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Catalytic cracking of heavy hydrocarbons on modified natural zeolite of the Shankanai deposit (Kazakhstan) with heteropoly acids

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Abstract

The purpose of this research work is to study the main aspects of catalytic cracking of heavy hydrocarbons on modified natural zeolite of the Shankanai deposit (Kazakhstan) with heteropoly acids. The leading methodological approach in this research work is a combination of a systematic analysis of the main aspects of performing catalytic cracking of heavy hydrocarbons with a practical study of the features of the functioning of the Shankanai deposit for obtaining and further practical use of modified natural zeolite and involving scientific experiments to determine the prospects for performing this kind of modifications, for the subsequent use of these zeolites in the processes of catalytic cracking of heavy hydrocarbons. The results obtained in this scientific study are clear evidence of the fact that more light oil fractions are obtained as a result of the catalytic cracking process using modified natural zeolites as a catalyst than as a result of thermal cracking under other similar initial conditions. The results obtained in this research work and the conclusions formulated on their basis are of significant practical importance from the standpoint of the prospects for the development of the Shankanai deposit and the use of the zeolite extracted from it after its modification in the processes of catalytic cracking of heavy hydrocarbons.

Keywords

Heteropoly acids, modified natural zeolite, Shankanai deposit, chemical industry.



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Introduction

Heteropolyacids (HPA) conditioned upon pronounced acidic functions are used to catalyse a wide range of chemical reactions. The activity of heteropoly acids is significantly higher than the activity of mineral acids; in particular, in various organic media, their molar activity is significantly higher than that of H_2SO_4 , and the difference in activity can be from 100 to 1000. Such a property of heteropoly acids allows the implementation of catalytic processes at lower temperatures and with lower loading of the catalyst or in its complete absence. During catalysis using heteropoly acids, the probability of adverse reactions tends to be zero. HPA are stable and relatively slightly toxic substances of crystal structure, are quite safe and do not cause problems with their storage.

Catalytic cracking of heavy hydrocarbons is a technological process in which the molecules of a given chemical element disintegrate into lighter molecules by passing through a special chemical reaction accelerator; as a rule, this happens when heated (Mercurio et al., 2018; Chuzlov et al., 2017). The process has several main advantages that should be highlighted. One of these is its significant flexibility of an operational nature, which enables the processing of heavy oil fractions to produce high-octane gasoline. Additionally, the process is able to utilise natural gas that is saturated with butane, propylene, and isobutane. Another advantage is the relative ease with which it can be combined with other processes, including hydrocracking, hydraulic cleaning, and adsorption cleaning.

Zeolites are the most effective adsorbing elements for water vapour. Unlike other adsorbents, in particular from silica gel, they have the ability to adsorb already at a water vapour temperature of 100°C. This property determines the broad prospects for the use of zeolites at gas-gasoline plants, including at other facilities of the oil refining industry for drying unsaturated hydrocarbons and for drying gases from vapours of volatile compounds (Parvulescu and Kemnitz, 2016; Fialko et al., 1994). Zeolites have a wide range of applications, particularly in the purification of gases from hydrogen sulfide and its compounds. Their adsorption ability sets them apart from other adsorbing substances used in the chemical and oil refining industry. The molecular sieve properties of zeolites give grounds to use them in the process of separation of various compounds, the values of the molecules of which are in the range of parameters of the radii of the entrances to the pores of zeolites (Gawande et al., 2021; Moldabayeva and Abileva, 2021).

Chemical modification of natural zeolites involves the production of synthetic samples that do not lag behind natural ones in their basic characteristics. X-ray phase and infrared (IR) spectroscopic analyses, including electron microscopic studies, are used to identify zeolite phases. The wide prevalence of zeolite rocks as a fairly cheap mineral raw material is of particular importance. The low cost of zeolite, combined with a unique set of both physical and physico-chemical characteristics and adsorption properties, determines their wide practical application in various sectors of the national economy of Kazakhstan (Shakiyeva et al., 2021). That is why the Shankanai deposit has been of significant interest since the end of the last century from the standpoint of conducting scientific research on the prospects for the practical use of zeolites for the needs of the national economy of the Republic of Kazakhstan (Kandiyoti et al., 2016; Moldabayeva et al., 2021). There is a dependence of zeolite properties on the content of the zeolite phase and the natural conditions in which residual rocks and impurities in their composition formed. This dependence is because zeolites are systems with many components that vary greatly in composition and constancy (Chatterjee and Bhattacharya, 2021).

The study aims to explore the potential of using modified natural zeolites from the Shankanai deposit as a catalyst for cracking heavy hydrocarbons. The practical study of catalytic cracking of heavy hydrocarbons on modified natural zeolite of the Shankanai deposit with heteropoly acids is crucial for improving the process and exploring new possibilities in oil refining products. The study holds significant importance for various industries and the national economy of Kazakhstan.

Material and Methods

The methodology of this research work involved a combination of systematic analysis and practical study. The systematic analysis focused on the main aspects of performing catalytic cracking of heavy hydrocarbons, while the practical study was aimed at understanding the functioning of the Shankanai deposit to obtain natural zeolite and perform its modifications for subsequent use. Scientific experiments were also conducted to determine the prospects of these modifications and the further use of zeolites in the processes of catalytic cracking of heavy hydrocarbons. A scientific study of the main aspects of the modification of natural zeolite, and the possibilities of obtaining zeolites at the Shankanai deposit, is being carried out to use them as a reliable raw material base to ensure the processes of catalytic cracking of heavy hydrocarbons.

The theoretical basis of this research work consists of scientific studies by a number of domestic and foreign authors devoted to the practical use of modified natural zeolites as raw materials for the implementation of catalytic cracking processes of heavy hydrocarbons. To create the most complete and objective picture of this scientific research and to facilitate the perception of the information provided, all the developments of foreign

researchers taken in the order of citation and presented in this scientific work have been translated into Russian. This study was carried out in several stages. In the first stage of the research, a systematic analysis was conducted on the main aspects of performing catalytic cracking of heavy hydrocarbons. This analysis is of fundamental importance as it provides an understanding of the general principles of the process and its specific features when implemented using raw materials from the Shankanai deposit. A theoretical study was also carried out on the practical use of modified natural zeolites as raw materials for implementing catalytic cracking processes of heavy hydrocarbons.

The next stage of this research work involved a practical study of the functioning of the Shankanai deposit to obtain natural zeolite and perform modifications for subsequent practical use. Scientific experiments were conducted to determine the prospects for these modifications and the application of zeolites in the processes of catalytic cracking of heavy hydrocarbons (Tab. 1). This practical study was based on the previously prepared theoretical basis of the research.

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Indicator	Units of measurement	Analysis results
Colour		Grey, dark brown
Mass fraction of zeolite	%	55-87
Hardness (Mohs)		4.8
Concentration of organic substances	%	Not marked
Resistance to an acidic environment	%	85-92
Imaginary density	g/cm ³	1.59-1.97
Actual density	g/cm ³	2.25-3.7
Pressure resistance	kg/cm ²	160-270
Shreddability	%	0.77-1.27
Abrasion resistance	%	0.08-1.18
Wear resistance	%	1
Resistance to water	%	(96)
Dew point	С	58-68
Concentration of radionuclides		In accordance with the standards of radiation safety
		according to NRB-78
Concentration of chemical elements		At the level of average values for igneous acidic
		rocks

Cracking of heavy hydrocarbons was performed on a standard catalyst layer in the reaction-regeneration mode, and natural zeolite of the Shankanai deposit with heteropoly acids – MO and W-12 series was used as a catalyst. Cracking was performed at a temperature of 450° C, in a pressure range of 0.5-0.7 MPa for 60 minutes, at the MAK-10 installation, manufactured by JSC BSKB Neftekhimavtomatika, Ufa, Russia (Tuktin et al., 2022). This installation is designed for the certification of cracking catalysts; purified air and nitrogen are used for purging, and operation in the reaction-regeneration mode is ensured. During the process, a catalyst with granules of no more than 2 mm was loaded into the quartz reactor of the MAK-10 installation, with parameters of thickness – 1.5 mm, height – 150 mm and diameter – 12 mm. After the process was completed, the reaction products were collected in the form of contact gases and hydrocarbons, solid and liquid, which were used for further research.

Chromatographic analysis of the hydrocarbon composition of the components of the cracking reaction products, and the target fractions, was performed on a 6890 N chromatograph manufactured in the USA (Agilent). Identification of the connection was performed automatically; the heating temperature of the thermostat increased from 50°C to 300°C, and the heating rate was 3°C per minute. The composition of cracking gases was determined by applying the gas-liquid chromatography technique on chromatographs Chrome-4 (1960s) and Chrome-5 (1970s) (former Czechoslovakia). The test gas in the volume of 200 μ l was injected with a syringe into the chromatograph input device at *t*=150°C. In the chromatograph Chromium-4, chromatom was used as a solid carrier, and squalane was used as a liquid stationary phase in a volume of 15% of the above carrier. At the final stage of this research work, conclusions were formulated based on the results obtained, summarising the results of the entire complex of studies performed.

Results

The conducted scientific study of catalytic cracking of heavy hydrocarbons on modified natural zeolite of the Shankanai deposit (Kazakhstan) with heteropoly acids gave the following results. Upgraded natural zeolites of the Shankanai deposit with heteropoly acids were used as catalysts for the oil cracking process at a temperature of 450°C, in a pressure range of 0.5-0.7 MPa for 60 minutes (Tab. 2).

Tab. 2. Elemental composition of natural zeolite of the Shankanai deposit (Kazakhstan), %										
Spectrum	0	Na	Mg	Al	Si	К.	Ca	Ti	Mn	Fe
1	52.38	1.18	1.36	9.16	26.80	1.76	3.26	0.42	0.08	3.86
2	52.6	1.02	1.58	8.9	26.25	1.78	3.35	0.46	0.09	3.92
3	52.44	0.85	0.98	17.35	20.66	1.22	2.86	0.48	0.11	3.26
Average	52.47	1.02	1.26	11.80	24.57	1.59	3.16	0.45	0.093	3.68

With zeolite modified by HPA, after passing through one layer of a stationary catalyst, the formed reaction products pass through the refrigerator and are concentrated in the assembly device. The total amount of carbon deposited on the catalyst was determined by the total volume of carbon dioxide released during the regeneration of the catalyst. At one pass at a temperature of 450°C, the yield of liquid products was 19.8% with a conversion rate of 43.3%. Decationation of the modified zeolite leads to the removal of alkaline and rare earth metal ions from its surface, which leads to an increase in acid centres and an increase in the overall activity of the cracking process as a whole (Krebayeva et al., 2021).

The nature of the hydrogen distribution is determined by the mutual transitions of oils, resins and altafenes, which leads to the development of light aromatic hydrocarbons, which are contained in gasoline fractions of thermolysis products. Most of the protons in olefins are present in gasoline fractions of hydrocarbon cracking products using upgraded zeolites. At the same time, an increase in the specific concentration of olefins, according to gas chromatography data, equalises the total number of protons in double bonds (Sadeghbeigi, 2020). This can be explained by an increase in the concentration of light olefins in the gasoline fractions of catalytic cracking products obtained under the condition of using upgraded zeolite as a catalyst for the process (Tab. 3).

Tab. 3. Composition of elements of liquid products of catalytic cracking of heavy hydrocarbons

	Hydrogen	Sulfur	Carbon	Other elements
Oil before refining	11.77	1.87	85.87	1.15
Catalytic cracking (zeolite) 60 minutes	11.66	1.65	83.84	1.82
Catalytic cracking (zeolite) 120 minutes	9.76	1.36	81.91	1.62
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Note: carried out at a temperature of 450°C pressure in the range of 0.5-0.7 MPa.

The data presented in Table 3 indicate that the composition of the elements of the final product undergoes insignificant changes with the duration of this process of 60 minutes compared to the initial composition of oil before the cracking process begins. This suggests that hydrogen and carbon are redistributed in the initial product, forming low-molecular compounds (Kendall, 2020). Increasing the duration of the catalytic cracking process from 60 minutes to 120 leads to a gradual decrease in the percentage of carbon to hydrogen. There is a systematic decrease in the total concentration of both elements in the final liquid product. The decrease in the concentration of carbon and hydrogen causes an increase in gas and coke formation. There are significant differences between the gasoline fraction of oil before the start of its refining process and the gasoline fractions of the products of catalytic and thermal cracking of this oil. The differences primarily concern the hydrocarbon composition, and the final fractions obtained during the refining process include a larger number of n-alkanes. On the other hand, the concentration of isoalkanes and naphthavenes is significantly lower (Fig. 1).

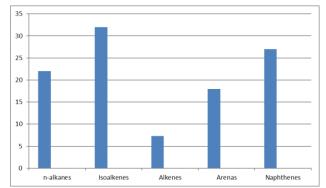


Fig. 1. Hydrocarbon composition of gasoline fractions obtained as a result of the catalytic cracking process Note: using modified natural zeolite from the Shankanai deposit with heteropoly acids as a catalyst.

The octane numbers of the final gasoline fractions obtained by catalytic cracking on modified natural zeolites of the Shankanai deposit with heteropoly acids are, on average, 7-8 units higher than the gasoline, straight-run fraction of the initial oil before processing. Significant differences in the mechanisms of processing petroleum hydrocarbons in the processes of thermal and catalytic cracking are reflected in the differences in the compositions of the resulting gasoline. Gasoline produced by thermal cracking of oil contains significantly more alkanes having a completely normal structure and slightly fewer isoalkanes, arenes, alkenes and naphthenes than

gasoline of the liquid product of catalytic cracking on upgraded natural zeolites (Tito et al., 2022; Moldabayeva et al., 2020). In the implementation of catalytic cracking of oil on this zeolite, the main reactions of hydrocarbon transformation should be considered cracking, dehydrogenation, isomerisation and aromatisation, while in thermal cracking – violation of C–C bonds and polycondensation.

An important aspect of the use of modified natural zeolites in oil cracking processes is the presence of impurities and mechanical additives in the feedstock that reduce the likelihood of achieving high-quality parameters of the final product and deactivating zeolite as a substance that catalyses the process itself. The most effective means of cleaning the feedstock before starting the catalytic cracking process on upgraded zeolites is solvent de-asphalting using a wide variety of hydrocarbon solvents from C3 to C5 or their mixtures; light gasoline is also very effective.

The modernisation of natural zeolites plays a significant role in the use of them as catalysts for the cracking of heavy hydrocarbons. The practical application of methods for the preparation of these elements with low flow rates of hydrogen transfer reactions contributes to a significant reduction in the amount of aromatic, polycyclic hydrocarbons, which are transformed into coke during subsequent processing (Shakiyeva et al., 2022). This significantly affects the overall quality of the catalytic cracking process since it increases the octane number of gasoline fractions obtained during oil refining. It also has a positive effect on the nature of the process itself since it eliminates its sharp jumps and problems with the disposal of oil refining waste. Thus, the practical use of modified zeolites of the Shankanai deposit with heteropoly acids as a catalyst in the cracking process also allows for achieving a significant increase in their quality. At the same time, there will be a significant increase in the volume of consumption of the catalysing substance per unit mass of refined oil, which necessitates further search for more economically advantageous ways of refining.

Discussion

The improvement of the adsorption properties of natural zeolites is facilitated by chemical modification to obtain aluminosilicate sorbents that have a hydrophobic surface. Scientific studies indicate that modifying natural zeolites with tetraethoxysilane provides the greatest adsorption capacity of zeolite for oil refining products. This finding suggests the potential use of modified natural zeolites for wastewater treatment and adsorption in the process of catalytic cracking of heavy hydrocarbons (Lesin and Eremin, 2019; Nadirov et al., 2017). Modified natural zeolites are actively used to dry the oil of transformers of oil refining plants, which is extremely important from the standpoint of the safety of their uninterrupted operation. Adsorption, in this case, involves direct contact of transformer oil with zeolites, which occurs in the usual temperature regime, which does not imply the presence of oxidation processes, which, as a rule, take place during heating. Adsorption using zeolites is widely used to purify transformer oils, to minimise dielectric losses of fresh transformer oils, including when drying oil with zeolites, in filters of constant regeneration of transformer oil, etc. (Ozdoyev and Tileuberdi, 2017).

A significant increase in motor fuel consumption causes oil refining companies to develop new deposits of bitumen of natural origin and heavy oil. The gradual improvement of existing technologies for processing these natural resources is gradually gaining popularity, which is facilitated by significant natural reserves of these fossil elements. The involvement of heavy oil in oil refining processes leads to the need to modernise existing oil refining schemes and to create the latest high-efficiency oil refining technologies associated with the use of secondary raw materials as a basis for processing oil residues (Zhu et al., 2019). The practical application of a catalyst based on natural zeolite modified with nickel nanopowder offers significant prospects for refining heavy oil under varying temperature conditions and the duration of the working process.

The final efficiency of the use of zeolite-based catalysts is estimated by the number of light fractions of oil that are formed during the implementation of catalytic cracking, and the method of thermal analysis is widely used. In the event that the mentioned catalysts are absent in the process of cracking oil, this leads to the development of liquid and gaseous products and a large number of heavy residues. The total number of light oil fractions leaving significantly increases within an hour after the completion of the catalytic cracking process. Two hours after the completion of the cracking process, there is an increase in the output of gasoline fractions, coke, and gas, which are by-products of this process (Murzin and Salmi, 2016; Nazarova et al., 2020a). Liquid products of catalytic cracking of oil contain in their composition the largest amounts of distillate, both medium and light, and it can be obtained by adding a catalyst based on modified natural zeolite having a concentration of no more than 5%. The need to deepen the refining process is becoming increasingly urgent due to the gradual decrease in the volume of industrial production of light oil. This, in turn, necessitates the modernisation of existing refining processes. It is worth noting that catalytic cracking is the most commonly used refining process, considered the most effective when using a fluidised catalyst. Catalysts based on modified natural zeolite, which are the most effective, include the zeolite itself, used as an active component and an aluminosilicate matrix. It also matters which additives are used in the catalyst to increase its efficiency (Sels and Kustov, 2016).

The gradual improvement of the principles of modification of natural zeolites is of fundamental importance from the standpoint of cracking heavy oil. The development of the latest ultramodern modifications of zeolites, characterised by low rates of hydrogen transfer reactions, contributes to a gradual decrease in the volume of polycyclic hydrocarbons, which are transformed into coke. In this context, the use of paraffin compounds of metals, in particular vanadium and nickel, contributes to the decomposition of the zeolite surface, which negatively affects the state of the catalyst, causing its poisoning. This causes the urgent need to create new catalysts for the process of catalytic cracking of heavy hydrocarbons or upgrade old samples in order to improve them (Basha et al., 2022). To date, it should be considered practical to completely exhaust the possibilities of oil refining by increasing the volume of its industrial production. In this context, a thorough study of the issues of deepening oil refining processes along with their chemicalisation is the most promising from the standpoint of the development of the oil refining industry in many countries, including in the context of expanding the needs for the use of motor fuels in the world (Maity et al., 2021). This is conditioned upon the gradual development and implementation of modern technological schemes that allow to intensify and improve the processes of oil refining and rational use of oil residues.

Catalytic cracking is of great importance from the standpoint of increasing the volume of gasoline production since it allows obtaining high-quality gasoline from heavy oil, the octane number of which is at the level of 85-95. This process contributes to the development of large quantities of gas saturated with propane-propylene and butane-butylene fractions, which are the raw material basis for the production on an industrial scale of various kinds of high-octane esters and other valuable components of motor fuels. The industrial equipment utilised for catalytic cracking processes regularly supplies raw materials for the chemical industry by extracting soot and naphthalene from cracking gas oils. Additionally, heavy gas oil can serve as raw materials for producing high-quality "needle" coke (Rey and Huettmann, 2020). Despite being similar to thermal processes of hydrogen redistribution to obtain more hydrogenated target products and hydrogen-depleted coke, the catalytic cracking process outperforms them in several parameters. It provides a higher yield and quality of products, especially gasoline, and does not produce by-products, as coke is burned in the regenerator. For all the time of its practical application, the catalytic cracking of heavy hydrocarbons has undergone significant improvement in terms of the choice of the contact option of the catalyst and the raw material base and in terms of the choice of catalysts for practical use (Nazarova et al., 2020b). Such changes and improvements have helped to gradually increase the yield of the final product, a motor gasoline component.

The progress made in the search for the optimal catalyst for the implementation of catalytic cracking of heavy hydrocarbons has allowed gradually involving heavier raw materials in the processing process. In the past, gas oil-kerosene fractions were commonly used as the initial stages of the cracking process, but in recent years, vacuum gas oils have been more commonly used. In the last two decades, many installations have been developed that use residual oil distillation products, such as fuel oil and deasphaltisates, including mixtures of these products with vacuum distillate, as the raw material base (Gruber and Plank, 2020; Ivanchina et al., 2018).

The cracking of heavy hydrocarbons required the development and practical implementation of special catalysts that have optimal selectivity for the coke yield parameter. They have large pores – up to 500 angstroms or more, which prevents the possibility of condensation of hydrocarbons in these pores and prevents their clogging. They include zeolites of a new sample, which have relatively low flow rates of hydrogen transfer reactions, which helps to reduce the total number of polynuclear compounds that precede the appearance of coke. Catalytic cracking is a chemical process accompanied by the splitting of heavy hydrocarbons into hydrocarbons with a lower molecular weight, and this process necessarily proceeds through the use of catalysts and when exposed to high temperatures. Vacuum gas oils, which can be obtained by direct distillation of oil under the influence of high pressure, are considered to be a typical raw material for cracking (Silim et al., 2022). Catalytic cracking significantly changes the composition of oil, and this is primarily facilitated by complex chemical reactions that significantly change the structure of hydrocarbons. The catalysts of this process ensure the proper efficiency of hydrocarbons' decomposition, which is possible at a lower temperature of the decomposition of raw materials. It is this kind of cracking that is called catalytic cracking.

Catalytic cracking is used to produce the bulk of modern automobile gasoline. The effectiveness of this technology is explained by the fact that it is the effect of the process catalysts that lead to the transformation of heavy unsaturated hydrocarbons into marginal ones. This fact determines the advantages of catalytic cracking over thermal cracking since the final quality of gasoline is much higher. Modified natural zeolites are recognised as effective catalysts of the catalytic cracking process, conditioned upon their high thermal stability and activity under the influence of high temperatures. Zeolites are actively used in the cracking process, during which heavy carbon raw materials, in particular vacuum gas oil, with high permissible boiling parameters (from 350 to 560-580°C) and large molecules (with a number of 30-40 carbon atoms) decompose into smaller-scale molecules (Fu et al., 2019). The key components of the cracking catalyst are the zeolite component and the matrix. The matrix provides high-quality primary cracking – decomposing raw materials into smaller molecules with a total number of atoms up to 20. After that, the main function of the zeolite is to destroy these fragments before they turn into a gasoline fraction. At the same time, the matrix allows the transport of reacting molecules directly to the zeolite

and provides the necessary parameters for the mechanical strength of the entire structure. High-quality and timely modernisation of zeolites is essential for the creation of effective catalysts for cracking residues – extremely stable, ultra-high-silica zeolites are actively used, causing a significant decrease in coke yield.

The need to develop and implement cracking catalysts in industrial production volumes arises from several factors. First, there is a significant reduction in the quality of the main raw materials used in the refining process. Additionally, the activity and selectivity of the catalysts currently used in the process deteriorate over time. This results in a decline in gasoline output and an increase in the volume of coke produced. Therefore, developing new, more efficient catalysts is crucial for improving the cracking process and increasing the overall yield of high-quality products. For this reason, the development of the use of modified natural zeolites as catalysts for the cracking of heavy hydrocarbons is of significant practical importance from the standpoint of the prospects for obtaining high-quality oil refining products, in particular, gasoline with high octane numbers (Jokar et al., 2021). In recent years, modern technologies have been developed and implemented involving the use of zeolites, particularly high-silica ones, as active components that increase the octane numbers of gasoline. The use of natural zeolite as a catalyst for the cracking process requires a significant amount of zeolites per unit volume of oil, which creates a need to find more economically advantageous options for the implementation of catalytic cracking of heavy hydrocarbons. An effective practical solution to this problem contributes to improving the oil refining technologies used today and producing high-quality products, with a view to their subsequent practical use in various fields.

Conclusions

A scientific study of the catalytic cracking of heavy hydrocarbons on modified natural zeolite of the Shankanai deposit (Kazakhstan) with heteropoly acids led to the following conclusions. The catalytic conversion of heavy hydrocarbons presupposes the presence of reactions that form end products with an increased oil content and significantly fewer resins than in refined products that are obtained by thermal cracking of oil. At the same time, the use of modified natural zeolites of the Shankanai deposit with heteropoly acids ensures the production of more light oil fractions than as a result of thermal cracking under the same initial conditions. The final gasoline fractions of catalytic cracking processes using modified natural zeolites of the Shankanai deposit (Kazakhstan) with heteropoly acids as the main catalysts of chemical reactions contain high-octane components in large quantities, resulting in their higher-octane number compared to gasoline fractions obtained by thermal cracking.

When cracking using modified natural zeolites with heteropoly acids obtained at the Shankanai deposit, the resulting gasoline fractions contain aromatic hydrocarbons in significantly smaller quantities than when performing thermal cracking or using other catalysts. Also, these gasoline frakes contain H-alkanes in their composition in a higher concentration than when cracking under other initial conditions or when using other catalysts. This is not accompanied by any significant changes in the qualitative composition of gasoline obtained as a result of the completion of the oil distillation process and a decrease in its octane number, which indicates the high efficiency of the upgraded zeolite and its significant isomerising and cracking activity.

In general, the results of the research have shown a high potential for the practical use of upgraded zeolite as a catalyst for cracking heavy hydrocarbons and are also a clear demonstration of the potential development of the Shankanai deposit to obtain natural zeolites for their subsequent modification and practical use as catalysts for cracking heavy hydrocarbons. Modification of natural zeolites with heteropoly acids in their practical application as catalysts for cracking heavy hydrocarbons allows for improving the process of obtaining alphaolefins as the target product of this process, conditioned upon reducing the load on the catalyst and eliminating side effects.

The need for this study is driven by the growing demand for efficient and cost-effective methods for refining heavy hydrocarbons and improving the quality of gasoline fractions obtained from the process. The significance of this study lies in its potential contribution to improving the oil refining industry worldwide. The practical application of this research could lead to the development of more efficient and cost-effective methods for refining heavy hydrocarbons and improving the quality of gasoline fractions obtained from the process.

References

Basha, I. K., Abd El-Monaem, R. M., Khalifa, R. E., Omer, A. M. and Eltaweil, A. S. (2022). Sulfonated graphene oxide impregnated cellulose acetate floated beads for adsorption of methylene blue dye: Optimization using response surface methodology. *Scientific Reports*, 12, 1-17. https://doi.org/10.1038%2Fs41598-022-13105-4.

- Chatterjee, S. and Bhattacharya, S. K. (2021). Size-dependent catalytic activity of PVA-stabilized palladium nanoparticles in *p*-nitrophenol reduction: Using a thermoresponsive nanoreactor. *ACS Omega*, 6(32), 20746-20757. https://doi.org/10.1021%2Facsomega.1c00896.
- Chuzlov, V. A., Ivanchina, E. D., Dolganov, I. M., Sejtenova, G. Z. and Ivanov, S. Y. (2017). The branched C5-C6 hydrocarbons synthesis on Pt-catalyst. *Current Organic Synthesis*, 14(3), 332-341. https://doi.org/10.2174/1570179413666161031123146
- Fialko, N. M., Prokopov, V. G., Meranova, N. O., Borisov, Yu. S., Korzhik, V. N. and Sherenkovskaya, G. P. (1994). Heat transport processes in coating-substrate systems under gas-thermal deposition. *Fizika i Khimiya Obrabotki Materialov*, (2), 68-75.
- Fu, Y., Li, J. and Li, J. (2019). Photo-improved hydrogen evolution reaction activity of the Pt/CdS electrocatalyst. *Progress in Natural Science: Materials International*, 29(4), 379-383. https://doi.org/10.1016/j.pnsc.2019.08.003.
- Gawande, M., Hussain, C. M. and Yamauchi, Y. (2021). Surface modified nanomaterials for applications in catalysis. Oxford: Elsevier.
- Gruber, S. and Plank, J. (2020). Preparation and effectiveness of a high-temperature anti-settling agent for well cement slurries. *Journal of Natural Gas Science and Engineering*, 81, 103416. https://doi.org/10.1016/j.jngse.2020.103416.
- Ivanchina, E. D., Ivashkina, E. N., Nazarova, G. Y. and Seitenova, G. Z. (2018). Influence of Feedstock Group Composition on the Octane Number and Composition of the Gasoline Fraction of Catalytically Cracked Vacuum Distillate. *Petroleum Chemistry*, 58(3), 225-236. https://doi.org/10.1134/S0965544118030106
- Jokar, S. M., Wood, D. A., Sinehbaghizadeh, S., Parvasi, P. and Javanmardi, J. (2021). Transformation of associated natural gas into valuable products to avoid gas wastage in the form of flaring. *Journal of Natural Gas Science and Engineering*, 94, 104078. https://doi.org/10.1016/j.jngse.2021.104078.
- Kandiyoti, R., Herod, A., Bartle, K. and Morgan, T. (2016). *Solid fuels and heavy hydrocarbon liquids*. Oxford: Elsevier Science.
- Kendall, K. (2020). Crack Control. Oxford: Elsevier.
- Krebayeva, L. U., Algabas, Z. D., Essenbayeva, A. N., Brodskyi, A. R. and Konuspayev, S. R. (2021). Cracking of the paraffins on catalysts from natural zeolite of Kazakhstan Shankanay field. *Chemical Bulletin of Kazakh National University*, 101(2), 20-27. https://doi.org/10.15328/cb1154.
- Lesin, V.I. and Eremin, N. A. (2019). Study on application of colloidal particles of metal oxides to increase the oil recovery factor. *IOP Conference Series: Materials Science and Engineering*, 700, 1-6. https://doi.org/10.1088/1757-899X/700/1/012061.
- Maity, S., Gayen, K. and Bhowmick, T. (2021). Hydrocarbon biorefinery. Oxford: Elsevier.
- Mercurio, M., Sarcar, B. and Langella, A. (2018). *Modified clay and zeolite nanocomposite materials*. Oxford: Elsevier.
- Moldabayeva, G. and Abileva, S. (2021). Study and determination of regularities in variability of oil rheological properties to enhance oil recovery. *Periodicals of Engineering and Natural Sciences*, 9(4), 44-60. http://dx.doi.org/10.21533/pen.v9i4.2299
- Moldabayeva, G. Zh., Suleimenova, R. T., Akhmetov, S. M., Shayakhmetova, Z. B. and Suyungariyev, G. E. (2021). The process of monitoring the current condition of oil recovery at the production fields in Western Kazakhstan. *Journal of Applied Engineering Science*, 19(4), 1099-1107. https://doi.org/10.5937/jaes0-30840
- Moldabayeva, G. Zh., Suleimenova, R. T., Turdiyev, M. F., Shayakhmetova, Zh. B. and Karimova, A. S. (2020). Scientific and technical substantiation of reducing oil viscosity. *International Journal of Engineering Research and Technology*, 13(5), 967-972. https://www.ripublication.com/irph/ijert20/ijertv13n5_19.pdf
- Murzin, D. and Salmi, T. (2016). Catalytic kinetics. Oxford: Elsevier Science.
- Nadirov, K. S., Moldabayeva, G. Z., Baibotayeva, S. E., Zeygman, Y. V. and Sadyrbayeva, A. S. (2017). Reagent preparation for oil treatment and its use in the process of dehydration. *Journal of Industrial Pollution Control*, 33(1), 1075-1084. https://www.icontrolpollution.com/articles/reagent-preparation-foroil-treatment-and-its-use-in-theprocess-of-dehydration.php?aid=86014
- Nazarova, G. Y., Ivashkina, E. N., Oreshina, A. A., Vymyatnin, E. K., Seytenova, G. Z. and Burumbaeva, G. R. (2020a). Vacuum distillate catalytic cracking technology modelling: Feedstock and products composition and properties investigation. *Petroleum and Coal*, 62(2), 380-389. https://web.p.ebscohost.com/abstract?direct=true&profile=ehost&scope=site&authtype=crawler&jrnl=133 53055&AN=143597290&h=BuFT9CfRabyQR4J5DJ%2btS4LstVl0sUDqepkM5Uic0PGyK2jLwovng99u1 PJuuqoGZKutwQ7HuwieOdsSFcoh1w%3d%3d&crl=c&resultNs=AdminWebAuth&resultLocal=ErrCrlN otAuth&crlhashurl=login.aspx%3fdirect%3dtrue%26profile%3dehost%26scope%3dsite%26authtype%3dc rawler%26jrnl%3d13353055%26AN%3d143597290

- Nazarova, G., Ivashkina, E., Shafran, T., Oreshina, A. and Seitenova, G. (2020b). Prediction of residue coke content and operating modes of regenerator in the catalytic cracking technology. *Petroleum Science and Technology*, 38(24), 1017-1025. https://doi.org/10.1080/10916466.2020.1825966
- Ozdoyev, S. M. and Tileuberdi, N. (2017). The geological prerequisites for increasing oil production at the North Karamandybas field. *News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology* and *Technical* Sciences, 4(424), 276-280. https://www.researchgate.net/publication/319345419_The_geological_prerequisites_for_increasing_oil_pro duction_at_the_North_Karamandybas_field

Parvulescu, V. I. and Kemnitz, E. (2016). New materials for catalytic applications. Oxford: Elsevier.

- Rey, A. R. and Huettmann, F. (2020). Telecoupling analysis of the Patagonian Shelf: A new approach to study global seabird-fisheries interactions to achieve sustainability. *Journal for Nature Conservation*, 53, 125748. https://doi.org/10.1016/j.jnc.2019.125748
- Sadeghbeigi, R. (2020). Fluid catalytic cracking handbook. Oxford: Butterworth-Heinemann.
- Sels, B. and Kustov, L. (2016). Zeolites and zeolite-like materials. Oxford: Elsevier.
- Shakiyeva, T. V., Sassykova, L. R., Dzhatkambayeva, U. N., Khamlenko, A. A., Zhakirova, N. K., Batyrbayeva, A. A., Azhgulova, R. N., Kubekova, S. N., Zhaxibayeva, Z. M., Kozhaisakova, M. A., Zhusupova, L. A., Sendilvelan, S. and Bhaskar, K. (2021). Optimization of the oxidative cracking of fuel oil on catalysts obtained from Kazakhstan raw materials. *Rasayan Journal of Chemistry*, 14(2), 1065-1071. http://dx.doi.org/10.31788/RJC.2021.1426152.
- Shakiyeva, T. V., Sassykova, L. R., Khamlenko, A. A., Dzhatkambayeva, U. N., Sassykova, A. R., Batyrbayeva, A. A., Zhaxibayeva, Z. M., Ismailova, A. G. and Semdilvelan, S. (2022). Catalytic cracking of M-100 fuel oil: Relationships between origin process parameters and conversion products. *Chimica Techno Acta*, 9(3), 1-8. https://doi.org/10.15826/chimtech.2022.9.3.01.
- Silin, M., Magadova, L., Malkin, D., Krisanova, P., Borodin, S. and Filatov, A. (2022). Applicability assessment of viscoelastic surfactants and synthetic polymers as a base of hydraulic fracturing fluids. *Energies*, 15, 1-19. https://doi.org/10.3390/en15082827.
- Tito, R., Salinas, N., Cosio, E. G., Boza Espinoza, T. E., Muñiz, J. G., Aragón, S., Nina, A. and Roman-Cuesta, R. M. (2022). Secondary forests in Peru: Differential provision of ecosystem services compared to other post-deforestation forest transitions. Ecology and Society, 27(3), 1-34. https://doi.org/10.5751/ES-13446-270312.
- Tuktin, B., Omarova, A., Sassykova, L., Saidilda, G., Subramanian, S., Tulepov, M. and Abimagzhanov, A. (2022). Development and testing of modified alumina catalysts for hydrotreating petroleum gasoline fraction. https://doi.org/10.20944/preprints202207.0052.v1.
- Zhu, C., Chen, Z., Gao, S., Goh, B.L., Samsudin, I.B., Lwe, K.W., Wu, C., Wu, Y. and Su, X. (2019). Recent advances in non-toxic quantum dots and their biomedical applications. *Progress in Natural Science: Materials International*, 29(6), 628-640. http://dx.doi.org/10.1016/j.pnsc.2019.11.007.