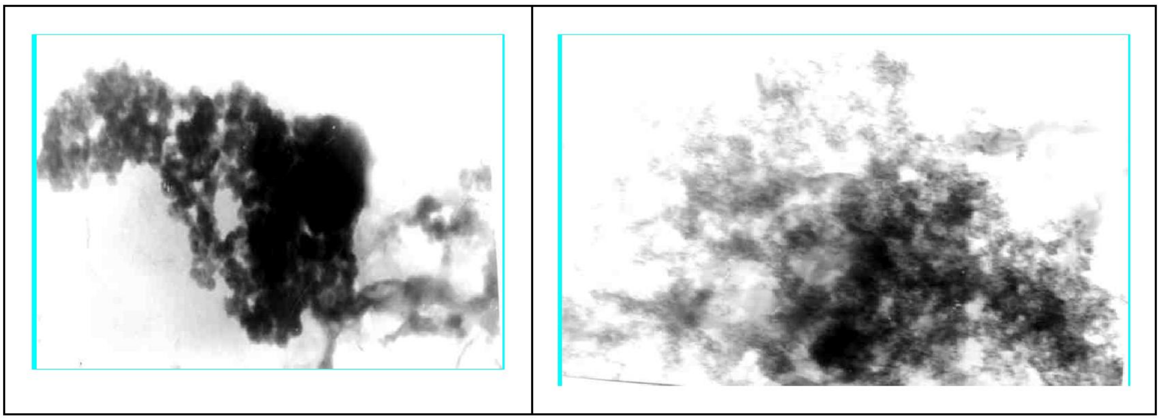

Figure 2 - Electron microscopic RMages of the catalyst KGO-18

It should be noted that the detected structures of AlNi2Si, AlMo3, AlNi, MoSi2, Al3Ce and CeAlO3 NiSi2 indicate the introduction of metals-active phase components into the zeolite structure with the formation of new centers that can function as Lewis acid sites [22, 23].

Conclusions. Thus, modified zeolite-containing catalysts for the hydroprocessing of gasoline fractions $CoO-MoO_3-Ce_2O_3-P_2O_5-Al_2O_3$-ZSM and $NiO-MoO_3-Ce_2O_3$ $-P_2O_5-Al_2O_3$-ZSM have been developed and synthesized, which hydrotreating and hydroisomerization in one step. The developed catalysts for activity in hydrotreatment processes of gasoline fractions of petroleum exceed the known industrial catalysts [1, 2]. The catalysts make it possible to obtain low-sulfur gasoline, and also to increase its octane number.

Source of research funding: The work is carried out in accordance with the scientific and technical program: No. BR05236739 "Creation of bases for the production of oil and gas products based on domestic technologies".

REFERENCES

[1] XavkinV.F., ChernyshevaE.A., GulayevaL.A., Gidrogenizatsionnyeprotsessypolucheniyamotornyhtopliv. Ufa, **2013**.259 .(in Russ)

[2] Smirnov V.K., Irisova K.N., Talisman E.L. Kataliz v promyshlennosti. **2003**, 2, 30-36. (in Russ)

[3] BarsukovO.V. TalismanE.L. Nasirov R.K. Neftepererabotka ineftehimia. **1996**, 9, 14-21. (in Russ)

[4] Gavrilov N.V., Durov O.V. Himiaitexnologiatoplivimasel. **2008**, 6, 9-13. (in Russ)

[5] Rodrıguez-Castellon E., Jimenez-Lopez A., Eliche-Quesada D. Fuel. – **2008**, 87, 1195-2006.(in Eng)

[6] Dengqian Zhang, Aijun Duan, Zhen Zhao, Chunming Xu. J. of catalysis. – **2010**, 274, 2, 273-286. (in Eng)

[7]YoussefSaih, KohichiSegawa. Applied catalysis A. **2009**, 353, 258-265. (in Eng)

[8] Iasian Iý .P., Kolesnikov A.G., Krahmalova I.S., Borovikova T.N., Ivanenko M.V., Ovchinnikova P.F.Himiaitexnologiatoplivi masel. **2009**, 5, 37-39. (in Russ)

[9] Nefedov B.K. Kataliz v promyshlennosti. **2003**, 2, 20-27. (in Russ)

[10]KuznetsovP.N. J.Catal. **2003**, Vol. 218, 12. – 23. (in Russ)

[11] RadchenkoE.D., NefedovB. K., AlievR. R.Promichlennii katalizatori gidrogenizassionnih processov. -Himia, **1987**, 224.(in Russ)

[12]Plantenga F.L, Leliveld R.G. Appl. Catal. A: General, **2003**, v.248, 1-7. (in Eng)

[13] OzorenkoA.A., ZamanovV. V.Neftepererabotka i neftehimia**2007**, 3, 28-32. (in Russ)

[14] RustanovM. I., Abat-ZadeH. I. PirievN.N., Gadtrov G.H., Muhtarova G.S., Ibragimov R.G.Neftepererabotka i neftehimia**2009**, 10, 8-13. (in Russ)

[15] EgorovO. I., ChigirinaO. A., BaimukanovA.S. Neftegazovyi kompleksKazahstana: problemyrazvitiai effektivnogo funktsionirovania.-Almaty, **2003**, 536.(in Russ)

[16] KashinO.N.,ErmolenkoA.D., FirsovaT.G., Rudin M.G.Neftepererabotka i neftehimia. **2005**,5, 32-38. (in Russ)

[17] Asaftei, I.V., Lungu, N.C., Birsa, L.M., Ignat, M., Sandu, I.G. Revista de Chimie. **2016**,67, 1523-1528(in Eng)

[18] Chavarria J.C., Ramirez J., Gonzalez H and Baltanas M.A. Catal.Today. **2004**, 98, 1-2, 235-242. (in Eng)

[19] Mota F.M., Bouchy C., Guillon E., Fécant A., Bats N., Martens J.A. J. of Catalysis. **2013**,V. 301, 20-29. (in Eng)

[20]ShimmelG. Metodika elektronnoimikroskopii. M.: Mir, **1972**. – 299.

[21]Schultz D. V., Howe J. M. Transmission electron microscopy and diffractometry of materials. **2011**. Technosphere. M. 305p.

[22] Paukshtis E.A. Инфракрасная спектраскопия в гетерогенном кислотно основном катализе.Infrakrasnaia spektroskopia v geterogennom koslotno- osnovnom katalize. Novosibirsk: Nauka, **1992**, 225 . (in Russ)

[23] Ione K.G Polifunktsionalnyh kataliz na tsiolitah.Novosibirsk: Nauka,**1982**, 272. (in Russ)

Б.Т. Туктин, А.С. Теңізбаева, Н.Н. Нұрғалиев, Л.Б. Шаповалова, В.И. Яскевич

" Д.В. Сокольскийатындағыжанармай, катализ және электрохимия институты", Алматы, Қазақстан

МОДИФИЦИРЛЕНГЕН Ni(Co)-Mo- Al_2O_3КАТАЛИЗАТОРЛАРЫНДА ТУРА АЙДАЛҒАН БЕНЗИН ФРАКЦИЯСЫН ГИДРОИЗОМЕРЛЕУ ЖӘНЕ ГИДРОӨҢДЕУ

Аннотация.Жұмыста жаңа цеолитқұрамды алюмоникель (кобальт) молибден, СЖЭ және фосформен модифицирленген CoO-MoO_3- Ce_2O_3-P_2O_5-Al_2O_3-ZSM (КГО-18); CoO-MoO_3-La_2O_3-P_2O_5-Al_2O_3-ZSM(КГО-20) жәнеCoO-MoO_3-Ce_2O_3-P_2O_5-Al_2O_3-ZSM-HY (КГО-16) катализаторларында тура айдалған бензин фракцияларын гидротазалау мен гидроизомерлеудің зерттеу нәтижелері көрсетілген. Шикізаттың көлемдікберілужылдамдығы мен қысымының температураға әсері зерттелді. Тура айдалған бензинді ағымды қондырғыда жоғары қысымда катализатордың стационарлы қабатының температурасы 320-400^{0}С, қысымы 3,0-4,0 МПа шикізаттың көлемдік берілу жылдамдығы 0,5-3,0 сағ$^{-1}$ гидроөңдеу процесі жүргізілді.Тура айдалған бензинді гидроөңдегенде жоғары күкіртсіздендіру активтілігіне КГО-18 катализаторы иеболды. Температураны 400^{0}С көтергенде сұйытықтағы күкірттің құрамы 0,0080 (Бастапқы бензин) 0,0015%-ға дейін төмендеді. 400^{0}С-та КГО-3 катализаторында тура айдалған бензин фракциясын гидроөңдегеннен кейін гидрожақсартылған бензиннің октан саны 79,0 (бастапқы бензин) 92,4 (З.Ә) және 62,4-тен 77,0 (М.Ә.) Осы жағдайда КГО-18 катализаторында гидрожақсартылған бензинді бастапқы мен салыстырсақ октан саны 78,9-дан 90,7(З.Ә) жәнемоторлы әдіспен 60,9-дан 71,7-ге өскен.

Электронды микроскопиялық зерттеулер модификацияленген Ni (Co) -Mo-Al_2O_3 катализаторларының жоғары дисперсті екенін көрсетті, белсенді фазаның металл компоненттері негізінен тотыққан күйде болып, бетінде кластерлі-ассоциаттар түзеді, дисперстілігі, құрылымы мен күйі катализатордың компоненттерінің табиғаты бойынша анықталады.

Түйін сөздер: цеолит, тура айдалған бензин, катализатор, гидроөңдеу.

Б.Т. Туктин, А.С. Тенизбаева, Н.Н. Нургалиев, Л.Б. Шаповалова, В.И. Яскевич

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

ИССЛЕДОВАНИЕ ГИДРООЧИСТКИ И ГИДРОИЗОМЕРИЗАЦИИ ПРЯМОГОННОЙ БЕНЗИНОВОЙ ФРАКЦИИ НА МОДИФИЦИРОВАННЫХ Ni(Co)-Mo- Al_2O_3- КАТАЛИЗАТОРАХ

Аннотация. В работе приведены результаты исследований гидроочистки и гидроизомеризации прямогонной бензиновой фракции на новых цеолитсодержащих алюмоникель (кобальт) молибденовых катализаторах, модифицированных фосфором и РЗЭ: CoO-MoO_3- Ce_2O_3-P_2O_5-Al_2O_3-ZSM (КГО-18) иNiO-MoO_3- Ce_2O_3-P_2O_5-Al_2O_3-ZSM (КГО-3). Исследовано влияние температуры, давления и объемной скорости подачи сырья. Исследование процессов гидропереработкипрямогонного бензина проводилосьв проточной установке высокого давления со стационарным слоем катализатора при температурах 320-400^{0}С, давлении 3,0 -4,0 МПа и объемной скорости подачи сырья 0,5- 3,0ч$^{-1}$.

При гидропереработке прямогонного бензина высокой гидрообессеривающей активностью обладает катализатор КГО-18. Содержание серы в катализате с ростом температуры до 400°С снизилось с 0,0080 (исходный бензин) до 0,0015%.После гидропереработки прямогонной бензиновой фракции на катализаторе КГО-3 при 400^{0}С октановое число гидрооблагороженного бензина растет от 79,0 (исходный бензин) до 92,4 (И.М) и от 62,4 до 77,0 (М.М).В этих условиях на катализаторе КГО-18 октановое число гидрооблагораженного бензина повышается по сравнению с исходным от 78,9 до 90,7 (ИМ) и по моторному методу от 60,9 до 71,7.

Электронно-микроскопические исследования показали что модифицированные Ni(Co)-Mo-Al_2O_3 катализаторы являются высокодисперсными, компоненты металлов активной фазы находятся преимущественно в окисленном состоянии, образуя на поверхности кластеры-ассоциаты, дисперсность, структура и состояние которых определяется природой компонентов катализатора.

Ключевые слова: цеолит, прямогонный бензин, катализатор, гидроочистка.

About the authors:

Tuktin BalgaTuctievich - Head of the laboratory of motor fuels, doctor of chemical science, JSC"DV Sokolsky Institute of Fuel, Catalysis and Electrochemistry", e-mail: tuktin_balga@mail.ru, w.ph. 8-727-2916826, mob.ph. 87026413597;

Tenizbayeva Aliya Serikovna - Lead engineer of the laboratory of motor fuels, JSC"DV Sokolsky Institute of Fuel, Catalysis and Electrochemistry", e-mail:aliya.85@mail.ru, mob.ph. 87772626004;

NurgaliyevNurzhan Nurlybekovich - Junior researcher of the laboratory of motor fuels, PhD, JSC "DV Sokolsky Institute of Fuel, Catalysis and Electrochemistry", e-mail: n.nurgaliyev@ifce.kz, mob.ph. 87013551823;

Shapovalova Larisa Borisovna - Chief researcherof the laboratory of motor fuels, doctor of chemical science, professor, JSC"DV Sokolsky Institute of Fuel, Catalysis and Electrochemistry", e-mail: larachemistry@mail.ru, mob.ph. 8-727-2916826;

Yaskevich Vladimir Ivanovich - Researcherof the laboratories of physical research methods, JSC "DV Sokolsky Institute of Fuel, Catalysis and Electrochemistry", w.ph. 8-727-290-79-19