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## HYDROPROCESSING OF DIZEL OIL FRACTIONS ON MODIFIED ALUMINA CATALYSTS

**Abstract.** The paper presents the results of a study of hydroforming diesel oil fractions on alumina catalysts modified with metals of variable valency, the addition of phosphorus and lanthanum. The study of the process of hydroprocessing of the diesel fractions was carried out in a high-pressure flow unit with a stationary catalyst bed at temperature of 320–400°C, a pressure of 3 - 4.0 MPa and a volume feed rate of 1–3 h<sup>-1</sup>. The results obtained during the tests of catalysts in the process of hydroprocessing of diesel oil fractions show that the greatest decrease in the pour point and turbidity occurs at a temperature of 380–400°C. During the hydroprocessing of the diesel fraction, the lowest residual sulfur content is observed at a temperature of 400°C.

During the hydroprocessing of the diesel fractions of oil, the catalyst CoO-WO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub>, has the greatest hydrodesulfurizing activity. The sulfur content of the catalysate with increasing temperature up to 400°C decreased from 0,560 to 0,0229%. The greatest decrease in the pourpoint and cloudpoint, during the hydroprocessing of the diesel oil fraction is observed on the catalyst NiO-MoO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub>: minus 58.9 and minus 57.7°C, respectively.

Physical and chemical characteristics of catalysts are studied. The method of temperature-programmed desorption of ammonia found that the highest concentration of acid centers has a catalyst NiO-MoO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub> (31.3•10<sup>-4</sup> mol NH<sub>3des</sub> /g cat) with T<sub>des</sub> = 215°C, which determines its high hydroisomerizing activity in the processes of hydroprocessing of diesel fractions.

The developed catalysts make it possible to obtain winter grades of diesel fuels with low sulfur content.

**Key words:** diesel fraction of oil, zeolite, catalyst, hydropurification.

### Introduction

Recently, due to the involvement in the processing of high-sulfur oil and the deepening of its processing, the requirements for catalysts for hydroprocessing gasoline and diesel oil fractions have increased. According to international standards, a significant restriction of the content of sulfur, benzene, aromatic and olefin hydrocarbons in motor fuels is required. Existing industrial catalysts for hydroprocessing of oil fractions in many countries of the world do not meet the increased requirements for the quality of motor fuels.

In the oil refining industry, hydroprocessing and hydroisomerization processes are increasingly used to produce high-quality diesel fuels. As a result of hydroprocessing, sulfur, nitrogen compounds, unsaturated hydrocarbons are removed, thermal stability is increased, the corrosion activity of fuels is reduced, the formation of sludge during storage is reduced, and the color and smell of motor fuel is improved. At present, there is a tendency to tighten the requirements for the composition of motor fuels, the insufficient quality of which is one of the causes of environmental pollution, so the main attention of many refineries is focused on increasing the depth of hydrodesulfurization. In this regard, catalytic processes of deep hydroprocessing of oil fractions are of great importance for the production of high-quality motor fuels at the present stage.

The practical implementation of this direction is associated with the creation of new multifunctional catalysts that can effectively carry out deep hydroprocessing of diesel fractions in one stage. Catalysts

based on high-silica zeolites, the activity and selectivity of which is determined by the unique acid-base and molecular-sieve properties, are very promising in this regard. One of the possible ways to regulate catalytic properties is the introduction of elements with variable valence into the catalyst and the use its as modifiers.

At the same time, more attention is paid to the development of a hydroprocessing catalyst for a certain type of oil product. [1 - 20].

In this work the results of research of catalytic hydroprocessing gasoline and diesel fractions of crude oil on the new aluminonickel(cobalt),tungsten, molybdenum catalysts supported on  $\text{Al}_2\text{O}_3$  and modified with additives of zeolite ZSM-5, phosphorus and lanthanum.

### Experimental part

New zeolite-containing aluminum oxide catalysts modified by the introduction of metals with variable valence and phosphorus were developed and prepared. The catalysts were prepared by simultaneous impregnation of a mixture of aluminum hydroxide with high-silica zeolite HZSM-5, water-soluble salts of Nickel, cobalt, molybdenum, tungsten, lanthanum and phosphoric acid. After impregnation, the catalyst samples were molded at  $150^\circ\text{C}$  for 5 hours, then dried at  $550^\circ\text{C}$  for 5 hours.

The activity of the synthesized catalysts was studied in the processes of hydroprocessing of diesel oil fractions. The process was carried out in a flow unit with a stationary catalyst bed at temperatures of  $320-400^\circ\text{C}$ , a volume feed rate of  $1-3 \text{ hour}^{-1}$ , a pressure of  $3.0-4.0 \text{ MPa}$ .

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

Physical and chemical characteristics of catalysts were studied using BET electron microscopy [21] and temperature-programmed desorption of ammonia [22].

### Results and discussion

The catalyst  $\text{CoO-WO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$  was tested in the process of hydroprocessing of diesel oil fraction (table 1). With an increase in the process temperature from  $320$  to  $400^\circ\text{C}$ , the pour point of the diesel fraction after its hydroprocessing decreased from minus  $18.3$  to minus  $37.6^\circ\text{C}$ . Cloud point in these conditions varies from minus  $11.3$  to minus  $36.1^\circ\text{C}$ . The yield of hydro-refined diesel fuel is  $95.0-100.0\%$ . The sulfur content after hydroprocessing of the diesel fraction at  $380-400^\circ\text{C}$  on the catalyst  $\text{CoO-WO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$  decreases from  $0.560$  to  $0.0229\%$ .

Table 1 - Hydroprocessing of diesel oil fraction on the catalyst  $\text{CoO-WO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ ,  $V=4 \text{ h}^{-1}$ ,  $P=4.0 \text{ MPa}$

Process temperature, $^\circ\text{C}$	Sulphur content, %	Pourpoint, $^\circ\text{C}$	Cloudpoint, $^\circ\text{C}$	Yield, %
Initial diesel fraction	0,560	-18,3	-11,3	-
320	-	-36,1	-28,5	100
350	-	-33,8	-32,0	97,5
380	0,0266	-37,6	-36,1	95,0
400	0,0229	-36,2	-34,6	95,0

When testing the catalyst  $\text{NiO-WO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$  during the hydroprocessing of the diesel fraction of oil, it is shown that the pour point of the diesel fraction at  $400^\circ\text{C}$  decreased to minus  $38.8^\circ\text{C}$ , while the pour point of the feedstock is minus  $18.3^\circ\text{C}$ . Cloud point in these conditions varies from minus  $11.3$  to minus  $28.8^\circ\text{C}$ . The yield of hydro-refined diesel fuel is  $96.1-100.0\%$ . The sulfur content is reduced from  $0.560\%$  in the initial fraction to  $0.102\%$  (table 2).

Table 2 - Hydroprocessing of diesel oil fraction on the catalyst  $\text{NiO-WO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ ,  $V=2 \text{ hour}^{-1}$ ,  $P=4.0 \text{ MPa}$

Process temperature, $^\circ\text{C}$	Sulphur content, %	Pourpoint, $^\circ\text{C}$	Cloudpoint, $^\circ\text{C}$	Yield, %
Initial diesel fraction	0.560	-18,3	-11,3	-
320	0,453	-30,2	-21,9	100
350	0,367	-35,1	-25,0	99,6
380	0,245	-38,1	-27,2	98,5
400	0,102	-38,8	-28,2	96,1

In the process of hydroprocessing diesel oil fraction at the catalyst  $\text{NiO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$  pour point of the diesel fraction with  $320^\circ\text{C}$  decreased from minus 18,3 to minus 35,9 $^\circ\text{C}$ . When the process temperature rises to  $400^\circ\text{C}$ , the pour point decreases to minus 58.9 $^\circ\text{C}$ . Cloud point in these conditions falls from minus 11.3 to minus 57.7 $^\circ\text{C}$ . The yield of hydroprocessing diesel fuel is 90.0-100.0% (table 3). Sulfur content is reduced to 0.0536%.

Table 3 - Hydroprocessing of diesel oil fraction  
on the catalyst  $\text{NiO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ ,  $V=4\text{ h}^{-1}$ ,  $P=4.0\text{ MPa}$

Process temperature, $^\circ\text{C}$	Sulphur content, %	Pourpoint, $^\circ\text{C}$	Cloudpoint, $^\circ\text{C}$	Yield, %
Initial diesel fraction	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

Table 4 presents the results obtained in the study of the effect of the bulk feed rate on the process of hydroprocessing of the diesel fraction of oil on the catalyst  $\text{NiO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$  at  $P=4.0\text{ MPa}$ ,  $400^\circ\text{C}$ . When the volume velocity decreases from 3.0 and  $1.0\text{ h}^{-1}$ , the amount of sulfur in the catalyst decreases from 0.1942% to 0.0536%. The greatest decrease in pour point and cloud point on this catalyst - to minus 58, 9 and minus 57.7, respectively - is observed at an optimal volumetric feed rate of  $2.0\text{ h}^{-1}$ . Reducing the activity of the catalyst with increasing feed rate is due to a decrease in the contact time of reacting substances with the active centers of the catalyst.

Table 4 - The effect of the volumetric feed rate of raw materials in the process of hydroprocessing the diesel fraction on the catalyst  $\text{NiO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ , with  $P=4,0\text{ MPa}$ ,  $400^\circ\text{C}$

$V, \text{ h}^{-1}$	Cloudpoint, $^\circ\text{C}$	Pourpoint, $^\circ\text{C}$	Yield, %	Sulphur content, %
Initial diesel fraction	-11,3	-18,3	-	0,560
1,0	-57,7	-58,9	84,0	0,0536
2,0	-60,5	-60,7	88,0	0,1848
3,0	-30,8	-31,4	100,0	0,1942

From the data presented in table 5, it can be seen that with an increase in pressure in the range of 3.0-4.0 MPa during the hydroprocessing of the diesel fraction of oil on the catalyst  $\text{NiO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ , the pour point and turbidity with an increase in pressure to 4.0 MPa decrease from minus 18.3 $^\circ\text{C}$  to minus 58.9 $^\circ\text{C}$ , and minus 11.3 $^\circ\text{C}$  to minus 57.7 $^\circ\text{C}$ , the sulfur content decreases from 0.560 to 0.0536%.

Table 5 -The pressure effect on the process of hydroprocessing of the diesel fraction  
on the catalyst  $\text{NiO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ ,  $V=2\text{ h}^{-1}$ ,  $400^\circ\text{C}$

$P, \text{ MPa}$	Cloudpoint, $^\circ\text{C}$	Pourpoint, $^\circ\text{C}$	Sulphur content, %	Yield, %
Initial diesel fraction	-11,3	-18,3	0,560	-
3,0	-32,1	-36,1	0,1110	93,0
3,5	-42,9	-43,1	0,0917	88,0
4,0	-57,7	-58,9	0,0536	84,0

When testing 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 process of hydroprocessing the diesel oil fraction, it was found that with an increase in the process temperature from 320 to  $400^\circ\text{C}$ , the pour point and turbidity of the diesel fraction decreases by 36.7 and 37.1 $^\circ\text{C}$ , respectively. The yield of hydroprocessing diesel fuel is 92.0-100.0%. The sulfur content after hydroprocessing of the diesel fraction at 380- $400^\circ\text{C}$  on the catalyst  $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$  decreases from 0.560 to 0.104% (table 6).

Table 6 - Effect of temperature on the process of hydroprocessing of the diesel fraction 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  $P=4.0$  MPa,  $V=2.0$  h<sup>-1</sup>

Process temperature, °C	Cloudpoint, °C	Pourpoint, °C	Sulphur content, %	Yield, %
Initial diesel fraction	-11,3	-18,3	0,560	-
320	-42,8	-47,5	0,448	100,0
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

During the hydroprocessing of the diesel fraction of oil containing 0.64% sulfur on the catalyst  $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-Fe}_2\text{O}_3\text{-ZSM-Al}_2\text{O}_3$  in the range of 320-400°C, A decrease in the pour point from minus 13.5 to minus 38.4°C (table 7) the cloud point under these conditions varies from minus 12.0 to minus 38.1°C. The yield of hydroblagged diesel fuel is 94.0-99.0%. The sulfur content is reduced from 0.64 % in the initial fraction to 0.0310% in the resulting catalyst.

Table 7 -Hydroprocessing of the diesel fraction of oil containing 0.64% sulfur on the catalyst  $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-Fe}_2\text{O}_3\text{-ZSM-Al}_2\text{O}_3$  at  $P=4.0$  MPa,  $V=2.0$  h<sup>-1</sup>

Process temperature, °C	Cloudpoint, °C	Pourpoint, °C	Sulphur content, %	Yield, %
Initial diesel fraction	-12,0	-13,5	0,64	-
320	-16,0	-16,3	0,39	97
350	-21,2	-21,5	0,28	99
380	-33,0	-33,3	0,11	99
400	-38,1	-38,4	0,031	94

The analysis of the test results of the developed catalysts in the process of hydroprocessing of diesel oil fractions shows that the greatest decrease in the pour point and cloud point of hydroblagged fuel occurs at temperature of 380 – 400°C. During the hydroprocessing of the diesel fraction, the lowest residual sulfur content is observed at temperature of 400°C.

In the study of the process of hydroprocessing of diesel oil fractions on the studied catalysts, it was established that the greatest decrease in the pour point and turbidity is observed on the catalyst  $\text{NiO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$  and is equal to minus 58.9 and minus 57.7°C, respectively, at an experiment temperature of 400°C. The hydrodesulfurizing activity of  $\text{CoO-WO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$  is significantly higher than that of other catalysts studied: the sulfur content decreases to 0.0229%.

During the hydroprocessing of the diesel fraction at 400°C and the bulk speed of the raw material from 2.0 h<sup>-1</sup>, the greatest hydrodesulfurizing activity varies in a number of catalysts (%):  $\text{CoO-WO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$  (0,0229%) <  $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-Fe}_2\text{O}_3\text{-ZSM-Al}_2\text{O}_3$  ( 0,031%) <  $\text{NiO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-HZSM-Al}_2\text{O}_3$  (0,0536%) <  $\text{CoO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$  (0,104%)

The studied catalysts make it possible to obtain winter grades of diesel fuels with low sulfur content.

The activity of catalysts is associated with the size of their surface and acid-base characteristics. Physical and chemical characteristics of catalysts were studied using BET methods and temperature-programmed desorption of ammonia. By the BET method it is established that the surface of the developed catalysts fluctuates within 211,0-274,0 m<sup>2</sup>/g of the catalyst. The catalysts are characterized by pores with  $d \approx 1.5\text{-}2.5$  nm and  $d \approx 7.0$  nm. The total volume of catalyst pores does not exceed 0.28-0.41 ml/g of catalyst.

Acid-base characteristics of catalysts are essential for the processing of hydrocarbons. Acid characteristics of catalysts were investigated by temperature-programmed desorption of ammonia (table 8).

Table 8 - Acid-base characteristics of catalysts

The catalysts	Temperature of the high peaks, °C		Amount of desorbed ammonia, 10 <sup>-4</sup> mol/gcat.		ΣNH <sub>3</sub> desorbed 10 <sup>-4</sup> mol/gcat.
	1	2	1	2	
NiO-WO <sub>3</sub> -La <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub> -ZSM-Al <sub>2</sub> O <sub>3</sub>	—	195	—	21,0	21,0
CoO-WO <sub>3</sub> -La <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub> -ZSM-Al <sub>2</sub> O <sub>3</sub>	—	210	—	26,0	26,0
NiO-MoO <sub>3</sub> -La <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub> -ZSM-Al <sub>2</sub> O <sub>3</sub>	—	215	—	31,3	31,3
CoO-MoO <sub>3</sub> -La <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub> -ZSM-Al <sub>2</sub> O <sub>3</sub>	175	220	10,2	9,5	19,7
CoO-MoO <sub>3</sub> -La <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub> -Fe <sub>2</sub> O <sub>3</sub> -ZSM-Al <sub>2</sub> O <sub>3</sub>	150	265	4,5	5,5	10,0

From the data presented in table 8, it can be seen that on the surface of the catalysts NiO-WO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub>, CoO-WO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub>, NiO-MoO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub>, there are strong acid centers with T<sub>des</sub> equal to 195, 210, 215°C, respectively. The amount of ammonia desorbed from the surface of NiO-WO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub> is 21.0•10<sup>-4</sup> molNH<sub>3des</sub>/g cat. The number of acid centers of CoO-WO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub> catalyst is 26.0•10<sup>-4</sup> mol NH<sub>3des</sub>/g cat. The concentration of acid centers on the catalyst NiO-MoO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub> above – 31.3•10<sup>-4</sup> molNH<sub>3des</sub>/g cat. Two forms of adsorbed ammonia with T<sub>des</sub> equal to 175 and 220°C were found on the surface of the catalyst CoO-MoO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub>. Their number is close to 10.2 and 9.5 mol NH<sub>3des</sub>/g cat, respectively. The total amount of NH<sub>3des</sub> = 19.7 10<sup>-4</sup> molNH<sub>3des</sub>/g cat. The total amount of ammonia desorbed from the surface of CoO-MoO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-Fe<sub>2</sub>O<sub>3</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub> is significantly lower than 10.0•10<sup>-4</sup> mol NH<sub>3des</sub>/g cat. This catalyst is characterized by the presence of the most loosely bound and most strongly bound forms of ammonia in comparison with other studied catalysts: with T<sub>des</sub> equal to 150°C and 265°C.

It should be noted that the highest concentration of acid centers has the catalyst NiO-MoO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub> (31.3•10<sup>-4</sup> molNH<sub>3des</sub>/g cat) T<sub>des</sub> = 215°C, which determines its high hydroisomerized activity in the processes of hydroprocessing diesel fractions.

Thus, the developed multifunctional modified alumina catalysts of hydroprocessing diesel oil fractions, which are simultaneously in one step carry out hydroprocessing, hydrocracking and hydroisomerization, which allows to obtain low-sulfur waxy diesel fuel.

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#### МҰНАЙДЫҢ ДИЗЕЛЬДІК ФРАКЦИЯЛАРЫН МОДИФИЦИРЕНГЕН АЛЮМООКСИДТІ КАТАЛИЗАТОРЛАРДА ГИДРОӨНДЕУ

**Аннотация** Жұмыста мұнайдың дизельдік фракцияларын ауыспалы валентті металдармен, фосфор және лантан қоспаларымен модифицирленген алюмооксидті катализаторында гидрожақсарту процесін зерттеу нәтижелері көрсетілген. Дизельдік фракцияларды гидроөндеу процестерінде зерттеулер 320-400°C температурада, қысымы 3-4,0 МПа және шикізат берілудің көлемдік жылдамдығы 1-3 сағ<sup>-1</sup> болып катализатордың тұрақты қабатында ағымды қондырғыда жүргізілді. Катализаторларды сынау нәтижесінде мұнайдың дизельдік фракцияларын гидроөндеу процестерінде лайлану және қату температураларының ең көп төмендеуі 380 - 400°C температураларда болатыны көрсетілді. Дизельдік фракцияларды гидроөндегенде ең аз күкірт мөлшері 400°C температурада байқалды. Мұнайдың дизельдік фракциясын гидроөндегенде ең үлкен гидрокүкіртсіздендіру активтілігін CoO-WO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub> катализаторы көрсетті. Температура 400C-қа дейін өскенде катализаттағы күкірттің мөлшері 0,560-тан 0,0229%-ға кеміді. Мұнайдың дизельдік фракцияларын гидроөндегенде қату және лайлану температуралары ең көп төмендеуі NiO-MoO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub> катализаторында байқалды: минус 58,9 қату және минус 57,7°C лайлану.

Катализаторлардың физика-химиялық қасиеттері зерттелді. Аммиактың температура-бағдарламалы десорбция әдісі бойынша қышқылдық орталықтардың ең үлкен мөлшері NiO-MoO<sub>3</sub>-La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-ZSM-Al<sub>2</sub>O<sub>3</sub>



катализаторында ( $31,3 \cdot 10^{-4}$  моль  $\text{NH}_{3\text{дес}}$  /г кат.  $T_{\text{дес}} = 215^{\circ}\text{C}$ ) болып, олар дизель фракцияларын гидроөндегенде жоғары гидроизомерлеу активтілігін анықтайды.

Жасалынған катализаторлар күкірті аз қыстық сортты дизель отындарын алуға мүмкіндік береді.

**Түйін сөздер:** мұнайдың дизельдік фракциясы, цеолит, катализатор, гидротазарту

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### **ГИДРОПЕРЕРАБОТКА ДИЗЕЛЬНЫХ ФРАКЦИЙ НЕФТИ НА МОДИФИЦИРОВАННЫХ АЛЮМООКСИДНЫХ КАТАЛИЗАТОРАХ**

**Аннотация** В работе приведены результаты исследования гидрооблагораживания дизельных фракций нефти на алюмооксидных катализаторах, модифицированных металлами с переменной валентностью, добавками фосфора и лантана. Исследование процесса гидропереработки дизельных фракций проводилось в проточной установке высокого давления со стационарным слоем катализатора при температурах  $320-400^{\circ}\text{C}$ , давлении  $3-4,0$  МПа и объемной скорости подачи сырья  $1-3$  ч<sup>-1</sup>. Результаты, полученные при испытаниях катализаторов в процессе гидропереработки дизельных фракций нефти, показывают, что наибольшее снижение температуры застывания и помутнения происходит при температурах  $380 - 400^{\circ}\text{C}$ . При гидропереработке дизельных фракций наименьшее остаточное содержание серы наблюдается при температуре  $400^{\circ}\text{C}$ .

При гидропереработке дизельных фракций нефти наибольшей гидрообессеривающей активностью обладает катализатор  $\text{CoO-WO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ . Содержание серы в катализате с ростом температуры до  $400^{\circ}\text{C}$  снизилось с  $0,560$  до  $0,0229\%$ . Наибольшее снижение температуры застывания и помутнения при гидропереработке дизельных фракций нефти наблюдается на катализаторе  $\text{NiO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$ : минус  $58,9$  и минус  $57,7^{\circ}\text{C}$  соответственно.

Изучены физико-химические характеристики катализаторов. Методом температурно-программированной десорбции аммиака установлено, что наибольшей концентрацией кислотных центров обладает катализатор  $\text{NiO-MoO}_3\text{-La}_2\text{O}_3\text{-P}_2\text{O}_5\text{-ZSM-Al}_2\text{O}_3$  ( $31,3 \cdot 10^{-4}$  моль  $\text{NH}_{3\text{дес}}$  /г кат-ра) с  $T_{\text{дес}} = 215^{\circ}\text{C}$ , что и определяет его высокую гидроизомерирующую активность в процессах гидропереработки дизельных фракций.

Разработанные катализаторы позволяют получать зимние сорта дизельных топлив с низким содержанием серы.

**Ключевые слова:** дизельная фракция нефти, цеолит, катализатор, гидроочистка

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