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ИЗВЕСТИЯ

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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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HYDROPROCESSING OF GASOLINE AND DIESEL FRACTIONS ON MODIFIED ALUMO-NICKEL-MOLYBDENUM CATALYSTS

Abstract. The paper presents the results of the study of hydroprocessing of gasoline and diesel oil fractions on alumina catalysts modified with variable valence metals, additives of phosphorus and lanthanum. The process of hydroprocessing gasoline and diesel fractions was studied in a high-pressure flow installation with a fixed catalyst bed at temperatures of 320-400°C, pressure 2.5-4.0 MPa and flow rate of the feedstock 1-3 h^{-1}.

The results obtained in tests of catalysts in the process of hydroprocessinggasoline and diesel oil fractions show that the greatest hydrodesulfurization activity is observed at a temperature of 380-400°C, a pressure of 4.0 MPa and a flow rate of 1 h^{-1}. Under optimal conditions, during the processing of straight-run gasoline fraction, the highest octane number is characteristic of the KGO-21 catalyst ($NiO-MoO_3-La_2O_3-P_2O_5$-ZSM-Al_2O_3): 91.8 (RM) and 72.4 (MM). The KGO-23 catalyst ($NiO-MoO_3-La_2O_3-P_2O_5$-BEA-Al_2O_3) has a high hydroabsorbing activity. After hydroprocessing of straight-run gasoline and catalytic cracking gasoline, sulfur was not detected on this catalyst. When hydroprocessing the diesel fraction of oil, the lowest pour point and cloud point of diesel fuel are achieved on the KGO-21 catalyst: minus 58.9 ° C and minus 57.7 ° C, respectively. Diesel fuel produced on this catalyst contains the least amount of residual sulfur compared with other catalysts.

By the method of temperature-programmed desorption of ammonia, it was found that the concentration of acid sites on the KGO-21 catalyst is $31.3 \cdot 10^{-4}$mol NH_{3des} / g cat. On the surface of the KGO-23 catalyst, two forms of adsorbed ammonia were found with a T_{des} = 175 and 220 ° C (10.2 and 9.5 molNH_{3des} / g cat, respectively). The total amount of NH_{3des} = $19.7 \cdot 10^{-4}$molNH_{3des} / g cat. The KGO-21 catalyst has the highest concentration of acid sites, which determines its high hydroisomerizing activity in the hydroprocessingof gasoline fractions.

Keywords: straight-run gasoline, diesel oil fraction, zeolite, catalyst, hydropurification.

Introduction

In connection with the involvement in the processing of high-sulfur oil and the deepening of its processing, the requirements for hydroprocessing catalysts for petroleum fractions increased. Currently, there is a tendency to tighten the requirements for the composition of motor fuels, the insufficiently high quality of which is one of the causes of environmental pollution; therefore the focus of many refineries is on increasing the depth of hydrodesulfurization. In this regard, for the production of high-quality motor fuels at the present stage, catalytic processes of deep hydroprocessing of petroleum fractions are of great importance [1–9]. In the world production of motor fuels, there is a constant trend of tightening their environmental performance. According to international standards, a significant limitation of the content of sulfur, benzene, aromatic and olefinic hydrocarbons in motor fuels is required. The effectiveness of hydroprocessing processes is mainly determined by the properties of the catalysts used. Existing hydroprocessing catalysts do not satisfy the increased quality requirements for motor fuels. For carrying out deep hydroprocessing of various fractions of oil, it is necessary to use new efficient catalysts and technologies.

Global priorities for the development of the oil sector are the creation and introduction of new catalytic technologies based on the use of catalysts that will improve the quality of oil refining. The creation of new catalysts for the directed refining of oil and its fractions will now and in the near future remain a relevant scientific and practical task. Industrial catalysts for hydroprocessing 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 (gasoline, diesel fuel), cheaper production for the

refineries of the Republic of Kazakhstan, the development of highly efficient multifunctional catalysts for the processing of oil fractions is an urgent and priority task.

The development of new efficient catalysts for the hydroprocessing of motor fuels is necessary for the creation of new technologies in this area. At the same time, much attention is paid to the development of a hydroprocessing catalyst for a certain type of crude oil. In this regard, the creation of new highly efficient catalysts for the hydroprocessing of gasoline and diesel oil fractions is very important [1-21].

This paper presents the results of the study of hydroprocessing of gasoline and diesel oil fractions on new alumonickel, tungsten, molybdenum catalysts modified with additives of ZSM-5, BEA, phosphorus and lanthanum zeolites.

Experimental part

New zeolite-containing alumina catalysts, modified by the introduction of metals with variable valence and phosphorus, were developed and prepared. The catalysts were prepared by impregnating a mixture of aluminum hydroxide with high silica zeolites HZSM-5, BEA, and water-soluble salts of nickel, molybdenum, lanthanum, and phosphoric acid. After impregnation, samples of the catalysts were molded and dried at 150°C for 5 hours, then calcined at 550 ° C for 5 hours.

The activity of the synthesized catalysts was studied in the hydroprocessingof gasoline and diesel oil fractions. The process was carried out in a flow-through installation with a stationary catalyst bed at temperatures of 320-400°C, bulk flow rate of feedstock 1-3 hours^{-1}, pressure 2.5-4.0 MPa.

Analysis of the sulfur content in the feedstock and products was carried out on the instrument SPECTROSCAN. Determination of the pour point and cloud point was carried out on the device LAZ M2.

The physicochemical characteristics of the catalysts were studied using BET, electron microscopy [22], and temperature-programmed desorption of ammonia [23].

Results and discussion

With enlarged laboratory tests of hydroprocessing of straight-run gasoline on the NiO-MoO_3-La_2O_3-P_2O_5-Al_2O_3-ZSM catalyst (KGO-21) at a temperature of 320°C, the content of isoalkanes increases from 36.8 to 44.3% compared to the initial (table 1). At a temperature of 400°C, the content of isoalkanes decreases and is equal to 30.7%. With an increase in temperature in the range of 320-400°C, the amount of aromatic hydrocarbons increases from 10.4 to 28.3%, the yield of naphthenic hydrocarbons increases from 20.3 to 30.3%. The amount of olefins in the catalyzate depends little on the process temperature and is 4.3–5.8%. The yield of the liquid phase with increasing temperature from 320 to 400°C decreases from 74.8 to 55.4%. The octane number of gasoline refined at 400°C is maximum and equal to 91.8 (RM) and 72.4 (MM). Under these conditions, the sulfur content in the resulting gasoline is reduced from 0.0092% to 0.0028%.

Table 1 - Effect of temperature on the process of hydroprocessing straight-run gasoline on the catalyst KGO-21

Products,%	Initialgasoline	T,ºC			
		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
The output of the liquid phase		74,8	65,7	59,0	55,4
The octane number by research method	78,9	84,3	89,8	90,0	91,8
The octane number bymotor method	60,9	70,4	69,2	71,8	72,4
Mass fraction of sulfur,%	0,0092	0,0036	0,0033	0,0030	0,0028
Note: V=2 h^{-1}, P=4,0MPa					

Studying the effect of pressure on the process of hydroprocessing straight-run gasoline on the KGO-21 catalyst showed that with an increase in pressure in the range of 2.5-4.0 MPa, the maximum amount of isoalkanes is observed at P = 2.5 MPa and is 34.9% (Table 2). With a further increase in pressure, their amount decreases to 30.7% at 4.0MPa, 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

varies between 27.3-29.7% and 4.6-5.8%, respectively. The yield of the liquid phase is 50.4-55.4%. The octane number of gasoline refined at 4.0 MPa is 91.8 (RM) and 72.4 (MM). The sulfur content in catalyzate is reduced from 0.0092% (initial gasoline) to 0.0028% at 4.0 MPa.

Table 2 - Effect of pressure on the process
of hydroprocessing straight-run gasoline on the catalyst KGO-21

Products,%	Initial gasoline	P, MPa			
		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 hydrocarbons	21,9	22,9	27,1	32,0	30,3
The output of the liquid phase		52,0	50,4	53,2	55,4
The octane number by research method	78,9	89,6	88,3	88,9	91,8
The octane number by motor method	60,9	72,9	71,8	70,1	72,4
Mass fraction of sulfur,%	0,0092	0,0047	0,0035	0,0033	0,0028
Note: T=400°C, V=2 h^{-1}					

During the hydroprocessing of straight-run gasoline fraction on the KGO-21 catalyst, the increase in the volumetric feed rate of the feedstock from 1.0 to 2.5 h^{-1} does not change the content of isoalkanes in the catalyst and is equal to 30.1 - 30.7% (Table 3). The amount of aromatic and naphthenic hydrocarbons in the resulting product also varies little with the change in the volumetric feed rate. The yield of olefinic hydrocarbons ranges from 4.9 to 5.8%. The octane number of the gasoline produced is increased compared with the initial (78.9) to 90.9-91.8 (RM), the residual sulfur content is reduced compared with the raw material from 0.0092 to 0.0036.

Table 3 - Effect of volumetric feed rate on the process
of hydroprocessing straight-run gasoline on the catalyst KGO-21

Products,%	Initial gasoline	V, h^{-1}			
		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
The output of the liquid phase	-	50,1	48,0	55,4	43,0
The octane number by research method	78,9	89,0	90,9	91,8	90,7
The octane number by research method	60,6	71,3	70,7	72,4	72,1
Mass fraction of sulfur,%	0,0092	-	0,0019	0,0028	0,0036
Note: T=400°C, P=4,0MPa					

The study of hydroprocessing of straight-run gasoline fraction on the KGO-21 catalyst showed that the greatest hydrodesulfurizing activity was observed at a temperature of 380-400°C, a pressure of 4.0 MPa and a space velocity of 1 h^{-1}.

In the process of hydroprocessing the diesel fraction of oil on the KGO-21 catalyst, the pour point of the diesel fraction at 320°C decreased from minus 18.3 to minus 35.9°C. As the process temperature rises to 400°C, the pour point decreases to minus 58.9°C. The cloud point under these conditions falls from minus 11.3 to minus 57.7°C. The output of hydrofluorised diesel fuel is 90.0-100.0% (Table 4). The sulfur content is reduced to 0.0536%.

Table 4 - Effect of temperature on the process of hydro processing
of the diesel fraction of oil on the catalyst KGO-21

Process temperature, °C	Sulfur content,%	Pour point, °C	Cloud point, °C	Yield, %
Initialdieselfraction	0,560	-18,3	-11.3	-
320	0,367	-35,9	-30,7	100
350	0,251	-51,3	-51,0	92,5
380	0,135	-54,9	-48,1	91,0
400	0,0536	-58,9	-57,7	90,0
Note: V=2 h^{-1}, P=4,0 MPa				

Studying the effect of the volumetric feed rate on the process of hydroprocessing the diesel fraction of oil on the KGO-21 catalyst showed that with a decrease in the volumetric rate from 3.0 to 1.0 h^{-1}, the amount of sulfur in the catalyzate decreases from 0.1942% to 0.0536%. The greatest decrease in the freezing and cloud point temperatures on this catalyst — down to minus 58.9°C and minus 57.7°C, respectively — is observed at an optimal flow rate of the feedstock of 2.0 h^{-1}. A decrease in catalyst activity with an increase in the feed rate of raw materials is due to a decrease in the contact time of reactants with active sites of the catalyst.

When hydroprocessing a straight-run gasoline fraction on the NiO-MoO_3-La_2O_3-P_2O_5-BEA-Al_2O_3 (KGO-23) catalyst at 320°C, the content of isoalkanes increases from 35.8 to 40.8%. With further increase in temperature to 400°C, their number reaches a maximum value of 44.6% (Table 5). The yield of the liquid phase in the range of 320 - 400°C decreases with increasing temperature from 95.0 to 86.4%, which is associated with an increase in hydrocracking. Under these conditions, the share of aromatic hydrocarbons in the obtained catalyzate increases from 9.5 to 11.4%, the content of naphthenic hydrocarbons decreases from 21.3% in the initial gasoline to 16.1% at 400°C. The concentration of olefinic hydrocarbons in the resulting catalyzate ranges from 5.8 to 7.3%. The octane number of gasoline hydroennobled in these conditions remains almost unchanged. The KGO-23 catalyst showed high hydrodesulfurization activity: after hydroprocessingof straight-run gasoline, sulfur was not detected on it.

Table 5 - Effect of temperature on the process
of hydroprocessing straight-run gasoline on the catalyst KGO-23

Products,%	Initial gasoline	T,°C			
		320	350	380	400
Paraffins C_5-C_6	27,6	25,3	23,9	21,8	22,3
Iso-alkanes	35,8	40,8	36,1	39,0	44,6
Olefins	5,8	5,8	7,3	6,7	5,6
Aromatic hydrocarbons	9,5	9,5	8,8	12,1	11,4
Naphthenic hydrocarbons	21,3	18,6	23,9	20,4	16,1
The output of the liquid phase		95	93,6	88,6	86,4
Octane number by research method	80,2	80,0	82,9	78,2	80,8
Octane number by motor method	61,1	62,2	66,5	62,5	66,9
Mass fraction of sulfur, %	0,0050	-	-	-	-
Note: V=2 h^{-1}, P=4,0 MPa					

The process of hydroprocessing of catalytic cracking gasoline on the KGO-23 catalyst was studied (Table 6). Studies have shown that at 320-400°C, the amount of isoalkanes and aromatic hydrocarbons increases from 25.8 to 41.8-48.6% compared to the initial and from 29.2 to 33.6-36.9%, respectively. The content of naphthenic hydrocarbons varies between 7.0 and 9.0%. The octane number of the gasoline produced at 400°C is 86.7 (RM) and 80.0 (MM). It should be noted that in catalytic cracking gasoline hydrated on the KGO-23 catalyst, as in the case of straight-run gasoline, sulfur was not detected, indicating a high hydrodesulfurization activity of this catalyst.

Table 6 - Effect of temperature on the process of gasoline hydroprocessing of catalytic cracking on the catalyst KGO-23

Products,%	Initial gasoline	T,°C			
		320	350	380	400
Paraffins C_5-C_6	5,6	9,8	10,1	14,5	8,4
Iso-alkanes	25,8	48,0	47,8	48,6	41,8
Olefins	31,5	4,8	3,9	4,3	4,9
Aromatic hydrocarbons	29,2	29,3	29,1	33,6	36,9
Naphthenic hydrocarbons	7,9	8,0	9,0	7,0	8,0
The output of the liquid phase		95	87,5	85	84,5
Octane number byresearch method	88,3	85,3	85,2	86,1	86,7
Octane number bymotor method	80,1	78,3	78,6	80,0	80,0
Mass fraction of sulfur,%		-	-	-	-
Note: V=2 h^{-1}, P=4,0 MPa					

With the consolidated testing of the KGO-23 catalyst in the process of one-stage hydroprocessing of the diesel fraction of oil with sulfur content of 0.6400%, it was shown that with increasing process temperature from 320 to 400°C, the pour point and cloud point of the diesel fraction after the hydroprocessing on the catalyst change little. The output of hydroennobled diesel fuel is 94.5-98.0%. The sulfur content after hydroprocessing the diesel fraction at 380-400°C on the catalyst KGO-23 is reduced to 0.1100%.

When hydroprocessing straight-run gasoline fraction of oil on the catalyst NiO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 (KGO-4) with increasing temperature from 320 to 400°C, the content of isoalkanes increases from 26.3% (initial), reaching a maximum value of 41.9% at 380 ° C, slightly decreasing at 400°C (Table 7). Under these conditions, the yield of aromatic hydrocarbons increases to 20.2% (380°C). The amount of olefins in the catalyzate is 4.4-5.0%. The octane number of refined gasoline obtained at 380°C is maximally 84.3 (RM) and 69.9 (MM).

Table 7 - Effect of temperature on the process of hydroprocessing of straight-run gasoline fraction on the catalyst KGO-4

Products,%	Initial gasoline	T, ˚C			
		320	350	380	400
ParaffinsC_5-C_6	33,4	23,9	10,9	16,6	19,2
Iso-alkanes	26,3	38,9	40,3	41,9	39,8
Olefins	3,7	4,7	5,2	4,4	5,0
Aromatic hydrocarbons	5,6	8,6	19,1	20,2	11,6
Naphthenic hydrocarbons	31,0	23,9	24,5	16,9	24,4
The output of the liquid phase		63,5	60,0	47,0	50
Octane number by research method	77,7	82,2	81,8	84,3	81,0
Octane number by motor method	53,8	67,1	66,8	69,9	65,9
Sulfur content, %	0,0370	0,0239	0, 0230	0, 0227	0,0220
Note: V=2 h^{-1}, P=4,0 MPa					

The yield of liquid catalyzate is equal to 47.0-63.5%. The sulfur content in the catalyzate after hydroprocessing decreased from 0.037 to 0.0220%.

The catalyst KGO-4 was also tested in the process of hydroprocessing the diesel oil fraction. The pour point of the diesel fraction after its hydroprocessing on the KGO-4 catalyst at 400°C has decreased to minus 38.8°C, whereas in the feedstock the pour point is equal to minus 18.3°C. The cloud point under these conditions varies from minus 11.3 to minus 28.2°C. The output of hydroennobleddiesel fuel is 96.1-100%. At the same time, the sulfur content decreases from 0.560% in the initial fraction to 0.1025% (Table 8).

Table 8 - Effect of temperature on the process of hydroprocessing of the diesel fraction of oil on the catalyst KGO-4

Experience temperature, °C	Sulfur content,%	Pour point, °C	Cloud point, °C	Yield, %
The original diesel fraction	0,560	-18,3	-11,3	-
320	0,3295	-30,2	-21,9	100
350	0,2198	-35,1	-25,0	99,6
380	0,1826	-38,1	-27,2	98,5
400	0,1025	-38,8	-28,2	96,1
Note: V=2 h^{-1}, P=4,0 MPa				

Acid-basic characteristics of catalysts are essential for the processing of hydrocarbons. The acidic characteristics of the catalysts were studied by the method of temperature – programmed desorption of ammonia (Table 9).

Table 9 - Acid-basic characteristics of KGO catalysts

Catalyst	Maximum peak temperature, °C		Amount of desorption ammonia bath, 10^{-4}mol/gcat		ΣNH_{3des} 10^{-4} mol/gcat
	1	2	1	2	
KGO-4	—	195	—	21,0	21,0
KGO-21	—	215	—	31,3	31,3
KGO-23	175	220	10,2	9,5	19,7

From the data presented in Table 9, it can be seen that on the surface of the catalysts NiO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 (KGO-4), NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 (KGO-21), NiO-MoO_3-La_2O_3-P_2O_5-BEA-Al_2O_3 (KGO-23), there are strong acid sites with T_{des} equal to 195, 215, 220°C, respectively. The amount of ammonia desorbed from the surface of NiO-WO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3(KGO-4) is 21.0 • 10^{-4}mol NH_{3des}/g cat. The concentration of acid sites on the NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3 catalyst is higher - 31.3 • 10^{-4}mol NH_{3des}/g cat. On the surface of the catalyst NiO-MoO_3-La_2O_3-P_2O_5-BEA-ZSM-Al_2O_3(KGO-23), two forms of adsorbed ammonia were found with a Td of 175 and 220°C. Their number is close to 10.2 and 9.5 mol NH_{3des}/g cat, respectively. The total amount of NH_{3des} = 19.7 10^{-4}mol NH_{3des}/g cat.

The analysis of the obtained results shows that under optimal conditions during the processing of straight-run gasoline fraction, the highest octane number is characteristic for the catalyst KGO-21: 91.8 (RM) and 72.4 (MM), respectively. It should be noted that the KGO-21 catalyst has the highest concentration of acid sites (31.3 • 10^{-4}mol NH_{3des}/g cat, T_{des} = 215°C), which determines its high hydroisomerizing activity in the process of hydroprocessing gasoline fractions. The catalyst KGO-23 has a high hydrodesulfurizing activity. After hydroprocessing of straight-run gasoline and catalytic cracking gasoline, sulfur was not detected on this catalyst.

When hydroprocessing the diesel fraction of oil, the lowest pour point and cloud point of diesel fuel are achieved on the KGO-21 catalyst: minus 58.9°C and minus 57.7°C, respectively. Diesel fuel produced on this catalyst contains the least amount of residual sulfur compared with other catalysts.

The new modified zeolite-containing KGO catalysts developed for the gasoline and diesel fractions hydroprocessing processes are hydrotreated, hydroisomerized and hydrocracked in one stage and allow to obtain low-sulfur, high-octane gasoline and low-coagulation diesel fuel. When hydroprocessing on KGO catalysts with dehydrating and hydrogenating abilities, n-alkanes on the metal centers of the catalyst start to dehydrate, the olefin formed on the acid center turns into carbonium ion, which is easily isomerized [24].

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МОДИФИЦИРЛЕНГЕН АЛЮМОНИКЕЛЬМОЛИБДЕН КАТАЛИЗАТОРЛАРДА БЕНЗИН ЖӘНЕ ДИЗЕЛЬ ФРАКЦИЯЛАРЫН ГИДРООҢДЕУ

Аннотация. Жұмыста ауыспалы валентті металдармен модифицирленген және фосфор мен лантан қосылған алюмооксидті катализаторларда мұнайдың бензин және дизель фракцияларының гидрооңдеу нәтижелері келтірілген. Бензин және дизель фракцияларын жоғары қысымды ағынды қондырғыда катализатордың стационарлы қабатында температура 320-400^{o}С, қысымы 2,5-4,0 МПа және шикізаттың көлемдік берілу жылдамдығы 1-3 сағ$^{-1}$ болғанда гидрооңдеу процесі жүргізілді.

Мұнайдың бензин және дизельді фракцияларын гидрооңдеу процесінде катализаторларды сынау нәтижесі бойынша ең жоғары гидрокүкіртсіздену 380-400^{0} С температурада, қысымы 4,0 МРа және көлемдік берілу жылдамдығы 1 сағ$^{-1}$ болғанда байқалды. Тура айдалған бензин фракциясын тиімді жағдайда өңдегенде октан саны ең жоғары көрсеткіші КГО-21 катализаторына ($NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$): 91,8 (ЗӘ) және 72,4 (МӘ) тән. КГО-23 катализаторы ($NiO-MoO_3-La_2O_3-P_2O_5-BEA-Al_2O_3$) ең жоғары гидрокүкіртсіздендіру активтілігін көрсетті. Осы катализатормен тура айдалған бензин және каталитикалық крекинг бензинін гидрооңдегеннен кейін күкірт мүлде байқалмады. Мұнайдың дизельдік фракциясын гидрооңдегенде КГО-21 катализаторы ең төмен қату және лайлану температурасына ие болды: сәйкесінше -58,9^{0}С және -57,7^{0}С. Осы катализатордан алынған дизельдік отын құрамындағы қалған күкірт мөлшері басқа катализаторлармен салыстырғанда ең аз мөлшерді құрады.

Аммиактың температуралық-бағдарламалы десорбция әдісі арқылы КГО-21 катализаторында қышқылдық орталықтарының концентрациясы $31,3\cdot10^{-4}$ моль $NH_{3дес}$ /г.катализатор құрады. КГО-23 катализаторының бетінде адсорбцияланған аммиактың екі түрі $T_{дес}$ 175 және 220^{o}С тең (10,2 және 9,5 моль $NH_{3дес}$ /г.катализатор сәйкесінше). Десорбцияланған аммиактың жиынтық мөлшері $19,7\cdot10^{-4}$ моль$NH_{3дес}$ /г.катализатор тең. Қышқылдық орталықтың ең жоғарғы концентрациясы КГО-21 катализаторында байқалып және бензин фракцияларын гидрооңдеу процестерінде жоғары гидроизомерлеу активтілігін анықтайды.

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

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ГИДРОПЕРЕРАБОТКА БЕНЗИНОВЫХ И ДИЗЕЛЬНЫХ ФРАКЦИЙ НА МОДИФИЦИРОВАННЫХ АЛЮМОНИКЕЛЬМОЛИБДЕНОВЫХ КАТАЛИЗАТОРАХ

Аннотация. В работе приведены результаты исследования гидропереработки бензиновых и дизельных фракций нефти на алюмооксидных катализаторах, модифицированных металлами с переменной валентностью, добавками фосфора и лантана. Процесс гидропереработки бензиновых и дизельных фракций изучали в проточной установке высокого давления со стационарным слоем катализатора при температурах 320-400^{o}С, давлении 2,5-4,0 МПа и объемной скорости подачи сырья 1-3 ч$^{-1}$.

Результаты, полученные при испытаниях катализаторов в процессе гидропереработки бензиновых и дизельных фракций нефти, показывают, что наибольшая гидрообессеривающая активность наблюдается при температуре 380-400^{o}С, давлении 4,0 МРа и объемной скорости подачи 1ч$^{-1}$. В оптимальных условиях при переработке прямогонной бензиновой фракции наиболее высокое октановое число характерно для катализатора КГО-21 ($NiO-MoO_3-La_2O_3-P_2O_5-ZSM-Al_2O_3$): 91,8 (ИМ) и 72,4 (ММ). Катализатор КГО-23 ($NiO-MoO_3-La_2O_3-P_2O_5-BEA-Al_2O_3$) обладает высокой гидрообессеривающей активностью. После гидропереработки прямогонного бензина и бензина каталитического крекинга на этом катализаторе сера не обнаружена. При гидропереработке дизельной фракции нефти наиболее низкие температуры застывания и помутнения дизельного топлива достигнуты на катализаторе КГО-21: минус 58,9^{o}С и минус 57,7^{o}С соответственно. Дизельное топливо, получаемое на этом катализаторе, содержит наименьшее количество остаточной серы по сравнению с другими катализаторами.

Методом температурно-программированной десорбции аммиака установлено, что концентрация кислотных центров на катализаторе КГО-21 составляет $31,3\cdot10^{-4}$ моль $NH_{3дес}$ /г кат-ра. На поверхности катализатора КГО-23 обнаружены две формы адсорбированного аммиака с $T_{дес}$, равной 175 и 220^{o}С (10,2 и 9,5 моль $NH_{3дес}$ /г кат-ра соответственно). Суммарное количество $NH_{3дес}$ = $19,7\cdot10^{-4}$ моль $NH_{3дес}$ /г кат-ра.

Наибольшей концентрацией кислотных центров обладает катализатор КГО-21, что и определяет его высокую гидроизомеризующую активность в процессах гидропереработки бензиновых фракций.

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

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