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Cracking of Heavy Hydrocarbons on the Shankanai Zeolite of Modified HPA for the Synthesis of Long-Chain α -Olefins

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Abstract. The relevance of the subject of this scientific research is determined by the importance of the problem of using zeolites as catalysts of process of the heavy hydrocarbons' cracking and studying the prospects for modifying heteropolyacids for the synthesis of long-chain α -olefins. The purpose of this scientific research is to study the prospects for the implementation of process of the heavy hydrocarbon cracking on Shankanai zeolite modified with heteropolyacids for the synthesis of long-chain olefins. The basis of the methodological approach in this research work is a combination of methods for system analysis of heavy hydrocarbon cracking processes using natural zeolites as catalysts for this process, with an analytical study of the prospects for implementing this process when modifying natural zeolites with heteropolyacids in order to synthesize α -olefins. In order to analyze the products of α -olefins, the method of gas-liquid chromatography and nuclear magnetic resonance spectrometry was used. The study is carried out under the condition of using the heavy hydrocarbon cracking process of natural zeolites of the Shankanai deposit as catalyst. The obtained results testify to the high efficiency of the practical application of the Shankanai deposit zeolites, upgraded with heteropolyacids when used as catalysts for the cracking of heavy hydrocarbons. The results obtained in the course of this scientific study, as well as conclusions formulated on their basis, are of significant practical importance for developers of chemical processes for oil cracking using natural zeolites modified with heteropolyacids as effective catalysts of this process, as well as for employees of oil refineries, whose professional duties include the quality control of the implementation of this process

Keywords: heteropolyacids, catalyst, gasoline fraction, feedstock, heavy oil



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INTRODUCTION

Heteropolyacids (HPA) are strong acids, much stronger than sulfuric acid, as well as all known other inorganic polyacids (Maity *et al.*, 2021). Heteropolyacids, together with some of their salts, are highly soluble in water and other acid-containing organic solvents, such as ethers, alcohols, ketones. They are relatively stable in neutral and acidic aqueous solutions, while rapidly decomposing in an alkaline environment. They are widely used as catalysts in the alkylation and dealkylation of phenol and benzenes with alkenes; they have the ability to catalyze the acetone condensation into mesityl oxide, as well as the formation of ethers: simple and complex (Sels & Kustov, 2016).

To date, the industrial processing of various types of hydrocarbon raw materials, as well as wet gases of oil refining, provides a number of important substances for the economy of any state (Kandiyoti *et al.*, 2016). The subsequent involvement of heavy hydrocarbons in oil refining processes requires a qualitative modernization of already existing schemes for processing oil products and the development of new and more efficient technological solutions that allow processing oil products on an industrial scale with obtaining a large amount of light oil fractions of high quality (Maity *et al.*, 2021). At the same time, today there are practically no effective methods for processing heavy oil, with the production of a sufficient amount of light fractions. There are only individual technological solutions that allow efficient processing of oil residues that are formed during the primary processing of light and medium grade oils. Industrial processing of heavy oil with the use of currently existing technologies implies the need for significantly higher costs per one ton of processed raw materials (McKeon *et al.*, 2016). It should also be taken into account that in order to improve the quality parameters of fuel fractions, it is necessary to introduce expensive secondary catalytic processes, in particular, such as hydrotreating and hydroforming (Sels & Kustov, 2016).

Issues related to various aspects of heavy oil refining are not new, but they remain relevant. The main negative impact of oil production and processing enterprises is on atmospheric air and water bodies. S. Yusup and N.A. Rashidi (2021) believe that the main sources of pollutants are the processes of sulfur extraction, regeneration of cracking catalysts, heaters, rectification columns, boilers, vessels for storing raw materials and finished products, water and oil separators, flares for burning a mixture of accompanying gases and air. According to J. Speight (2019), the industry annually emits up to 1,650,000 tons of harmful substances (the main share of emissions is liquid and gaseous substances). G.P. Da Ponte Jr (2021) is convinced that the negative impact on the environment is manifested in the following aspects: extraction of land resources for the construction of wells; land pollution; emissions of gaseous substances into the atmosphere; extraction of highly

mineralized associated waters with oil; emergency oil spills with subsequent evaporation.

According to R. Kandiyoti *et al.* (2016), for now, the bulk of the oil refining companies of the Republic of Kazakhstan have not implemented high-quality technologies for the industrial processing of heavy oil, which leads to their preliminary mixing with light and medium oils during the implementation of this process. At the same time, the processing of oil with a high degree of viscosity causes significant difficulties, since the lack of a clear technology for implementing this process stipulates low profitability and difficulties in its implementation. This explains the need to find effective methods for implementing oil cracking processes using the catalytic elements, one of which is natural zeolites modified with heteropolyacids (HPA) for the synthesis of long-chain α -olefins. The technologies developed to date in different countries of the world for processing heavy high-viscosity oils into "synthetic" oil are mainly based on a combination of classical methods for processing oil residues. At the same time, T. McKeon *et al.* (2016) agree that the specific characteristics and complex composition of heavy hydrocarbon raw materials indicate that the classical recycling methods of light oils do not show proper efficiency. The problem can be effectively and timely solved by introducing the heavy hydrocarbon cracking technique using the modified zeolites as a catalyst.

To date, a large number of scientific studies (Yusup & Rashidi, 2021; Speight, 2019; Da Ponte Jr, 2021) have been devoted to the search for non-standard methods for solving the problem of ensuring the high quality of oil distillation processes using catalysts, which only emphasizes the seriousness and relevance of the problem under consideration. The main disadvantage of the conducted scientific research devoted to the comprehensive study of issues related to various aspects of the heavy hydrocarbons' cracking on natural zeolites is the insufficient knowledge of the problem of the implementation of the zeolites preliminary modification with heteropolyacids in the context of synthesis of the long-chain α -olefins. The task of this scientific research is to study the prospects for implementation of heavy hydrocarbon cracking processes on the Shankanai zeolite of modified HPA for the synthesis of long-chain olefins, as well as to obtain practical results that are important from the point of view of optimizing heavy oil cracking processes using natural zeolites as catalysts for this chemical process.

The aim of the article is to study the prospects for implementation of heavy hydrocarbon cracking processes on the Shankanai zeolite of modified HPA for the synthesis of long-chain olefins.

MATERIALS AND METHODS

The study was carried out under the condition of using the heavy hydrocarbon cracking process of natural zeolites of the Shankanai deposit as catalyst. In this scientific

study, nuclear magnetic resonance (NMR) and gas chromatography (GC) analyzes of al-olefins were implemented in practice, as well as certification of modified zeolite catalysts for cracking processes was carried out. TEM analysis of zeolites modified with heteropolyacids was made. The theoretical basis of this research work consists of a number of studies of authors dedicated to the issues of cracking of heavy hydrocarbons on natural zeolites used as catalysts for this process, as well as the problems of modifying natural zeolites with heteropolyacids and the synthesis of long-chain α -olefins.

This scientific study was carried out in three main stages. At the first stage of this research work, a theoretical study of available publications dedicated to various problematic aspects of the cracking of heavy hydrocarbons on zeolite modified with heteropolyacids for the synthesis of long-chain α -olefins was made. On the basis of the formed theoretical background of scientific research, at this stage of scientific work, a systematic analysis of the processes of cracking of heavy hydrocarbons was performed using natural zeolites as catalysts for this process.

At the next stage, an analytical study of the prospects for the implementation of this process was carried out when modifying natural zeolites with heteropolyacids in order to synthesize α -olefins. The study proceeded under the condition that natural zeolites of the Shankanai deposit are used as a catalyst for the cracking of heavy hydrocarbons. Factual information was used regarding the characteristics of this kind of zeolites and the current state of their development processes, directly in the conditions of the Shankanai deposit of the Republic of Kazakhstan. To study the hydrocarbon composition of the cracking reaction products, as well as the target fractions, 6890N chromatograph with a plasma ionization type detector was used. Separation was carried out on HP-5 capillary column with the following characteristics: length – 30 m, inner diameter – 0.25 mm, film thickness in a nitrogen flow – 0.25 μ m. The increase in temperature of the thermostat was increased sequentially from 50 to 300°C, at a heating intensity of 3° per minute.

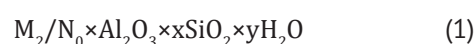
To determine the composition of cracking gases, the gas-liquid chromatography method was used using Chromium-4 and Chromium-5 chromatographs (Czech Republic). On the Chromium-4 chromatograph, chromaton was used as a solid carrier, and squalane was used as an immobile liquid reagent, in a volume of 15% of the total mass of the solid carrier. The column of chromatographs separates saturated hydrocarbons, which are the components of source gas. For NMR analysis of α -olefin products, it was used NMR spectrometer Bruker AVANCE IIIITM 400 MHz (Germany) with a superconductivity magnet, optimized for experiments on solid objects.

Also, at this stage of the research work, an analytical comparison of the main results obtained during its conduction with those obtained by other scientists

during parallel studies of the stated problem was made. All this in combination provides an objective and high-quality picture of the performed scientific research. At the final stage of this research work, based on the results obtained during it, the final conclusions were formulated, acting as a logical presentation of these results and summing up the entire range of scientific studies that were carried out within the framework of the stated theme. In general, the results obtained in this research work and the conclusions formulated on their basis can subsequently serve as a qualitative methodological basis for further research in studying the processes of catalytic cracking of heavy hydrocarbons on natural zeolite that has passed the stage of modification using HPA.

RESULTS

Natural zeolites of the Shankanai deposit are pure aluminosilicate raw materials of multipurpose use. According to the mineralogical classification, zeolites can be referred to the highest class of zeolites of natural origin (Speight, 2019). Modification of natural zeolites with heteropolyacids improves their adsorption properties, which is essential for their subsequent use in hydrocarbon cracking processes as catalysts. The main chemical formula of zeolites (1):



where: Al_2O_3 – alkali or alkaline earth metal; yH_2O – the degree of its oxidation.

Table 1 presents data regarding the content of oxides and auxiliary natural elements in the zeolites of the Shankanai deposit. Natural zeolites of the Shankanai deposit, modified with heteropolyacids, are used as an active component of the oil cracking process. The catalytic effect of such zeolites is determined by many components, among which it should be single out their acidic properties that can be regulated, with a change in the nature and concentration of exchange cations, the molar ratio, SiO_2/Al_2O_3 , and also the main conditions of heat treatment. Heteropolyacids are extremely strong protonic acids, which are much stronger than all known inorganic acids. The specific acid characteristics of heteropolyacids are of significant interest for acid catalysis and the theory of acids and bases, since HPAs have a fairly high oxidizing potential. These and a number of other properties make it possible to use HPA in practice as selective catalysts for oxidation and reduction processes. Heteropolyacids have a wide variability in chemical composition and physico-chemical characteristics, by having a stable molecular structure (Da Ponte Jr, 2021).

In the course of experiment, the efficiency of the action of zeolite catalysts modified with heteropolyacids was estimated by the amount of light fractions formed in the process of oil cracking at $t=350^\circ C$. Figure 1 shows gas chromatographic analysis of al-olefin products.

Table 1. The content of oxides and auxiliary natural elements in the zeolites of the Shankanai

Element	Concentration. %	Content. atom. %	Oxides. %	Chemical formula
O	52.38	66.34	–	–
Si	39.57	28.85	85.28	SiO ₂
Al	4.45	6.65	9.58	Al ₂ O ₃
Ca	1.18	0.56	1.62	CaO
Fe	0.96	0.44	1.16	FeO
K	0.66	0.38	0.90	K ₂ O
Na	0.45	0.33	0.54	Na ₂ O
Mg	0.35	0.28	0.62	MgO
Total	100	–	–	–

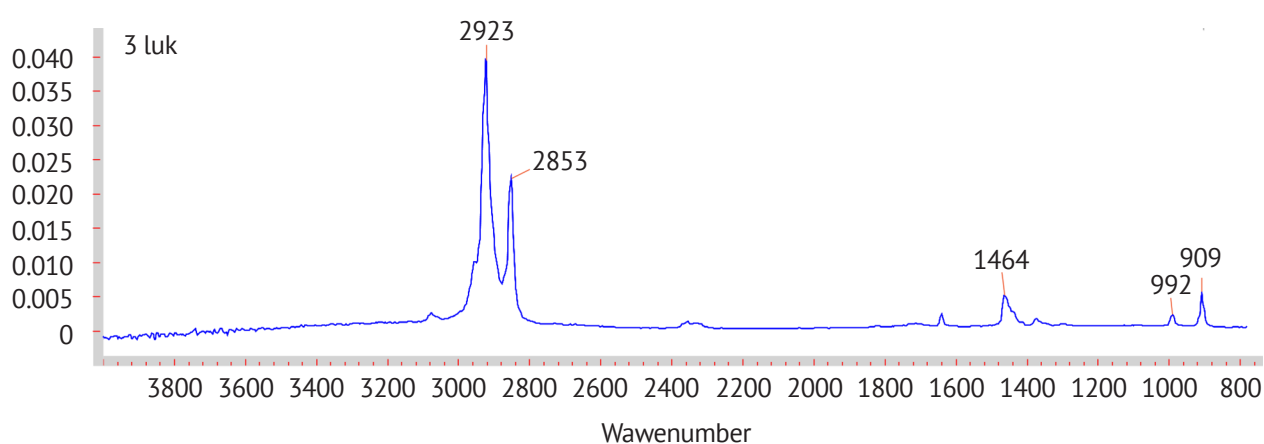
**Figure 1.** GC analysis data for α -olefin products

Table 2 presents the results of GC analysis of the composition of gaseous products of cracking of heavy hydrocarbons on the natural zeolites of the Shankanai deposit that have not undergone the HPA modification.

Table 2. Results of GC analysis of the composition of gaseous products of cracking of heavy hydrocarbons using unmodified zeolite

Element	1	2	3
Butadiene	0.09	0.02	0.04
Hydrogen	0.28	0.24	0.27
n-Butane	3.95	4.68	3.98
Methane	0.75	0.88	1.05
Propan	1.17	1.42	1.85
Propylene	5.86	6.65	7.62
Isobutane	0.87	1.01	1.16
Olefins C ₄	6.56	6.82	6.97
Ethan	0.55	0.58	0.66
Ethylene	0.79	0.95	1.12

As follows from the data presented in Table 2, in the process of catalytic cracking, it is possible the formation of a significant amount of C1-C17 hydrocarbons, in particular C17 olefins and propylene, as well as hydrogen. These elements are of significant interest for

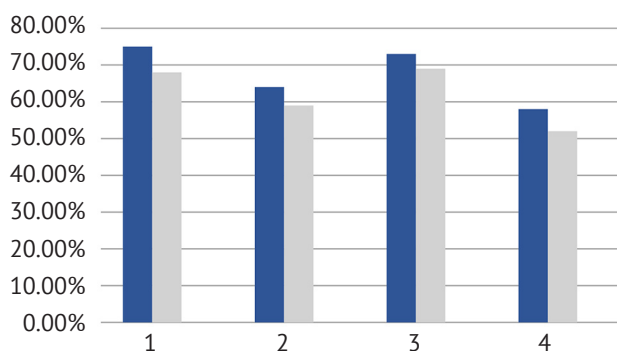
the processes of alkylation and petrochemical synthesis of α -olefins. Table 3 presents the results of GC analysis of the composition of gaseous products of cracking of heavy hydrocarbons on natural zeolites of the Shankanai deposit modified with HPA.

Table 3. Results of GC analysis of the composition of gaseous products of cracking of heavy hydrocarbons using a zeolite modified with HPA

Element	1	2	3
Butadiene	0.03	0.02	0.02
Hydrogen	0.12	0.11	0.1
n-Butane	3.81	4.55	3.62
Methane	0.73	0.82	1.06
Propan	1.06	1.22	1.45
Propylene	5.25	6.33	7.54
Isobutane	0.93	1.02	1.18
Olefins C4	6.57	6.99	6.94
Ethan	0.56	0.59	0.69
Ethylene	0.72	0.84	1.09

Figure 2 shows the main results of the validation of modified zeolite catalysts of cracking, expressed as the

dependence of the conversion of heavy hydrocarbons into light gasoline fractions on the type of cracking catalyst used.

**Figure 2.** Dependence of the conversion value obtained in the process of heavy hydrocarbons' cracking of the type of catalyst used

Experimental data confirm the higher efficiency of using HPA-modified zeolites as catalysts for the cracking of heavy hydrocarbons, which is reflected in a greater amount obtained as a result of C_{17} long-chain alpha-olefins. Thus, the cracking of heavy hydrocarbons on the zeolite of the Shankanai deposit, modified with HPA, ensures obtaining the target product – long-chain C_{17} alpha-olefins. In the course of this scientific study, it has been proven the high efficiency of using natural zeolite when modified with heteropolyacids to convert alkanes into long-chain olefins.

This means a proof of the practical feasibility of modifying the natural zeolites of the Shankanai deposit with heteropolyacids in order to enhance their catalytic properties, as well as to reduce the total volume of gaseous cracking products. The results of comparative tests of modified and unmodified natural zeolites as catalysts for cracking processes have shown that the adsorption properties of zeolites modified with heteropolyacids increase significantly, which leads to a significant increase in the efficiency of their use as catalysts for the cracking of heavy hydrocarbons (Mantas, 2019).

Modification of natural zeolites with heteropolyacids plays an important role in their practical application as catalysts for oil cracking processes at modern oil refineries. The practical use of heteropolyacids as modifying elements increases the adsorption properties of natural zeolites, and it has a positive effect on the efficiency of their use as cracking catalysts.

This explains the possibility of obtaining long-chain C_{17} alpha-olefins, which are the target product of the process at the output. In addition, the use of heteropolyacids as modifying elements for the conversion of alkanes into long-chain olefins has a positive effect on the nature of the process under consideration, since it minimizes the likelihood of sharp jumps and problems with the subsequent use of secondary products of oil refining. Thus, the cracking of heavy hydrocarbons on the Shankanai zeolite modified with HPA for the synthesis of long-chain α -olefins contributes to the production of a significant amount of long-chain C_{17} alpha-olefins, which generally indicates the high efficiency of this process. It should be noted that in this context, the purity of the catalytic substance and

the high level of preparation of petroleum products for the process of their processing are of great importance, since the contamination of the modified natural catalyst used significantly complicates the process and negatively affects its final results. To date, there is a significant potential of the Shankanai deposit as a proven source of natural zeolites, which can be successfully used as effective catalysts for the cracking of heavy hydrocarbons, subject to the implementation of their high-quality modification with HPA. This is of great importance from the point of view of increasing the efficiency of the development of the Kazakhstan oil refining industry as a whole.

DISCUSSION

According to G. Mantas (2019), one of the critical problems of the oil refining industry is the irreversible loss of hydrocarbons during oil processing. These emissions enter the atmospheric air, water basin, or soil, polluting them. That is why the problem of emissions is not only a technical and economic one but also a global ecological one. Research by J. Jarvis *et al.* (2018) showed that among the causes of hydrocarbons entering reservoirs, the discharge of oil-containing effluents and the entry of oil products into groundwater are the most significant. R. Wang *et al.* (2020) believe that heavy oil products destroy microorganisms that participate in the process of self-purification of water. As a result of the decay of sediments contaminated with oil products, harmful substances have released that poison the water.

J. Jarvis *et al.* (2018) assert that today, in the context of a large-scale decrease in reserves, as well as in the volume of oil production, including the so-called "light" oil, the need to use new, non-standard methods for refining hydrocarbon sources is becoming more acute, primarily for bitumen and heavy oils. First of all, it concerns the bitumen and heavy oils. The subsequent increase in the production of heavy oils necessitates an increase in the efficiency of options for their industrial processing to obtain the maximum possible volume of light oil products with qualitatively better characteristics. According to R. Wang *et al.* (2020), the steadily growing consumption of motor fuels in the economically developed countries of the world, encourages leading oil companies to start developing new methods of oil production, as well as developing new oil and bitumen deposits amid the general decline in the share of light oil in the overall balance of oil production. In recent years, the issues of improving the processing of oil and bitumen have become increasingly important, since the natural reserves of raw materials of this kind are several times higher than the natural reserves of medium and light oils. According to numerous expert estimates, it is expected a steady increase in their share in the total volume of hydrocarbon production, taking into account the current balance of production and processing of hydrocarbons.

The task of deepening the oil refining is one of the most urgent tasks of chemical technology for building oil refining processes using catalysts. The processes of catalytic cracking of oil, along with thermal, hydrocracking and visbreaking, are the main methods for processing heavy oil residues. The high energy cost of these processes and their material and capital intensity do not allow timely and full implementation of these processes at most enterprises of the modern oil refining industry. In particular, according to A. Hameed *et al.* (2021), technologies for the industrial processing of vacuum gas oil through catalytic cracking include two additional stages (in addition to the main one) such as hydraulic purification from sulfur compounds of the initial vacuum gas oil, as well as the final products of its cracking. While the hydrocracking process implies the need of practical application of complex technology, it is combined with a high hydrogen pressure. Catalytic cracking ensures the production of high-quality products, and this technique is distinguished by the possibility of processing oil and oil fractions in order to obtain high-quality final products. At the same time, there is a real possibility of combining this process with technological operations of alkylation, adsorption purification. The main disadvantage of this technique is its relative high cost, which predetermines the need to stop the spread of catalytic cracking in many modern enterprises of the oil refining industry. For medium power plants, this process may not always justify itself and fully pay off.

An analysis of the currently existing technologies for cracking of heavy oil residues indicates that catalytic cracking requires significant financial costs and, in fact, is a very expensive operation. S. Chattaraj *et al.* (2016) think that the possibility of obtaining light oil products in sufficient quantities should be considered an undoubted advantage of such technologies. The possibility of practical use in the process of natural zeolites' cracking as catalysts for this process contributes to a significant reduction in its cost and increase in overall efficiency per unit time. Actual high rates of activity of catalysts' cracking when starting these processes in industrial plants can be obtained through the purposefully reducing its specific surface area and thorough deterioration of the active part. According to K.M. Zohdy *et al.* (2021), catalytic cracking should be considered the leader among all processes for improving the efficiency of oil distillation processes in the modern oil refining industry, since one fourth of the world's gasoline is produced through the use of this technology. In addition to gasoline, cracking should also be considered a key producer of diesel fuel and propane-propylene, butane-butylene fraction – the main feedstock for petrochemical processes. The role of catalytic cracking in the development of the economy, especially for countries that are large exporters and producers of oil, is very significant, since it has a significant impact on the depth and thoroughness of oil refining. It also determines the final

volume of oil and oil products consumption, including per capita and for specific types of fuel, by exerting a key influence on the growth rate of the actual gross domestic product of the state (2021).

Zeolites of type X, Y and ZSM-5 (Zeolite Socony Mobil-5) are widely used in the production of cracking catalysts in the fluidized bed. Aluminum oxide and amorphous aluminosilicates are most often used as the catalyst matrix. A. Atmayudha *et al.* (2021) consider that the active matrix makes the main contribution to the overall performance of the catalyst, because the zeolite pores can have a small size for the cracking of especially large molecules of heavy hydrocarbons with a boiling point of more than 480°C. In addition, with an increase in the level of activity of the catalytic substance, various components are added to it that can activate the combustion process (CO) and reduce the concentration of SO_x and NO_x. Various distillate fractions can be used as feedstock components of the catalytic cracking process, and during their conversion, it is observed a catalyst coking and contamination with heavy metals (V and Ni) and sulfur. For now, there is a continuing trend towards an increase in the total weight of the fractional composition of the feedstock that is involved in the catalytic cracking process, which inevitably becomes one of the reasons for the increase in the concentration in the feedstock of polynuclear aromatics, as well as sulfur, nitrogen and heavy metals. All this, in turn, leads to an increase in the coking capacity of raw materials. Today, the most urgent tasks should be considered the tasks of gradually increasing the depth of the catalytic cracking process and increasing its selectivity, as well as maintaining the activity level of the selected catalyst for a long time of operation (2018).

Nowadays, many countries of the world have almost completely exhausted the possibilities for improving oil refining processes in order to meet the real needs for fuels of various types, which can only be realized by increasing the volume of industrial oil production. Various options for solving this problem are proposed, one of which is a gradual transition to the use of catalysts for cracking processes of natural origin. Zeolites are one of these variants (2021). The practical use of natural zeolites as cracking catalysts makes it possible to achieve a high intensity and efficiency of this process, with a significant reduction in energy and material costs. The implementation of secondary catalytic processes requires preliminary upgrading of the initial feedstock. Dementalization and denasalizing should be attributed to the category of refining processes, while the thermal adsorption variety of these processes can also be attributed to the indicated type. According to A. Al-Qasim *et al.* (2020), in all these processes, partial thermdestructive transformations can act as methods for refining the hydrocarbon residues, at the same time there is a parallel and simultaneous adsorption of the resins formed, asphaltenes and carboids, as well

as organometallic, organosulfur and organonitrogen compounds on the surface of the resulting adsorbing substances.

The processing of heavy hydrocarbon residues is carried out in various ways and methods, which should be grouped for subsequent selection when developing the proposed schemes for oil refineries. In this context, the use of heavy hydrocarbon residues as the main components of fuels significantly reduces the depth of processing of hydrocarbon raw materials at oil refineries. This necessitates a high-quality organization of the processes of industrial processing of hydrocarbon residues at oil refineries in order to increase the efficiency of these enterprises and obtain high-quality oil refining products. A. Al-Qasim *et al.* (2020) believe that such processes are characterized by significant technological complexity and require a qualitatively new approach to their organization in order to obtain optimal results, which can be expressed in the high quality of the oil distillation products obtained as a result of oil refining processes. Adding a certain amount of zeolite to the processed oil helps to increase the volume of output of light fractions, as well as coke and gas. When conducting studies of the composition of gaseous products released during the implementation of oil cracking processes, it is found that catalytic cracking products contain a significantly larger number of lower olefins, including propylene, butenes and pentenes, as well as a smaller number of alkanes compared to the gas phase that occurs in thermal cracking.

In addition, J.A. Curiale & J.B. Curtis (2016) are convinced that a significantly higher content of isostructural alkanes (15.2%) and a significant amount of hydrogen (1.7%) can be detected in the gas formation products that are released during oil cracking in the presence of catalyst, which is clear evidence of the development of dehydrogenation reactions and further redistribution of hydrogen. At the same time, the oil straight-run gasoline fraction immediately before the start of the catalytic cracking process and the products' gasoline fractions of its thermal and catalytic cracking differ significantly in the group concentration of hydrocarbons. The gasoline fractions obtained contain a significantly larger amount of n-alkanes and a significantly lower concentration of nevtenes and alkenes. At the same time, the octane numbers of gasolines produced through the implementation of catalytic and thermal cracking processes are significantly higher than similar indicators of the straight-run gasoline component of the original oil. The composition of the resulting gasolines also determines significant differences in the technology of thermal and catalytic cracking of oil. In this context, it should be noted that gasoline obtained through the implementation of thermal cracking processes contains more alkanes of normal structure and less naphthenes and alkenes than gasoline obtained as a result of catalytic cracking. When catalytic cracking is implemented on natural

zeolites as catalysts for the process, the cracking itself with dehydrogenation, isomerization and aromatization is the key reactions for the conversion of hydrocarbons. However, in the thermal cracking, disconnection of C-C connection in combination with polycondensation is observed.

CONCLUSIONS

To date, science offers various options for improving the processes of industrial oil refining, one of which is the use of zeolites upgraded with heteropolyacids as catalysts for the cracking of heavy hydrocarbons. In almost every case of launching an oil refining process through catalytic cracking, the best option for upgrading zeolites in order to obtain a larger amount of light oil fractions amid the synthesis of long-chain α -olefins can be selected. It should also be noted that the gasoline fractions of catalytic cracking processes using the Shankanai zeolites (Kazakhstan) modified with heteropolyacid include a large number of components with a high-octane number, which significantly exceeds the octane number of their analogues that were obtained by thermal cracking.

The preparedness of the feedstock should be considered the most important aspect that directly affects the results of the catalytic cracking process on modified natural zeolites in order to avoid contamination of the natural catalyst used for this process. Before starting the cracking process, it is necessary to prepare the feedstock in order to prevent poisoning of the natural zeolite acting as a catalyst, which will adversely affect the results of the synthesis of long-chain α -olefins. In addition, the cracking of heavy hydrocarbons on the Shankanai zeolite, which has undergone the HPA modernization, implies the need for a careful selection of zeolites, taking into account their actual characteristics, which can be significant in terms of the actual results of this process, expressed in obtaining a significant amount of light gasoline fractions. In general, the results obtained in the course of this research work showed the high practical efficiency of modifying the natural zeolites of the Shankanai deposit with heteropolyacids when they are used as catalysts for the cracking of heavy hydrocarbons. This indicates the significant prospects for the subsequent mass use of zeolites modified with HPA in processes of catalytic cracking of heavy hydrocarbons for the synthesis of long-chain α -olefins.

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Крекінг важких вуглеводнів на шанканайському цеоліті модифікованого ГПА для синтезу довголанцюгових α -олефінів

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Анотація. Актуальність теми наукового дослідження визначається важливістю проблеми використання цеолітів як каталізаторів процесу крекінгу важких вуглеводнів та вивченням перспектив модифікування гетерополікислот для синтезу довголанцюгових α -олефінів. Метою наукової роботи є вивчення перспектив реалізації процесу крекінгу важких вуглеводнів на шанканайському цеоліті, модифікованому гетерополікислотами, для синтезу довголанцюгових олефінів. Основою методологічного підходу в цій науково-дослідній роботі є поєднання методів системного аналізу процесів крекінгу важких вуглеводнів з використанням природних цеолітів як каталізаторів цього процесу, з аналітичним дослідженням перспектив реалізації цього процесу при модифікуванні природних цеолітів гетерополікислотами з метою синтезу α -олефінів. Для аналізу продуктів синтезу α -олефінів використано метод газорідної хроматографії та ядерно-магнітно-резонансної спектроскопії. Дослідження проведено за умови використання в якості каталізатора процесу крекінгу важких вуглеводнів природних цеолітів Шанканайського родовища. Отримані результати свідчать про високу ефективність практичного застосування цеолітів Шанканайського родовища, модернізованих гетерополікислотами, при використанні в якості каталізаторів крекінгу важких вуглеводнів. Отримані в ході наукового дослідження результати, а також сформульовані на їх основі висновки мають практичне значення для розробників хімічних процесів крекінгу нафти з використанням природних цеолітів, модифікованих гетерополікислотами, як ефективних каталізаторів цього процесу, а також для працівників нафтопереробних заводів, до професійних обов'язків яких входить контроль якості здійснення даного процесу

Ключові слова: гетерополікислоти, каталізатор, бензинова фракція, сировина, важка нафта