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CONVERSION OF C_4-FRACTION OF LIQUEFIED PETROLEUM GAS ON ZEOLITE-CONTAINING CATALYST MODIFIED WITH CHROMIUM AND PHOSPHORUS

Abstract: *A zeolite-containing catalyst modified with chromium and phosphorus additives has been developed. The technological conditions of its optimal activity in the dehydrogenation reaction and oligomerization of the C4 fraction of liquefied petroleum gas to produce gasoline components are determined.*

A study of the physicochemical properties of a 5% Cr/Al_2O_3*+ HZSM catalyst promoted with 5% phosphoric acid was carried out. The structure of the catalyst was studied by electron microscopy in combination with microdiffraction. The reflections of HZSM and* Al_2O_3 *were detected using the X-ray diffraction method. It was also shown by the EPR method that the PFK-9 catalyst is characterized by a narrow singlet symmetrical EPR signal with a g-factor of 1.96 and a width* $\Delta H=60$ *Gauss against the background of a broad signal with* $\Delta H=1000$ *Gauss. The narrow EPR signal is due to* Cr^{5+} *ions in the matrix and HZSM zeolite. The intensity of the Cr5+ signal in the PFK-9 catalyst is 205 conventional units. The specific surface area of the catalyst is 176,5 m2/g, the pore volume is 0,137 ml/g.*

The catalyst at contact with C_4*-alkanes (400-600°C, P=0,1 MPa) makes dehydrogenation with reception olefins with the subsequent them oligomerisetion. A study of the conversion of the* C_4 *fraction of LPG on the PFK-9 catalyst was also carried out in the presence of water vapor.*

The yield of C_5*-C10-hydrocarbons depending on technological conditions fluctuates within 40-50%, at the degree of conversion raw material 80-90%.*

Key words: *dehydrogenation, alkanes, oligomerization, olefins, zeolite-containing catalyst, chromium, phosphorus.*

Introduction

Despite the anticipated rapid growth of renewable energy, it is projected that fossil fuels will continue to dominate the energy landscape until at least 2050 [1]. This persistence is attributed to the increasing global demand for energy, the superior energy intensity and reliability of fossil fuels, and the formidable challenges associated with replacing them on a large scale. The Republic of Kazakhstan possesses substantial reserves of light hydrocarbons, including oil, gas condensate, and natural and associated petroleum gases. However, a challenge arises as total hydrocarbon reserves decrease, leading to an imbalance between oil production and the processing of associated petroleum gases. This imbalance results in an increased annual flaring of these associated gases. Additionally, a considerable portion of light gases is currently used inefficiently as technological and household fuel, causing significant environmental harm. Simultaneously, in the current stage of development, there is a consistent rise in the consumption of motor fuels, accompanied by stricter requirements for their operational and environmental characteristics.

Associated, waste and natural gases are more cheap energy resources compared to oil and coal. In the production of unleaded gasoline there is a constant tendency to increase octane numbers, which can be achieved by increasing the content of olefins (up to 15-18%), isoalkanes and aromatic compounds (up to 30%), including benzene (0,8-1,0%). One of the important directions of high-octane gasoline production is alkylates synthesis by isobutane alkylation with industrial butane-butylene fraction, which is a waste gas of oil cracking. However, the existing industrial alkylation technologies are based on the use of toxic liquid catalysts (H_2SO_4, HF, etc.). Given these circumstances, the rational utilization of natural and associated petroleum gas, along with waste gases from oil refining and petrochemical production, emerges as a paramount objective for the oil and gas complex of the Republic of Kazakhstan [2]. This approach is essential to address environmental concerns, optimize resource usage, and meet the evolving demands for high-performance motor fuels. Therefore, development of solid acidic heterogeneous catalysts operating in stationary flow-through units is an important challenge.

In [3] the study of the effectiveness of the CaLaHPtX catalyst derived from molded NaX zeolite in alkylation of isobutane with butylenes was conducted. The catalyst showed stable performance for at least 24 hours, achieving impressive conversion of butylenes (97,1 wt.%) and alkylate yield of 94,1 wt.%, with high selectivity (76,4 wt.%) towards trimethylpentanes.

The hierarchically porous BEA zeolite, featuring trimodal micro-/meso-/macroporosity, synthesized in [4], demonstrated significantly enhanced alkylation selectivity towards trimethylpentanes and an extended lifetime. The authors explain such remarkable catalytic properties by highly interconnected secondary macro- and mesoporous structures, which promote movement of hydride donors and alkylation products to the micropores of zeolite or from them.

Bimolecular alkylation reactions in the presence of strong Brønsted acid centers (BACs) proceed according to the mechanism based on the carbocation theory by generation of primary active particles and development of initial C_4-hydrocarbons transformation [5, 6].

Another way to produce motor fuel components from light hydrocarbons is the oligomerization process, which also makes it possible to simultaneously obtain olefins when processing natural gas. In industry, butene oligomerization is carried out on silicon-phosphate catalysts [7, 8].

Among the catalysts considered as promising systems are zeolites [9-11]. Catalysts prepared by base-acid treatment modification of commercially available ZSM-5 demonstrate improved performance characteristics: butenes conversion rate of up to 86%, space-time yield of 852 mg/g(cat)·h, and a diesel to naphtha cuts mass ratio of 2,2 [11].

The impact of process conditions on H-ZSM-5 zeolite catalyst performance in 1-butene oligomerization reaction at ambient pressure was explored [12]. The study reveals that higher temperatures, partial pressures, and contact times enhance catalyst activity, with increased partial pressure improving selectivity to dimers (C_8-hydrocarbons). The selectivity to C_8-hydrocarbons is maximal at 200°C and 50 kPa partial pressure, with a decreased contact time. At higher temperatures, the decrease in selectivity is linked to the prevalence of cracking reactions, resulting in lighter olefins (C_5-C_{11}). The major component is the dimer (42 wt.%) with approximately 40 wt.% of various side products. Catalyst deactivation due to coke formation is directly correlated with operating temperature.

High-silica zeolites modified with metals exhibit bifunctional properties, in which the metal or metal oxide has dehydrogenation activity [12-16]. The development and synthesis of a polyfunctional solid acid catalyst, that allows the dehydrogenation and isomerization reactions of alkanes with their subsequent oligomerization into higher molecular weight hydrocarbons in a single pass of feedstock, is of the greatest interest.

A series of hierarchical HZSM-5 zeolite catalysts, prepared by treating HZSM-5 with LiOH, NaOH, KOH, and CsOH aqueous solutions at the same concentration [17], were tested for butene oligomerization, demonstrating greater resistance to deactivation through pore blockage compared to commercial ZSM-5 catalyst. The CsOH-treated hierarchical HZSM-5 catalyst exhibited suitable acidity, higher molar ratio of Lewis to Bronsted acid sites, interconnected open-mesopores, and a smaller crystal size, resulting in enhanced catalytic activity and stability due to shorter diffusion paths. The HZSM-5 catalysts treated with CsOH aqueous solution, with optimal characteristics, prolonged the catalyst lifetime for butene oligomerization. It achieved approximately 92% butene conversion and 85% selectivity to C_8-hydrocrbon within 12 hours.

Oligomerization of C_3 and C_4 olefins into gasoline products using phosphorus-treated MTW zeolite-based catalysts was studied [18]. Modification of the binding matrix during phosphorus treatment resulted in a notable reduction in catalyst surface area and pore volume, although the crystallinity of MTW remained unaffected. The increase in phosphorus content substantially diminishes the Bronsted acidity of the catalyst. The augmentation of phosphorus content in MTW/Al_2O_3 catalysts lead to a decrease in the production of liquid products heavier than gasoline. The 10% H_3PO_4 catalyst displayed selectivity for triisobutylenes of nearly 50%.

The purpose of the present work is development of solid acid catalysts for oligomerization of C_4-alkenes into high molecular weight liquid hydrocarbons and motor fuel components.

Methods

The catalyst 5% Cr/ Al_2O_3 + 30% HZSM was prepared by impregnation of Al_2O_3+HZSM mixture with aqueous solution of $Cr(NO_3)_3$•$9H_2O$ salt while heating on a water bath with constant stirring to form a dough-like mass, which was then molded into granules (D=2.0-2.5 mm), dried and calcined at 200-400°C (1 h) and 500°C (5 h). To increase the acidic properties of the catalyst, the granules were impregnated with 5% aqueous solution of phosphoric acid under stirring, dried and treated with air at 500°C. Prior to the experiment, the PFC-9 catalyst was treated with air at 550°C (3 h) in a flow-through reactor.

Structure and composition of catalyst was studied by electron microscopy in combination with microdiffraction, extended X-ray absorption fine structure (EXAFS), electron paramagnetic resonance (EPR), and X-ray fluorescence analysis (XRF) methods.

The composition of feedstock and reaction products were analyzed by "Gas-Chromium 3101" chromatographs with molecular sieve CaX, LHM-8D, and γ-aluminum oxide (Supelco) columns. C_4-fraction of liquefied petroleum gas (LPG) was used as feedstock. The composition of C_4-fraction was the following: isobutane – 56,0%, butane – 39,6%, propane – 2,8%, isobutylene – 0,9%, butylene – 0,7%.

The conversion of C_4-alkanes was studied varying the temperature in the range of 400-600°C (P=0.1 MPa). The volumetric feed rate (V) was varied from 70 to 200 h^{-1}.

Results and Discussion

The C_4-fraction conversion rate over PFC-9 catalyst increases from 19,4 to 86,4% with temperature rise from 400 to 600°C (V=70 h^{-1}). C_2-C_5-olefins (3,4-14,4%), H_2 (1,0-10,2%), methane and ethane (0,4-6,6%) are detected in the reaction products (Table 1).

Table 1 – Effect of temperature on conversion of C_4-fraction of LPG on PFC-9 catalyst (V=70 h^{-1})

Indicators	**Temperature, °C**				
	400	**450**	**500**	**550**	**600**
Conversion, % wt.	19,4	25,5	42,9	74,7	86,4
Product yield, % wt.:					
C_5-C_{10}- hydrocarbons	1,9	1,7	1,8	29,2	50,6
C_2-C_5- olefins	3,4	7,3	12,0	14,9	14,4
hydrogen	1,0	3,6	5,2	9,0	10,2
C_1-C_2- alkanes	0,4	1,7	3,2	5,9	6,6

The presence of C_5-C_{10}-hydrocarbons are determined in the liquid products mixture, content of C_5-C_{10}-hydrocarbons increases from 1.9 to 50,6% at the transition from 400 to 600°C. High-molecular-weight hydrocarbons consist of n-alkanes (pentane, nonane, decane), isoalkanes (C_5, C_8, C_{10}), olefins (isobutene, butene, isopentene); their yields are 27,0, 23,2, and 5,0%, respectively.

The C_5-C_{10}-hydrocarbons, formed during oligomerization, are components of gasoline. The productivity of PFC-9 catalyst in terms of liquid phase yield at the maximum is 40 g/l cat.·h (600°C, V=70 h^{-1}).

Figure 1 shows the results obtained during the conversion of C_4-fraction (V=100 h^{-1}) on 5% Cr/Al_2O_3+30% HZSM catalyst promoted with 5% H_3PO_4 (PFC-9). As temperature rises (V=100 h^{-1}) the feedstock conversion increases from 16,2 (400°C) to 80,1% (600°C), the yield of C_2-C_5-olefins and H_2 at 600°C is 14,1 and 14,5%, respectively. Maximum yield of C_5-C_{10} liquid hydrocarbons is observed at 600°C with prevalence of octane, isononane, isodecane, and decane. The productivity on C_5-C_{10}-hydrocarbons is 50 g/l cat.·h. It is likely that oligomerization proceeds not only with the participation of olefins, but also their precursors - alkyl surface adsorbed structures, the formation of which follows the mechanism [9]:

$$C_4H_{10} + 2Z \rightarrow ZC_4H_9 + ZH_{ads},$$
$$ZC_4H_9 + ZC_4H_9 \rightarrow ZC_8H_{18},$$
$$ZC_4H_9 + Z \rightarrow ZC_4H_8 + ZH_{ads},$$
$$ZH_{ads} + ZH_{ads} \rightarrow 2Z + H_2,$$

where Z is the active center.

The mechanism of isobutane dehydrogenation was determined using deuterium [9]. The first stage is the detachment of the hydrogen atom from the adsorbed molecule. Formation of semi hydrogenated form is a slow process, while the detachment of the second hydrogen atom and desorption of isobutylene go faster. It was found by EXAFS method that metal particles localize on zeolite near Bronsted acid centers [10]. Alkyl structures, especially at high contact time, can migrate from Cr^{n+}– centers to nearby acid centers and dimerize to form octane or isooctane, which is confirmed by the presence of 9.7% isooctane in the reaction products (V = 70 h^{-1}, 600°C).

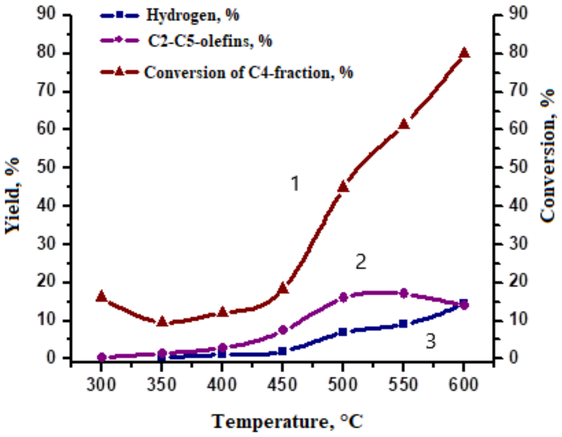

Fig. 1 – Effect of temperature on the degree of conversion of LPG C_4-fraction (1), yield of C_2-C_5-olefins (2) and hydrogen (3) over PFC-9 catalyst in the absence of water vapor (V = 100 h^{-1}).

As the feedstock flow rate increases at t = 550°C, the conversion rate of the C_4-fraction varies in the range of 74.7-84.6% (Table 2). The yield of C_2-C_5-olefins varies extremely, the maximum yield of 17.0% is observed at V =100 h^{-1} which then declines to 12.5%. When the flow rate rises, the share of olefins in the oligomerization reaction increases, which leads to a decrease in their yield from 17.0 to 12.5% and an increase in the degree of C_5-C_{10}-hydrocarbons formation from 24.3 to 43.1-48.4% (see Table 2). Under these conditions, the migration of the half-hydrogenated form adsorbed on the Cr^{n+}– centers to the acid centers is probably a slow stage, and the dehydrogenation process to form olefins predominates. The dimerization of pentene on the acid centers produces the decane, which is found in the product mixture, whereas nonane appears as a result of possible interaction between pentene and butene, although there are conditions for C_2-C_5- olefins participation in reaction. Narrow EPR signal characteristic to chromium (V) bound to the zeolite framework and aluminum oxide was detected by EPR method. The combination of metal and acidic centers facilitates sequential dehydrogenation to form olefins or precursors and their oligomerization [14].

Table 2 – Dependence of C_4-fraction conversion degree over PFC-9 catalyst and yield of reaction products on feedstock flow rate at 550°C

Indicators	**Feed rate, h^{-1}**			
	70	**100**	**150**	**200**
C_4 conversion, % wt.	74,7	61,3	85,6	84,6
Product yield, % wt:				
C_2-C_5- olefins	14,9	17,0	12,2	12,5
C_5-C_{10}- hydrocarbons	29,2	24,3	48,4	43,1
hydrogen	9,0	9,1	8,2	9,1
C_1-C_2- alkanes	5,9	5,4	3,6	2,8

According to literature data [5,11,12], when the catalyst is promoted with phosphoric acid, P-OH centers are formed on the surface of the matrix (Al_2O_3) and zeolite HZSM, which are manifested by an absorption band at 3670 cm^{-1} in the IR spectrum. Phosphorus atoms with acidic oxygen atoms create a four-coordinated state, which underlies the strong Bronsted acid centers active in the reaction of olefins and their precursors oligomerization.

It should be noted that the formed liquid products mainly consist of high-molecular-weight C_8-C_{10}- hydrocarbons. The yields of hydrogen and C_1-C_2-alkanes as a result of cracking by >C-H and >C-C< bonds, are ~9.0-9.1 and 5.9-2.8% respectively (V = 70-200 h^{-1}). Evidence for the appearance of strong acid centers was obtained by studying the structure of PFC-9 catalyst. Two structures: $AlPO_4$ (JCPDS, 20-45) and $AlPO_4$ (JCPDS, 31-29) were detected by electron microscopy and microdiffraction methods, the presence of these structures indicates the interaction of H_3PO_4 with Al_2O_3 and zeolite [14].

The study of C_4-fraction of LPG conversion over PFC-9 catalyst was also carried out in the presence of water vapor. Fig. 2 shows that the degree of conversion of C_4-alkanes varies within 75.8-88.5% when the feed rate increases from 70 to 200 h^{-1}. Liquid and gaseous carbohydrates were found in the reaction products at 550°C, H_2 yield varies extremely from 9.1 to 4.6% with increasing feed rate, maximum of ~12.1% is observed at V=150 h^{-1}. Olefins formation tends to increase with rising feed rate of C_4-alkanes, and at V = 200 h^{-1} their yield is 23.8%. Under these conditions (t = 550°C, P_{H2O} = 150 mm Hg), the yield of liquid C_5-C_{10}-hydrocarbons, the formation of which is limited by contact time of raw materials with the surface of catalyst, sharply decreases to 11.9%. The maximum oligomer yield is 41.5% at V = 100 h^{-1}. Drop in the degree of olefins and their precursors oligomerization is explained by competitive adsorption of water molecules on acid centers and by migration rate of olefins from Cr^{n+}-centers to Bronsted acid centers. This is confirmed by the increase in olefin yield up to 23.8% with increasing feed rate. The content of individual olefins at 600°C falls in the line: propene (10.3%) > ethylene (7.9%) > isobutene (5.0%) > butene (2.4%). Isopentene was found in the product mixture in temperature range 450-550°C (0.7-1.4%).

It is known [13] that in the presence of water vapor, which is heat carrier, adsorption of H_2O molecules occurs mainly on the acid centers of the matrix and zeolite, formation of chromium oxide-H_2O bond is not excluded. It follows from the results obtained during the C_4-alkanes conversion at the feed rate of 200 h^{-1}, that the reduction of the contact time between feed and catalyst surface and the presence of H_2O_{ads} inhibit alkyl intermediates and olefins dimerization and trimerization, the yield of liquid hydrocarbons decreases to 13.6% (see Fig. 2).

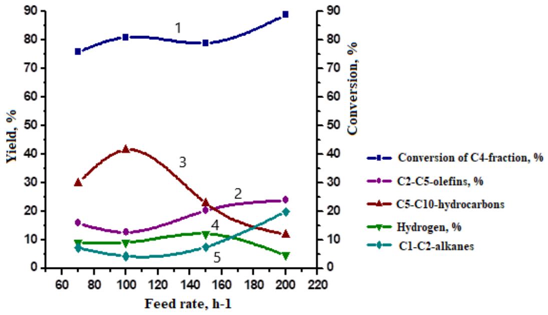

Fig. 2 – Effect of feed rate on the degree of C_4-alkanes conversion (1) and yield of C_2-C_5-olefins (2), C_5-C_{10}-hydrocarbons (3), hydrogen (4) and C_1-C_2-alkanes (5) over PFC-9 catalyst at 550°C in the presence of water vapor (P_{H2O} = 150 mm Hg).

Physical-chemical properties of 5% Cr/Al_2O_3+ HZSM catalyst promoted with 5% phosphoric acid (PFC-9) were investigated. The reflexes of HZSM and Al_2O_3 were detected by XRF analysis method. The structure of HZSM is represented by reflexes: 11.0Å; 9.8Å; 3.83Å; 3.7Å; 3.6Å, and that of Al_2O_3 by 1.98Å; 2.48Å; 1.40Å. The structural elements related to Cr and P are characterized by low intensity, which indicates their high dispersity.

It was shown by EPR method that the PFC-9 catalyst is characterized by a narrow singlet symmetric EPR signal with g-factor of 1.96 and width of ΔN=60 Gauss against the background of a broad signal with ΔN=1000 Gauss. The narrow EPR signal is due to Cr^{5+} ions in the matrix and in HZSM zeolite. The intensity of the Cr^{5+} signal in the PFC-9 catalyst is 205 units. Phosphoric acid modification reduces the intensity of the Cr^{5+} signal.

The catalyst's specific surface area is 176.5 m^2/g and the pore volume is 0.137 mL/g.

The presence of an extensive cluster of dense particles of ~80 Å size on the zeolite surface is determined (Fig. 3 a). The microdiffraction pattern is represented by a large set of rings and reflections and can be assigned to the phases: Cr_2O_3 (JCPDS, 6-564); SiP_2O_7 (JCPDS, 22-1274); $AlPO_4$ (JCPDS, 20-45) and CrO(OH) (JCPDS, 9-331).

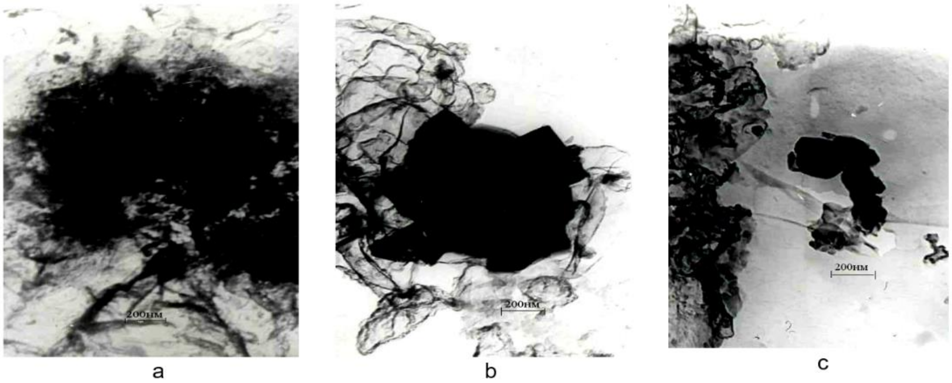

Fig. 3 – Electron microscopic images of PFC-9 catalyst: a – cluster of dense particles;
b – aggregate of dense crystals with rectangular faceting motif;
c – aggregate of dense crystals with hexagonal faceting motif

Fig. 3b presents a 1000-3500 Å aggregate of dense crystals with signs of a rectangular faceting motif. Its microdiffraction pattern is represented by rows of reflexes and can be attributed to a mixture of phases: CrO_2 (JCPDS, 9-332); CrP (JCPDS, 29-456); Cr_3Si (JCPDS, 7-186) and CrO(OH) (JCPDS, 9-331). Formation of Cr_3Si structure indicates the entry of chromium into the zeolite framework, where it stabilizes in the zeolite structure as ions and has off-lattice ligands [14]. The narrow EPR signal indicates the entry of Cr^{5+} ions into the HZSM zeolite structure, which agrees with the data of [15].

Fig. 3c shows a small 1000 Å aggregate of dense crystals with evidence of a hexagonal faceting motif. The microdiffraction pattern is represented by reflexes that can be attributed to $AlPO_4$ (JCPDS, 31-29). The formation of two $AlPO_4$ structures indicates the interaction of phosphoric acid with Al_2O_3 (matrix) and aluminum included in the crystal structure of zeolite.

Conclusion

The solid acid catalyst PFC-9 (5% Cr/Al_2O_3+ HZSM catalyst promoted with 5% H_3PO_4) has been developed, its structure and physical-chemical properties were studied. The catalyst's specific surface area is 176.5 m^2/g and the pore volume is 0.137 mL/g. Evidence for the appearance of strong acid centers was obtained by studying the structure of PFC-9 catalyst. An extensive cluster of dense particles of ~80 Å size, 1000-3500 Å aggregate of dense crystals with signs of a rectangular faceting motif and small 1000 Å aggregate of dense crystals with evidence of a hexagonal faceting motif are determined on the zeolite surface. It was established that Cr^{5+} ions entered into the HZSM zeolite structure, and that phosphoric acid interacted with Al_2O_3 (matrix) and aluminum included in the crystal structure of zeolite.

Conditions of optimal activity of PFC-9 in dehydrogenation and oligomerization of C_4-fraction of liquefied petroleum gas to produce gasoline components have been determined. The C_4-fraction conversion rate over PFC-9 catalyst and the content of C_5-C_{10}-hydrocarbons increase with temperature and are maximal at 600°C: 86.4% and 50.6% respectively. The productivity of PFC-9 catalyst in terms of liquid phase yield at the maximum is 40 g/l cat.·h (600°C, $V=70\ h^{-1}$). The results obtained during the conversion of C_4-fraction ($V=100\ h^{-1}$) on PFC-9 catalyst show that as temperature rises ($V=100\ h^{-1}$) the feedstock conversion increases from 16.2 (400°C) to 80.1% (600°C), the yield of C_2-C_5-olefins and H_2 at 600°C is 14.1 and 14.5%, respectively. Maximum yield of C_5-C_{10} liquid hydrocarbons is observed at 600°C with prevalence of octane, isononane, isodecane, and decane. The productivity on C_5-C_{10}-hydrocarbons is 50 g/l cat.·h.

The effect of feedstock flow rate on reaction over catalyst was studied. The conversion rate of the C_4-fraction varies in the range of 74.7-84.6%. When the flow rate rises, the share of olefins in the oligomerization reaction increases, which leads to a decrease in their yield from 17.0 to 12.5% and an increase in the degree of C_5-C_{10}-hydrocarbons formation from 24.3 to 43.1-48.4%. It was determined that the formed liquid products mainly consist of high-molecular-weight C_8-C_{10}-hydrocarbons. The yields of hydrogen and C_1-C_2-alkanes as a result of cracking by >C-H and >C-C< bonds, are ~9.0-9.1 and 5.9-2.8% respectively (V = 70-200 h^{-1}).

The degree of conversion of C_4-alkanes in the presence of water vapor varies within 75.8-88.5% when the feed rate increases from 70 to 200 h^{-1}. The reduction of the contact time between feed and catalyst surface at the feed rate of 200 h^{-1} and the presence of H_2O_{ads} inhibit alkyl intermediates and olefins dimerization and trimerization, the yield of liquid hydrocarbons decreases to 13.6%.

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ПРЕВРАЩЕНИЕ C_4-ФРАКЦИИ СЖИЖЕННОГО НЕФТЯНОГО ГАЗА НА ЦЕОЛИТСОДЕРЖАЩЕМ КАТАЛИЗАТОРЕ, МОДИФИЦИРОВАННОМ ХРОМОМ И ФОСФОРОМ

Разработан цеолитсодержащий катализатор, модифицированный добавками хрома и фосфора. Определены технологические условия его оптимальной активности в реакции дегидрирования и олигомеризации C_4-фракции сжиженного нефтяного газа с получением компонентов бензина.

Проведено исследование физико-химических свойств 5% Cr/Al_2O_3+ HZSM катализатора, промотированного 5%-й фосфорной кислотой. Электронно-микроскопически в сочетании с микродифракцией исследована структура катализатора. Методом РФА были обнаружены рефлексы HZSM и Al_2O_3. Также методом ЭПР было показано, что катализатор ПФК-9 характеризуется узким синглетным симметричным ЭПР-сигналом с g-фактором 1,96 и шириной $\Delta H=60$ Гаусс на фоне широкого сигнала с $\Delta H=1000$ Гаусс. Узкий ЭПР-сигнал обусловлен ионами Cr^{5+} в матрице и цеолите HZSM. Интенсивность сигнала Cr^{5+} в катализаторе ПФК-9 составляет 205 усл.ед. Удельная поверхность катализатора равна 176,5 $м^2/г$, объем пор – 0,137 мл/г.

Катализатор при контакте с C_4-алканами (400-600°C, P=0,1 МПа) проводит дегидрирование с получением олефинов с последующей их олигомеризацией. Исследование превращения C_4-фракции СНГ на катализаторе ПФК-9 было также проведено в присутствии паров воды. Выход C_5-C_{10}-углеводородов в зависимости от технологических условий колеблется в пределах 40-50% при степени превращения сырья 80-90%.

Ключевые слова: *дегидрирование, алканы, олигомеризация, олефины, цеолитсодержащий катализатор, хром, фосфор.*

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ХРОМ ЖӘНЕ ФОСФОРМЕН МОДИФИЦИРЛЕНГЕН ЦЕОЛИТҚҰРАМДЫ КАТАЛИЗАТОРДА СҰЙЫТЫЛҒАН МҰНАЙ ГАЗЫНЫҢ C_4-ФРАКЦИЯСЫНЫҢ ӨЗГЕРІСКЕ ҰШЫРАУЫ

Хром және фосформен модифицирленген, цеолит құрамды катализатор дайындалды. Бензин компоненттерін алумен бірге сұйылтылған мұнай газы С4-фракциясының сутексіздену және олигомерлену реакцияларында катализатордың тиімді белсенділігінің технологиялық шарттары анықталды.

5% Cr/Al2O3+HZSM және 5%-ті фосфор қышқылымен промоторланған катализаторлардың физикалық-химиялық қасиеттеріне зерттеулер жүргізілді. Микродифракцияға сәйкес электронды-микроскопиялық әдіспен катализатордың құрылымы зерттелді. РФТ әдісімен HZSM және Al2O3 рефлекстерінің бар екендігі анықталды. Сонымен қатар ПФК-9 катализаторы $\Delta H=1000$ кең сигнал аймағында g-факторы 1,96 және ені $\Delta H=60$ Гаусс тар синглет симметриялы ЭПР сигналымен сипатталатыны ЭПР әдісімен көрсетілді. Тар ЭПР сигналы матрицадағы Cr 5+ иондарына және HZSM цеолитіне байланысты болады. ПФК – 9 катализаторындағы Cr^{5+} қарқындатылу сигналы 205 ш.б. тең болды. Катализатордың меншікті беті – 176,5 $м^2/г$, саңылау көлемі – 0,137 мл/г тең.

Катализатор C_4-алкандармен әрекеттесу кезінде (400-600°C, P=0,1 МПа) олефиндер түзілетін сутексіздену реакциясы жүріп, ол әрі қарай олигомерлену реакциясына өтеді. ПФК-9 катализаторында СМГ-ның C_4- фракциясының өзгеріске ұшырауы су буының қатысында жүргізілді. Технологиялық шарттарға байланысты C_5-C_{10}-көмірсутектерінің шығымы шикізаттың 80-90% өзгеріске ұшырау дәрежесінде шамамен 40-50% аралығында болады.

Түйін сөздер: *сутексіздену, алкандар, олигомеризация, олефиндер, цеолитқұрамды катализатор, хром, фосфор.*

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ОСОБЕННОСТИ ХИМИЧЕСКОГО СОСТАВА И ПОЛУЧЕНИЯ САПРОПЕЛЯ ЭВТРОФНЫХ ОЗЕР СЕВЕРО-КАЗАХСТАНСКОЙ ОБЛАСТИ

Аннотация: *Донные отложения эвтрофных озер Северо-Казахстанской области отличаются наличием сапропеля, который может найти применение в сельском хозяйстве. Для создания эфективной технологии переработки сапропелей необходимо знать особенности их химического состава, который в конечном итоге влияет на показатели посевных качеств семян культур. В статье на основе изучения химического состава донных отложений трех эвтрофных озер выделен сырьевой источник получения сапропеля с оптимальным органическим и минеральным составом. Предложен способ переработки донных отложений. Полученный сапропелевый продукт*