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The Role of Zeolite Catalysis in Modern Petroleum Refining: Contribution from Domestic Technologies

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Abstract—The problems of zeolite catalysis associated with the introduction of domestic technologies are considered. Particular attention is paid to works related to the use of alternative components of catalytic systems, the introduction of new environmentally friendly materials that improve the quality of the fuels produced with their use. The processes of catalytic cracking, processing of heavy petroleum residues, solid-acid alkylation, and synthesis of light olefins and the problems of renewable feedstock processing are discussed in detail.

Keywords: zeolites, catalytic cracking, alkylation, olefins, heavy petroleum residues, bio-oil

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Zeolites have long been proven to be effective components of catalysts for a large number of chemical processes due to their high acidity and thermal stability, as well as molecular sieve properties, which ensure high selectivity. Zeolites are widely used in almost all processes of the chemical industry: hydrocracking, catalytic cracking, hydrotreating, the Fischer–Tropsch process, alkylation, etc. On their basis, catalysts are created to neutralize harmful compounds in industrial off-gases and automobile exhausts.

CATALYTIC CRACKING

Catalytic cracking is one of the main refining processes aimed at deepening oil refining. By cat cracking high-quality components of motor fuels are obtained, as well as petrochemical feedstock including lower olefins and amylenes. The capacity of all cat cracking units is about 700 million tons/year, which is about one fifth of all the capacities for primary petroleum processing [1]. For the first time, the conversion of hydrocarbons in the presence of an acid catalyst (aluminum chloride) was observed by Russian chemist G.G. Gustavson [2]. More profound studies followed by a pilot trial of the catalytic cracking of crude oil were carried out by N.D. Zelinsky [3, 4] in Russia and A.M. McAfe [5, 6] in the United States. The rapid increase in the automobile production in the first decades of the twentieth century contributed to a sharp increase in demand for gasoline with improved antiknock characteristics. In 1936, the first industrial cracking unit using the Houdry process with a new catalyst was built; in the future, at least 20 large units of this type were commissioned [7, 8]. Despite the process discontinuity caused by the need for frequent catalyst regeneration and the low degree of automation at that time, it was the Houdry process that could be considered the first important milestone in the history of catalytic cracking. A new surge of interest in the process arose with the beginning of the Second World War. The huge demand for aviation high-octane gasoline could not be met by straight-run or cracked gasoline. In 1941, the largest oil companies in the United States signed the Recommendation 41 agreement, under which companies joined efforts to develop a new process for the production of high-octane gasoline [9]. As a result, a method for making synthetic aluminosilicate catalysts was developed, and the "Thermofor" moving-bed process with a granular catalyst was created by 1945. In the USSR, the flagship of research-and-development works in the field of catalytic cracking was the Grozny Scientific Research Institute (GrozNII). The first research in the field of catalytic cracking was launched at the Institute in 1938 under the guidance of V.S. Fedorov and B.K. Amerik, and full-scale scientific and design work was launched in 1941 to create the first Soviet catalytic cracking unit. The full completion of these works was the construction and start-up in 1952 of the 43-102 unit designed with the participation of experts from VNIPINeft [10]. Units of this type made it possible to obtain aviation gasoline with an octane rating of 80–87 and a yield of up to 27% from kerosene–gas oil fractions as feedstock [11].

The discovery of catalytic activity of zeolites in the late 1950s marked the beginning of a new chapter in the history of catalytic cracking. It was found that coarse-pores type X and Y zeolites in exchangeable forms show high activity in the cracking of both kerosene and gas oil fractions—standard cracking feedstock of those times—and vacuum distillates with boiling points up to 500°C [12]. The first zeolite-containing cracking catalysts were developed almost immediately: in 1969, the production of zeolites NaA, MgA, NaY and the cracking catalyst Tseokar [13] was organized on the basis of a GrozNII pilot plant and the Novogroznensky refinery. The introduction of a zeolite-containing catalyst in domestic cracking units made it possible to raise the yield of aviation gasoline from 20.5 to 31.1% in the industry on average using heavy cracking feedstock [14].

One of the pioneers of the use of zeolites in catalytic cracking was S.N. Khadzhiev, at that time a young PhD after postgraduate school at Moscow State University. Returning to the Grozny Research Institute in 1967, Khadzhiev was actively involved in the development of the production technology of NaY zeolite and the Tseokar cracking catalyst [15]. Subsequently, under his leadership, extensive research was carried out in the field of cracking on zeolites, later incorporated into the project of an advanced domestic cracking unit with a continuous-flow reactor using a microspheric catalyst containing Y zeolite in exchange form with rare-earth elements. In 1969–1970, a new stage began in the development of the catalytic cracking process associated with the development and introduction of highly active and selective zeolite-containing catalysts. In the early 1970s, for the first time in this country, the GrozNII and VNIINP specialists, together with manufacturers, transferred all industrial catalytic cracking units to a zeolite-containing catalyst with rare-earth elements. In 1976, the project was implemented as a G-43-107 type unit, subsequently replicated to ten different Soviet and foreign refineries and for the first time allowing the production of a gasoline component with an octane rating of at least 92 to reach an output of 50–55% when operating on heavy feedstock [14]. To maximize the high activity and selectivity of zeolite-containing catalysts, a unique catalytic cracking system was developed, which allows the process to be carried out at elevated temperatures (up to 530–550°C) and weight hourly space velocities (10–130 h^{-1}), with a high intensity of coke burning at catalyst regeneration (80–150 kg/t h) and maximum afterburning of carbon monoxide to dioxide.

The production volume of cracking catalysts is more than 850 thousand tons/year [16, 17], which makes it the most widely used catalyst in petroleum refining. A modern cracking catalyst is a multifunctional material based on zeolites Y and ZSM-5, distributed in an oxide or aluminosilicate matrix. A cracking catalyst is a very high-tech product; its development and modification is directly related to scientific and applied research in the field of zeolites.

Further development of the catalytic cracking process is directed both towards increasing the degree of oil refining and towards creating modifications for processing new types of feedstock and producing fuels and petrochemicals that are in demand. Separately, it is necessary to consider the prospects for the use of cracking for the processing of renewable feedstock.

PROCESSING OF HEAVY RESIDUES AND BITUMINOUS OILS

The increase in the share of heavy feedstock in the structure of world oil reserves, as well as the indisputable need to increase the depth of oil refining leads to the problem of involving heavy petroleum residues in catalytic cracking [18]. As the cracking feedstock becomes heavier, the concentration of polycyclic aromatic and naphthenic–aromatic hydrocarbons, as well as asphaltenes and resins, sharply increases with increasing temperature at the end of boiling. The molecules of these hydrocarbons are characterized by a strong affinity for the acid sites of the zeolite catalyst, which leads to their strong adsorption and blocking the pores of the zeolite [19]. Cracking of heavy feedstocks is characterized by lower conversion rates and selectivity to target products (gasoline components, lower olefins). In addition, during the processing of feedstock at standard cracking units, an increase in coke yield leads to an increase in regenerator temperature up to 750–800°C, which, in turn, leads to burnout and failure of separation devices.

In the first approximation, the problem of heavy feedstock cracking is solved by technological means. The catalyst is regenerated in two steps, special solid-phase refrigerators have been developed for cooling the catalyst from the regenerator. The most widely used units designed exclusively for refining residual feedstock are RCC (residual catalytic cracking) units with two-stage regeneration and separate flue gas withdrawal (UOP) and R2R units with two regenerators (IFP). However, even taking into account advances in cracking technology, the refining of feedstock with a carbon residue of greater than 10 wt % and a metal content of more than 30 ppm without prior preparation is unprofitable [20].

One of the most effective ways of refining heavy residues is preliminary hydrofining. Specialists of GrozNII showed that the combination of catalytic cracking with hydrotreating or light hydrocracking can significantly improve the technical and economic indicators of the refining of heavy residues [21]. Further development of this approach led to the creation of a domestic combined complex KT-1 with a typical throughput of 4 million tons/year, including vacuum distillation, hydrotreating and catalytic cracking of a vacuum distillate on a microspherical zeolite-containing catalyst, and visbreaking of the vacuum residue [22]. The complex was implemented in our country and abroad at the Pavlodar, Mažeikiai, Omsk, and Bourgas refineries. The creation of the domestic hydroconversion process using nanoscale catalysts led to the development of a project for a new combined unit like KT-2, which includes a vacuum-resid hydroconversion block to produce an additional amount of feedstock for cracking. The implementation of the complex made it possible to increase the depth of refining of heavy residues to 93–97% and to improve the range and quality of the products [23].

Further work of the Grozny Research Institute and the Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences (TIPS RAS) is primarily related to the creation of a catalytic cracking process for heavy vacuum distillates and fuel oil, the development of combined plants for the deep processing of fuel oil, including catalytic cracking units, as well as research projects aimed at developing a catalytic cracking process. The research works performed make it possible to involve heavier types of petroleum feedstock into refining, including vacuum distillates with boiling points of 540–560°C. In some cases, it is economically feasible to apply the catalytic cracking of high-sulfur straight-run feedstock without prior hydrotreatment, providing that the obtained components of motor fuels will be subjected to the subsequent hydrogenation after-treatment. Such a situation has developed in TAIF-NK (Nizhnekamsk) in the Republic of Tatarstan, where sour, hard-to-crack oil is processed. At the request of TAIF in 2001, VNIPINeft together with VNIINP and TIPS RAS developed a unique domestic technology for catalytic cracking of vacuum gas oil, which is not inferior in its performance to the best foreign analogues. This technology was successfully introduced in 2006 during the reconstruction of the reactor unit of the isopentane dehydrogenation plant at TAIF-NK (Nizhnekamsk) based on the existing equipment (capacity 880 thousand tons/year). The yield of the desired product gasoline fraction at this unit amounted to 48.5 wt % on a feedstock basis. After desulfurization, gasoline is characterized by a research octane number of 90 (MON 80) and the sulfur content less than 50 ppm. On its basis, high-volume production of gasoline according to GOST R51105-97: Normal-80, Regular-92, and Premium-95, corresponding to modern European quality standards was organized at TAIF-NK. The adopted technical solutions can be used as the basis for the development of other refineries in Russia, taking into account the need to produce gasoline of world-class quality. The development of a powerful combined catalytic cracking unit for high-sulfur heavy feedstock at TAIF-NK fully confirmed the design parameters of this plant, ensuring a high economic and environmental effect from its implementation. Due to uniqueness and novelty of the technical solutions of this work, its authors were honored the 2008 Prize of the Government of Russia in the field of science and technology (the research group was headed by TIPS RAS director, academician Salambek Khadzhiev).

Progress has been recently observed in the intensification of the cracking of heavy feedstocks as a result of the development of methods for the synthesis of new mesoporous and nanocrystalline zeolites. The use of sequential desilication/dealumination [24, 25] or the introduction of structure-directing agents during the synthesis [26, 27] allows the formation of zeolites of conventional structural types with an increased volume of mesoporous structures. Mesoporous zeolites exhibit increased activity in the cracking of heavy molecules, a high selectivity for the gasoline fraction, and a reduced coke yield [28]. In another approach, the size of the zeolite crystal is reduced, which leads to an increase in the external surface accessible to heavy feedstock molecules. A decrease in the zeolite crystal size from 100 to 25–40 nm leads to an increase in the selectivity for gasoline by 10% and a decrease in the selectivity for heavy gas oil by 5–10% [29].

A fundamentally new approach to increasing the conversion of raw materials is being developed at the Institute of Chemical and Technical Research, RAS. The method consists in dispersing the promoting composition on the basis of Group VII metals in heavy oil fractions and their subsequent cracking. The introduction of the promoting additive in the amount of up to 0.1% for raw materials allows increasing the selectivity for the gasoline fraction by 7–10% by reducing the yield of heavy gas oil and coke [30].

SOLID-ACID ALKYLATION

The possibility of catalytic alkylation of isoalkanes by alkenes was discovered by V.N. Ipatiev back in 1932. Aluminum chloride was used as an acid catalyst [31]. In 1938, there were reports of successful testing of concentrated sulfuric acid as a catalyst for the alkylation of isobutane with C_3 and C_4 alkenes [32]. Somewhat later, liquid hydrogen fluoride was also found to exhibit activity in the alkylation reaction [33]. There are more than 700 refineries over the world that have about 170 alkylation units [34]. However, modern industrial alkylation does not fundamentally differ from the processes developed in the middle of the last century and is still based on the use of sulfuric or hydrofluoric acid. Industrial alkylation processes are still being retrofitted by improving the hardware design, a development that makes it possible only to alleviate the disadvantages of liquid-acid catalysis, which are due to the toxicity and high corrosive activity of the catalysts [34]. The solution of production problems and reduction of capital costs and the cost of process safety management can be achieved by switching to solid-acid (zeolite) alkylation catalysts.

Table 1. Results of testing the starting (H-EMT, H-FAU, Si/Al = 3.5) and dealuminated (H-EMT, H-FAU, Si/Al = 5–6) zeolites in the isobutane alkylation reaction with 2-butylene at 80°C after 8 h in a slurry reactor

Parameter	Zeolite form			
	H-EMT	dealumd. H-EMT	H-FAU	dealumd. H-FAU
Butene-2 conversion, wt %	88	98	66	67
Alkylate yield[a]	3.8	4.8	1.4	2.1
Selectivity[b]	1.8	2.0	1.0	1.3
Product distribution, wt %				
Paraffins C_5–C_7	9.6	7.6	23.0	18.1
Paraffins C_8	81.9	76.4	64.4	69.3
Olefins C_8	0.5	0.0	3.1	2.9
Paraffins C_{9+}, olefins	7.9	15.8	9.3	9.8
Isooctanes, wt %				
2,3-DMH	4.9	6.1	4.8	6.2
2,4-DMH	1.4	2.4	4.0	4.2
3,4-DMH	2.3	2.1	3.6	2.7
2,2,3-TVP/2,5-DMH	14.7	7.9	7.1	6.4
2,2,4-TMP	24.4	18.3	26.9	24.4
2,3,3-TMP	29.5	34.1	29.1	29.8
2,3,4-TMP	22.1	28.5	24.2	26.3
Isooctenes in C_8 products, wt %	0.6	0.0	4.6	4.0

[a] Alkylate yield: g of C_5–C_8 paraffins/g of dry catalyst.
[b] Selectivity: g of C_5–C_8 paraffins/g of converted butene-2.

The study of the effect of dealumination on the catalytic activity of EMT and FAU zeolites was studied in [35]. The process of isobutane alkylation with butylenes was carried out at 80°C on various zeolites with faujasite structure—the initial and dealuminated samples of H-EMT zeolites with hexagonal structure and H-FAU with cubic structure. The Si/Al atomic ratio was 3.5 and 5–6 for the initial and dealuminated structures, respectively. The results of catalyst testing in the alkylation reaction are given in Table 1.

As follows from the data in Table 1, a higher alkylate yield and a higher TMP selectivity after 3 h on stream are observed for the dealuminated forms. The dealuminated zeolite H-EMT showed the best results in alkylation. In the alkylate composition, 76% C_8 hydrocarbons for dealuminated H-EMT and 70% for dealuminated H-FAU were observed. In both cases, trimethylpentanes prevailed in the C_8 fraction. A higher yield of dimethylhexanes was observed for dealuminated H-FAU. For dealuminated H-EMT, a lower olefin yield was observed in the C_8 fraction even after 5 h of the reaction.

A comparative study of the activity in the alkylation of isobutane with butylenes in the presence of various zeolites was performed in [36]. The alkylation reaction was carried out in a flow mode at a temperature of 50°C and a pressure of 2.5 MPa. The distribution of alkylation products is given in Table 2. It has been established that high conversion of olefins is accompanied by a high cracking rate. The yield of trimethylpentanes (TMP) on zeolite MCM-22 is less than that on wide-pore zeolites, such as Y, Beta, mordenite, but higher than on ZSM-5 with similar butene-2 conversions. This zeolite is more active in the dimerization of olefins than in their alkylation with isobutane. Zeolite MCM-22 is an active catalyst for the alkylation of isobutane with butene-2 at lower reaction temperatures. It was noted that the concentration of TMP in gasoline decreases much slower with time for zeolite MSM-22 than for the other zeolites studied.

In [37], it was shown that the acidity of catalysts plays a major role in coking. At low acidity, the reaction does not proceed and a small amount of coke is formed. With an increase in acidity, the adsorption of olefins increases and the polymerization reaction results in catalyst deactivation. Zeolite Y, partially exchanged with lanthanum, is an example of a catalyst with optimum acidity. This catalyst is deactivated by loss of acidity and pore blocking. It was shown that high catalyst activity is accompanied by intense coking. Coke formed at the reaction temperature has an aliphatic structure. With increasing temperature, aliphatic coke converts into aromatic coke. Using the TPO technique, it was shown that the removal of coke

Table 2. Activity and selectivity at the beginning of the reaction (1 min) (50°C, molar ratio $i\text{-}C_4/2\text{-}C_4^= = 15$, olefin WHSV = $1\ h^{-1}$ on different zeolites [36]

	Zeolites				
	USY	BETA	Mordenite	ZSM-5	MCM-22
Conversion of $2\text{-}C_4^=$, wt %	100.0	97.4	93.7	99.8	95.2
Alkylate yield (g C_{5+}/g $2\text{-}C_4^=$)	0.48	0.47	0.67	0.03	0.12
Distribution of C_{5+}, wt %					
C_5–C_7	32.8	29.9	7.9	6.2	63.4
C_8	40.9	50.6	70.2	83.5	33.0
C_{9+}	26.3	19.5	21.9	10.3	3.6
Distribution of C_8, wt %					
2,2,4-TMP	27.9	40.3	44.0	5.7	1.5
2,2-DMH	0.0	0.0	0.4	0.0	0.0
2,5-DMH	1.7	4.3	3.8	4.1	8.2
2,2,3-TMP	6.6	5.9	8.1	6.1	2.7
2,4-DMH	2.4	1.6	1.3	20.4	2.5
2,3,4-TMP	19.6	20.2	12.1	7.4	13.0
2,3,3-TMP	20.0	10.5	12.7	1.7	19.7
2,3-DMH	11.0	12.8	11.0	43.0	12.4
3,4-DMH	10.5	2.4	1.3	3.4	10.0
dimethylhexenes	0.3	2.0	5.3	8.2	30.0
TMP distribution, wt %					
2,2,4-	37.7	52.4	57.2	27.3	4.1
2,2,3-	8.9	7.7	10.5	29.2	7.3
2,3,4-	26.5	26.3	15.7	35.4	35.2
2,3,3-	26.9	13.6	16.6	8.1	53.4

deposits in a stream of hydrogen at 80°C for 12 h leads to the removal of half of these deposits. However, the toxicity of the remaining deposits in this case is significantly lower than those that remain after catalyst regeneration in the presence of oxygen at high temperatures.

Many companies and research institutes are conducting active research in this area, but only four solid-acid alkylation technologies have been proposed for licensing (Table 3) [37].

Despite the high initial activity in the alkylation reaction, these catalysts are quickly deactivated because of the oligomerization of olefins, and ensuring their on-stream stability still remains an unsolved problem. There is advertising information about the demonstration facilities of Haldor Topsoe together with Kellogg (FBA process) and UOP (Alkylene process). The technologies being tested, however, are not without drawbacks, since the heterogeneous catalysts used require maintaining constant activity by introducing a superacid: aluminum chloride (Alkylene process) or supported trifluoromethanesulfonic acid CF_3SO_3H (FBA process), which ultimately requires the protection of equipment against possible corrosion. In August 2015, the Chinese company Shandong Wonfull Petrochemical Group announced the launch of the first industrial solid-acid alkylation plant based on the AlkyClean technology developed by Albemarle, CB & I and Neste Oil CB & I/Albemarle (the United States). To maintain a constant catalyst activ-

Table 3. Development of solid alkylation catalysts

UOP	HAL-100 ($AlCl_3/Al_2O_3$)
Lummus	USY
HaldorTopsoe	CF_3SO_3H/SiO_2
INEEl	USY
DuPont	CF_3SO_3H/SiO_2 + Nafion/SiO_2
Mobil	Zeolite
Shell	Zeolite

Table 4. Material balance of the alkylation test bench

No.	Taken		Obtained	
		wt %		wt %
1	Total C_1–C_3	1.9	Total C_1–C_3	1.2
2	Isobutane	76.8	Isobutane	59.7
3	*n*-Butane	6.1	*n*-Butane	5.9
4	Total butylenes	15.2	Alkylate	29.6
5		–	Loss by sweeping**	3.6
	Total	100	Total	100

ity, frequent catalyst regeneration is proposed. Such a short-cycle version of the technology requires the use of several reactors. TIPS RAS, Elinp, and Gazprom Neft have developed a demonstration plant for the alkylation technology on the solid catalyst Alkyran-GPN, which can compete with the existing technologies of sulfuric and hydrofluoric acid-catalyzed alkylation. The Alkyran-GPN process provides unique advantages:

(a) use of noncorrosive medium;

(b) giving a product with a higher octane number (with almost the same material balance of the process);

(c) lower capital costs compared with sulfuric acid alkylation (eliminating the costly and environmentally harmful unit for the regeneration of spent sulfuric acid, the product alkalizing and water washing blocks, the sulfuric acid transport and storage system, and comprehensive measures for protecting the environment from the effects of sulfuric acid).

The material balance of the test run is presented in Table 4.

In the test run, the conversion of butylenes was 96 wt %, and the yield of alkylate from feedstock butylenes was 94% (relative to the theoretical value). The alkylate octane numbers were 92 (MOC) and 97 (RON). Using the results of the research, a basic project of the first industrial domestic alkylation unit on solid catalysts with an annual capacity of 100 thousand tons of alkylate, scheduled for construction at the Gazpromneft-Moscow Refinery, will be developed. In Russia, there are currently seven refineries that have sulfuric acid and hydrofluoric acid alkylation units in operation with a total capacity of about 1.5 million tons/year. These units are easy to switch to the Alkyran-GPN process by replacing the reactor block, with the rectification unit (about 50% of the capital costs) remaining almost unchanged. In order to achieve modern levels of oil refining efficiency (this value is 85% in Europe and 96% in the United States), it is necessary to have a catalytic cracking unit at almost each of the 28 existing refineries, which is the source of the butane–butylene fraction as the feedstock of the alkylation process. Thus, there is potential for the construction of at least ten more plants for the production of alkylate with a total capacity of 1.5–2 million tons/year with a gross output of about 70 billion rubles a year. The development of projects and the industrial implementation of domestic industrial units based on the Alkyran-GPN technology will ensure the independence of the Russian refining industry concerning this strategically important and very interesting process.

The production of ethylbenzene is becoming an increasingly significant process in which zeolite catalysts have found industrial application. Ethylbenzene is mainly used to produce styrene, one of the most important petrochemical products. The general scheme for producing ethylbenzene is similar to that for producing isoalkanes using olefins. In the earliest technologies developed since the beginning of the 20th century, strong mineral acids (for example, H_2SO_4, HF) were used as catalysts [38]. In the 1950s. the Friedel–Crafts catalyst $AlCl_3$ acquired very wide use as a catalyst for the production of ethylbenzene, but its application was complicated by the high sensitivity of the catalyst to the smallest impurities; therefore the process of ethylbenzene production was rather complex and time consuming [39]. The first solid acid catalysts were obtained in the middle of the last century [40] and, already in 1966, it was shown that wide-pore X and Y zeolites exhibit high activity in the production of ethylbenzene [41]. In the USSR, research in the field of ethylbenzene production using synthetic zeolites was actively conducted under the guidance of Academician Kh.M. Minachev [42]. The first industrial application of a zeolite-containing catalyst was implemented in 1980 by Mobil and Badger. The process was carried out in the gas phase on the catalyst HZSM-5, with the on-stream time being 60–90 days. The effectiveness of this technology is evidenced by the fact that more than 35 units using the Mobil–Badger process with a total capacity of about 8 million tons/year have been licensed since 1980 [43]. In the 1990s, the same company developed the "third-generation" ethylbenzene production process, which involved an additional transalkylation reactor. The duration of the cycle increased to 1 year [44]. In early 1990, Chevron patented a liquid-phase alkylation and transalkylation process using zeolite Beta [45], and EniChem (PolimeriEuro-pa) announced the creation of a similar process in 1991 in Europe [46]. In Russia, the process for synthesizing ethylbenzene on zeolite catalysts under both gas-phase and liquid-phase conditions was developed by the Grozny Research Institute and Institute of Organic Chemistry of the Russian Academy of Sciences in the late 1980s. The implementation of the process was started on a retrofitted unit with a capacity of 230 thousand tons/year at Salavatnefteorgsintez in the 1990s. Based on the foreign practice of that time, preference was given to the gas-phase version of the process. For a number of well-known economic reasons, the construction and commissioning of the unit were completed as late as 2003 [47].

SYNTHESIS OF LIGHT OLEFINS

The development of polymer production determines a significant increase in demand for petrochemical feedstock, in particular, propylene. The production of this monomer in 2011 amounted to approximately 82 million tons/year with a forecast of growth to 132 million tons by 2025 [48]. Obviously, the conventional propylene manufacture process—pyrolysis of gaseous and gasoline feedstock—cannot fully satisfy this demand, since the yield of propylene in the pyrolysis process does not exceed 8–9% even from optimal feedstock and 1.5–2.0% in the case of ethane pyrolysis. Meanwhile, the Russian economy in terms of the pace of development of complexes for the production of olefins and the consumption of polymer products is currently far behind the economies of industrialized countries. The pyrolysis units operating in Russia, producing ethylene and propylene, have exhausted their capabilities, and a shortage of basic monomers has arisen on the domestic market. The demand for polymer products significantly exceeds supply, and in order to reduce the dependence on imports of polymers, new ethylene and propylene production facilities are being created. In accordance with the decision of the Russian government [49], the production facilities under construction are largely focused on the use of gaseous feedstock [50].

Catalytic cracking of petroleum fractions, on the other hand, already now provides over 30% of world production of propylene. The monomer yield in the cracking process is usually 3–5%, depending on the reaction conditions and the type of feedstock. To increase the production of propylene, in addition to elevating the temperature and increasing the catalyst/feedstock ratio, zeolites of other structural types in the catalyst composition are used. The basic principle of the choice of zeolite is the presence of narrow pores in combination with a high strength of acid sites. Materials, such as MCM-22, ZSM-11, ZSM-23, Beta [51], and ITQ-7 [51], having these properties were successfully used; however, ZSM-5 zeolite has found the widest application. For the purpose of hydrothermal stabilization, zeolite is usually modified with rare-earth elements and phosphorus [52, 53].

There are a variety of cracking processes with a higher yield of light olefins: DCC (RIPP and SINOPEC) [47], PetroFCC (UOP) [54], and others [55–58]. The yield of propylene can reach 19–20% by the processing of traditional cracking feedstock and up to 23–25% with a total yield of C_2–C_4 olefins up to 40–45% when using paraffinic feedstock. In addition to olefins, a concentrate of C_6–C_8 aromatic hydrocarbons is produced in an amount of up to 20% suitable for the production of individual aromatic hydrocarbons. An additional advantage of catalytic cracking for the production of olefins is the ability to flexibly adjust the ratio between ethylene, propylene, and butylenes by varying the value of the SiO_2/Al_2O_3 molar ratio in the zeolite. An increase in the SiO_2/Al_2O_3 ratio from 33 to 487 leads to an increase in the C_4/C_3 ratio from 0.60 to 0.70 without reducing the degree of conversion when used in a mixture with zeolite Y [59–61]. Due to the current situation, there is a great demand for new technologies for processing cheap gaseous feedstock, which, on one hand, could eliminate the "propylene hole" formed in the olefin world complex, and, on the other hand, would provide deep processing of the "methane" component of natural gas.

Technologies that meet these conditions have been actively developed in recent years by a number of foreign companies (UOP, Lurgi, INEOS, Total, JGC, Mitsubishi, and many others) and Russian research centers. In particular, at the Topchiev Institute of Petrochemical Synthesis conducts research on the conversion of methane-containing feedstock into valuable petrochemicals, which have made a significant contribution to the development of new natural gas processing processes.

Olefins can be obtained from synthesis gas in different ways, in one stage by the Fischer–Tropsch process or through intermediate synthesis of methanol or dimethyl ether with their subsequent conversion into olefins on zeolites or molecular sieves. The processes of synthesis gas conversion to lower olefins through methanol provide deep conversion of synthesis gas and make it possible to obtain ethylene and/or propylene with yields at the level of 70–90%, with a purity of 99.6–99.8% (polymer grade products) [62, 63]. The high efficiency of such processes is partly due to the high productivity and relatively low feedstock consumption per unit product in the manufacture of methyl alcohol from CO and H_2 [64]. But a key component of the success of such methods is well-developed technologies for converting methanol to lower olefins, which have been developed for over 40 years. Today they are brought to commercial use by a number of companies and research centers (UOP, HydroNorsk, INEOS, Total, Lurgi, Mobil Oil Corporation, Exxon Mobil, DICP, SINOPEC, etc.). The developers offer numerous options for methanol-based lower olefin production technologies, which differ in the catalysts and technological nuances used (Table 5). In some processes, a mixture of ethylene with propylene (MTO, MTO/OCP, DMTO, SMTO) is obtained, and some technologies are focused on targeted production of propylene (MTP, FMTP, DTP, OTP) or ethylene (MTE). For the synthesis of lower olefins from oxygenates (from both methanol and DME), catalysts are being actively developed on the basis of ZSM-5 zeolite, which differs from other molecular sieve structures by increased stability under conditions of olefin synthesis and selectivity for propylene. The physical and chemical properties of catalytic systems (for example, total acidity, channel structure, pore volume and size, crystal size) and operating conditions have a significant impact on the selectivity of ethylene and propylene production [65–67]. Thus, Exxon Mobil and Mobil Oil Corporation have patented a process for converting methanol to zeolites in combination with the cracking of hydrocarbons. They proposed to use a selective ZSM-5 catalyst modified with phosphoric acid or gallium compounds and add C_{9+} aromatic hydrocarbons to the initial methanol for accelerating the reaction to [68]. Under these conditions, C_2–C_4 olefins are formed with a selectivity of more than 75% with methanol conversion of more than 74%.

The MTO (methanol-to-olefins) process developed by UOP/Norsk Hydro, was carried out on a silicoaluminophosphate catalyst (SAPO-34, SAPO-17) in a fluidized bed reactor at temperatures of 420–500°C and was mainly oriented on ethylene production. The use of SAPO-34, due to the small pore size of silicoaluminophosphate (0.4 mm), makes it possible to obtain lower C_2–C_4 olefins with quite high selectivity (above 80%). In addition, about 10% of methanol is converted to butenes, which themselves are a valuable feedstock for making a variety of products; however, with all the obvious advantages of the process proposed, there is one significant drawback, the extremely rapid deactivation of the SAPO-34 catalyst by coking, which often requires the regeneration or replacement of the catalyst in the reactor [69]. In 2004, the company announced the creation of large-scale production of ethylene and propylene from methanol (up to 400 thousand tons of ethylene per year) and, in 2008, UOP patented a process for the selective production of ethylene or propylene from methanol diluted with water [70]. On a bifunctional catalyst containing SAPO-34 and ZSM-5, propylene was obtained with a selectivity of 71%, and the selective formation of ethylene (70–76%) was carried out on the ELAPO catalyst. Zeolite HZSM-5 has a huge advantage in this process, compared with SAPO-34 molecular sieves, because its deactivation does not proceed so rapidly, even though ZSM-5 is less selective for lower olefins [71–74]. At the same time, ZSM-5-based catalysts have a higher propylene selectivity, the demand for which is significantly higher than for ethylene. In the MTP (methanol-to-propylene) process developed by Lurgi in cooperation with German companies (MG Technologies AG, Metallgesellschaft AG, Süd-Chemie AG), propylene is selectively obtained in the presence of HZSM-5-modified zeolite catalysts (~0.05 wt %) [75, 76]. In contrast to the developments by MOBIL and UOP, Lurgi researchers use an equilibrium mixture consisting of methanol, DME, and steam in the ratio of 32, 34, 34 vol %, respectively, as the feedstock. As a result, it is possible to process up to 99% of methanol at a temperature of 435–440°C and a pressure of 0.18 MPa, obtaining 70% propylene [77]. Along with it, depending on the reaction conditions, ethylene and higher olefins are formed, the by-products being fuel gas and liquid gasoline hydrocarbons.

PROCESSING OF ALTERNATIVE FEEDSTOCK

The world economy is traditionally based on fossil raw materials: coal, oil, and gas provide more than two thirds of world energy production and 100% cover the needs of mankind in hydrocarbons - valuable chemical feedstock [78]. The world is difficult to imagine today without transport vehicles with internal combustion engines and without polymer materials, varnishes, drugs, and other essential products. Accordingly, the development of the world economy leads to an increase in the extraction of fossil raw materials.

From 2005 to 2012 the world proven oil reserves increased from 187.5 to 230.3 billion tons [17]. However, starting from 2012, the increase in reserves becomes extremely small; Moreover, in 2015, there was a decrease in global oil reserves by 300 million tons compared with 2014. In Russia, the situation with oil reserves is no less alarming: the decline in proven reserves began in 2007 and continues; the current level is 14.0 billion tons, which is 500 million tons less than in 2007. In addition, most of the newly discovered reserves are represented by relatively heavy types of oil concentrated in small and medium-sized fields.

The only real substitute for fossil raw materials is the renewable feedstock plant biomass. Biomass in elemental composition contains carbon, hydrogen, and oxygen; accordingly, it can be used both for the production of electricity and (potentially) for the production of fuels and chemicals. The main advantages of using biomass as an energy source and chemical feedstock are:

—extremely large amount of available resources; thus, the annual volume of forestry waste only and in Russia alone is at least 1 billion m^3 [79];

—rapid reproduction of biological feedstock and the possibility of extensive expansion of its production. The annual global increase in biomass is about 220 billion tons, of which only one tenth is used [80];

—no violation of the carbon balance in the biosphere when burning biomass-derived fuels. Biomass generation occurs as a result of absorption and assimilation of atmospheric carbon dioxide. Accordingly, the gas to be released into the atmosphere by burning this fuel will be only the one uptaken from air and it can be converted again to the same amount of biomass.

From the technological and economic point of view, the most suitable for processing lignocellulosic biomass is the use of two-stage processes: liquefaction/gasification/pyrolysis of biomass to produce intermediate products (biogas and bio-oil) and the subsequent conversion to fuels or petrochemicals. The

Table 5. Methanol-based processes for production of lower olefins

Process[a]	Developer company	Catalyst	T, °C	Conver-sion, %	Product yield, wt %			Technological features			Total olefin production volume, thousand tons/year
					ethylene	propylene	gasoline	feedstock[b] + diluent	reactor type[c] (number)	recycle	
Production of lower olefins from methanol											
MTO [64]	MobilOil	HZSM-5	350–400	47–75	7–24	20–28	30	$CH_3OH + H_2O$	I (1)	C_{6+}[e]	–
MTO [68]	ExxonMobil	GaZSM-5	450	~100	21–73	17–44	0	CH_3OH + He + C_{6+}[d]	I (1)	C_{6+}[e]	–
					6	50	0	CH_3OH (r.g.) + He	I (1)	–	
MTO [76]	UOP, Norsk Hydro	SAPO-34	450	95–97	40	30	0	CH_3OH(c) + H_2O	II (1)	–	0.3
MTO/OCP [69]	UOP, Total, INEOS	SAPO-34	450–550	~100	31–48	34–45	0	CH_3OH(c) + H_2O	II (1) + Cr	DME, C_{4+}	**>3600**
DMTO [62, 63]	DICP[d]	SAPO-34	450–500	~95	30	40	0	CH_3OH(c) + H_2O	II (1)	–	**5170**
DMTO-II		SAPO-34	450–500	~100	35–45	35–45	0	CH_3OH(c) + H_2O	II-K (1)	C_{4+}	**670**
SMTO [76]	SINOPEC	SAPO-34	450–500	~100	35–45	35–45	0	CH_3OH(c) + H_2O	II (1)	–	230
FMTP [76]	Tsinghua University	SAPO-18/ SAPO-34	450–550	~100	N.d.	>67	N.d.	CH_3OH (r.g.)	II (2) + Cr	$C_2^=, C_4^=$	230
OTP [70]	UOP	ZSM-5/ SAPO-34	430–490	99	<0.1	>71	19	CH_3OH(c) + H_2O	III (3)	H_2O, $C_2^=$, C_{4+}	–
Production of lower olefins from methanol through dimethyl ether											
MTP [77]	Lurgi	ZSM-5	430–450	~ 99	0	68–70	26	CH_3OH (r.g.) + DME + H_2O	D + I (≥3)	$C_2^=, C_{4+}^=$	**~2000**
DTP [76]	JGC, Mitsubishi Chemical	ZSM-5	450–550	~100	0	>70	16	CH_3OH (r.g.) + DME + $C_{4+}^=$	D + I (1)	C_{4+}	–
MTE [76]	Van Dijik	SAPO-34	450	70	34	0	0	CH_3OH (r.g.) + DME + H_2O	D + I (4)	H_2O, C_{2+}	–

[a] MTO (Methanol-to-olefins); OCP (Olefin Cracking Process); DMTO (DICP Methanol-to-olefins); SMTO (Sinopec Methanol-to-olefins); FMTP (Fluidized Methanol-to-propylene); OTP (Oxygenate-to-propylene); DTP (Dominant technology for the propylene production); MTE (Methanol-to-ethylene): [b] CH_3OH(r.g.)—reagent-grade methanol, CH_3OH(c) crude—methanol; [c] I—adiabatic fixed bed MTO reactor, II—MTO fluidized bed reactor, III—moving bed MTO reactor, D—methanol dehydration reactor, and Cr—hydrocarbon cracking reactor; [d] Dalian Institute of Chemical Physics (DICP); [e] aromatic hydrocarbons.

Table 6. Typical biomass composition, wt % [86–89]

Biomass	Extracts	Ash	Lignin	Hemicellulose	Cellulose	Reference
Poplar	3.6	0.9	23.3	27.8	43.7	[86]
Pine	2.7	0.3	25.9	23.0	41.7	[87]
Millet	17.0	5.8	17.4	27.3	30.8	[88]
Corn	7.6	6.8	17.2	26.3	37.8	[89]

thermochemical processes gasification and pyrolysis are the most widely used (and implemented in the industry) for biomass processing. The products obtained by thermochemical processing are characterized by low quality. Synthesis gas contains up to 5% hydrogen sulfide and up to 50% carbon dioxide, which make it impossible to use the gas in further syntheses without additional purification. Bio-oil consists of water (20–30 wt %, depending on the feedstock) and a complex mixture of oxygen-containing compounds [81], the main components of which are carboxylic acids, aldehydes, ketones, alcohols, glycols, esters, ethers, phenols, and their derivatives, as well as carbohydrates and lignin oligomers [82]. Separation of bio-oil into individual components is not cost-effective due to the high complexity of its composition. Development of methods for processing bio-oil to produce chemical feedstock and motor fuels is in the experimental stage. There are a number of approaches, among which the following can be noted: steam reforming/gasification of the bio-oil itself [83], chemical modification of corrosive components, for example, alkylation and esterification [84], and also hydrogenation/hydrocracking of bio-oil to hydrocarbons [85]. The latter method is one of the most popular lines of research in upgrading bio-oil. The process takes place at temperatures of 200–400°C, hydrogen pressure of 8–30 MPa in the presence of catalysts based on noble metals, of transition metal (cobalt, nickel, molybdenum) sulfides, and others. The refined bio-oil contains up to 70% hydrocarbons, and the oxygen content is reduced to 5–10%. The balance of oxygen-containing compounds is represented by phenols, which are most difficult to hydrogenate.

Table 7. Classes of bio-oil compounds [89]

Class	Content, wt %
C_1 compounds: formic acid, methanol, formaldehyde	5–10
C_2–C_4 linear hydroxyl- and oxo-substituted aldehydes and ketones	15–35
C_5–C_6 hydroxyl-, hydroxymethyl- and oxo-substituted furans, furanones and pyranones	10–20
C_6 anhydrosugars and anhydrooligosaccharides	6–10
Water-soluble carbohydrates, substituted oligomeric and polymeric compounds of unknown composition	5–10
Monomeric methoxyphenols	6–15
Lignin	15–30

Biomass consists of three main biopolymers: cellulose, hemicellulose, and lignin; it is these components that produce solid, liquid, and gaseous substances upon decomposion (Table 6).

Radlein et al. [89] determined the composition of bio-oil taking into account the classes of compounds contained in it and the size of their molecules (Table 7).

The problem of refining bio-oil to produce fuels and chemical feedstock comes down to the difficulty of removing oxygen without losing carbon from the composition of the compounds it contains. Direct hydrogenation proceeds at high hydrogen pressure, which significantly impairs economy and energy efficiency. The decrease in hydrogen pressure or process temperature leads to a sharp drop in the degree of hydrogenation. The water content in bio-oil ranges from 15 to 30%. With this percentage, bio-oil is not separable into fractions, but remains in the form of a stable pseudo-emulsion. When going beyond the specified range, separation of the emulsion into two phases is observed [91]. Water in bio-oil appears from the moisture contained in the biomass itself and as a result of dehydration reactions occurring during pyrolysis. The presence of water can be damaging to refining catalysts. Extraction is an acceptable method for the removal of the aqueous component of the bio-oil, however, this will result in loss of the organic phase and increase the requirements for wastewater treatment.

Depending on various factors (water content in bio-oil, its nature, amount of light fractions, degree of aging, etc.), the viscosity of bio-oil can vary from 25 to 1000 cP (measured at 40°C). Polymerization reactions leading to an increase in viscosity are accelerated at higher storage temperatures. It was shown that the rate of viscosity change may increase from 0.009 cP per day when stored at −20°C to more than 300 cP per day at 90°C [92].

At room temperature, bio-oil is a viscous, dark-brown liquid with a strong odor [93], it has the same appearance as vacuum gas oil (VGO) although their compositions differ significantly. Table 8 presents the

Table 8. Comparative characteristics of crude bio-oil and VGO [94]

Physical property	Bio-oil	Vacuum gas oil
Water content, %	15–30	0.1
pH	2.5	–
Specific gravity	1.2	0.94
Elemental composition, wt %		
C	54–58	85
H	5.5–7.0	11
O	35–40	1.0
N	0–0.2	0.3
Ash	0–0.2	0.1
Calorific value, MJ/kg	16–19	40
Viscosity, (50°C, cP*)	40–100	180
Salt content, wt %	0.2–1	1
Residue after distillation, wt %	up to 50	1

comparative characteristics of bio-oil and the VGO fraction. Bio-oil contains more water and oxygen, in addition, it contains a significant amount of organic acids (4.2–6.8 wt %), as a result of which the TAN (total acid number) value usually exceeds 100 mg KOH kg^{-1}. For comparison, conventional oil has a TAN value below 2 mg KOH kg^{-1}.

A solid phase is formed from the sand and inorganic compounds contained in the biomass, as well as from the coke and polymerization products formed during the pyrolysis. Its presence facilitates the aging and polymerization of bio-oil, an increase in viscosity, poisoning of catalysts.

Processes for converting bio-oil into more usable materials can be divided into two categories: low-temperature and high-temperature. The low-temperature processes include extraction in alcohols and other solvents [95]. High temperature processes are of the following types:

—noncatalytic heat treatment at high pressure (high pressure thermal treatment, HPTT) [96, 97].

—cracking at atmospheric pressure using crystalline aluminosilicate catalysts (zeolites) [98, 99].

—catalytic hydrotreatment at elevated pressure, hydrodeoxygenation (HDO) [100].

The main conditions of high-temperature processes are given in Table 9.

A significant advantage of catalytic hydrofining before catalytic cracking and HPTT is a low level of coking and, as a result, lower carbon losses and a longer catalyst life [97].

The vapor-phase catalytic cracking of bio-oil is carried out both in situ and ex situ. An example of an in situ process is catalytic fast pyrolysis, in which pyrolysis vapors are immediately passed through a catalyst bed. Contact of thermal pyrolysis vapors with a catalyst in a separate reactor is an example of ex situ bio-oil refining. This mode of operation has several advantages, including the ability to vary the process conditions (temperature, pressure, contact time).

At temperatures from 350 to 500°C and using zeolite catalysts, oxidized organic compounds undergo cracking, dehydration, decarboxylation, aromatization, alkylation, condensation, and polymerization. Dehydration is the dominant process when acid catalysts (e.g., ZSM-5) are used. The result of bio-oil refining is a mixture of aromatic hydrocarbons and lower olefins.

In a set of studies by Adjaye and Bakshi [101–103], the cracking of bio-oil in a microreactor was investigated at temperatures ranging from 290 to 410°C over various catalysts: HZSM-5, HY zeolite, H-mordenite, silicalite, and amorphous aluminosilicate. Hydrocarbon yields ranged from 5 to 29.7% for silicalite and ZSM-5, respectively. At higher temperatures, increased coking was observed, significantly reducing the yield of the product.

Chang et al. [104] showed that adding hydrogen-rich compounds can significantly reduce coking and increase the yield of hydrocarbons on crystalline aluminosilicate catalysts. A number of model compounds were studied [105–109]. High conversions (>90%) were obtained for alcohols, aldehydes, ketones, acids, and esters, whereas phenols and ethers did not react. Aromatic hydrocarbons were obtained from alcohols and ketones in high yields; acids and esters were converted to gas, water and coke with a low yield of liquid hydrocarbons.

In the case of bio-oil deoxygenation on zeolites, hydrocarbon yields typically range from 10 to 30%. Note that a certain amount of oxygen-containing compounds in the modified product can be beneficial, since they enhance the combustion process and,

Table 9. High-temperature of bio-oil upgrading processes [97, 101]

	HPTT	Cracking	HDO
Temperature, K	473–623	573–873	523–673
Pressure, MPa	15–30	–	10–30
Catalyst	–	Zeolites	Supported metals
Coking	High	High, 26–39 wt %	Low, <5 wt %

therefore, reduce coking [110]. Intense coke formation and rapid deactivation of catalysts are associated with the high acidity of the materials used, which induce dehydration reactions. Hydrogen deficiency in bio-oil [111] partially facilitates these processes. The presence of transition metals in catalysts facilitates the removal of oxygen, with the formation of more carbon oxides and less water, which promotes the hydrodeoxygenation of bio-oil to hydrocarbons [112].

Recently, research has been conducted on the involvement of bio-oil in the cracking process. Catalytic cracking of bio-oil in its pure form does not hold promise, since there is a high yield of coke, dry gas, and heavy residue due to a high coking value of certain components of bio-oil [113–116]. Therefore, it was proposed to introduce bio-oil into the cracking process together with conventional hydrocarbon feedstocks. The viability of this approach is related to the following factors:

—catalytic cracking of hydrocarbons is based on the reactions of intermolecular hydrogen transfer catalyzed by zeolites. The transfer of the hydride ion from one hydrocarbon molecule to another and hydrogenation of one of the molecules occur in these reactions. The introduction of bio-oil into the bio-oil cracking process leads to the involvement of its oxygen-containing components in these reactions. Being hydrogen acceptors, the bio-oil components are hydrogenated to form hydrocarbons and water;

—the hydrogen required for the hydrogenation of bio-oil components in the catalytic cracking process is provided by hydrocarbon molecules during their joint conversion.

The cracking of model bio-oil components, such as sorbitol [117], guaiacol [118, 119], glycerol, and acetone [120], has been most widely studied. It has been found that below a certain concentration of an oxygenated additive, the reaction can occur via hydrogen transfer from hydrocarbons; oxygen in this case is utilized in the form of water. At a high concentration of the additive, the yield of coke and dry gas sharply increases and carbon oxides appear in the products. Thus, bio-oil or its components can be successfully introduced into the cracking process in an amount up to 5% without a significant deterioration in the process performance characteristics [120]. At high concentrations, preliminary preparation of bio-oil is necessary to reduce its coking value. Thus, preliminary hydrodeoxygenation of bio-oil at 290 bar and 330°C can increase its amount for use in cracking feedstock up to 20% [121].

Catalytic cracking of bio-feedstock is currently being at the research-and-development stage. There are separate reports on a pilot implementation of the process using a pilot cracker with a capacity of 200 kg/h [122–124]. The widespread use of bio-oil in refining processes is hampered by its thermal instability and related technical problems.

Another area of involvement of renewable feedstock in the catalytic cracking process is the production of biofuels by cracking vegetable oils. As catalysts for the cracking of vegetable oils, MCM-41 [125], SBA-15 [126], zeolites BETA and ZSM-5 [127], and composites on their basis are used. The main reaction in the conversion of vegetable oils under cracking conditions is decarboxylation with carbon dioxide evolution and the formation of various hydrocarbons [128]. The yield of the gasoline fraction in the oil cracking process is 40–77%, depending on the catalyst and oil type. The advantage of the production of biogasoline from vegetable oils in the cracking process is the absence of the need to retrofit the reactor–regenerator unit of existing catalytic crackers, which significantly reduces the cost of oil conversion products. The absence of oxygen-containing waste, as well as the need for special purification of the product also makes the cracking process more economically attractive compared to the transesterification of oils with methanol—the traditional biofuel production process [129].

The data presented in this review show that zeolite catalysts from the time of their discovery to the present are used in a wide variety of refining and petrochemical processes. Combining the properties of various crystalline aluminosilicates, various polyfunctional catalysts of a new type are being developed for the refining of both heavy petroleum residues and biofeedstock. It is noteworthy that domestic petroleum refining industry possesses its own zeolite catalysis technologies that are not inferior to the best foreign analogues.

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