

Development of Efficient Zeolite-Containing Catalysts for Petroleum Refining and Petrochemistry

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Received November 18, 2004

Abstract—The role of various technologies in oil refining and petrochemistry changes due to amendments to the requirements for fuel quality. The development of these technologies requires the improvement of catalysts. This paper outlines main procedures for the production of dealuminated zeolites, as well as the advantages and drawbacks of these procedures. Catalysts with a high desulfurizing ability for the hydrocracking of vacuum gas-oil to gasoline and diesel fractions and catalysts for the isomerization of fuel hydrocarbons can be prepared using ultrastable Y-type zeolites. The results of testing of zeolite-containing binary catalytic systems in Fischer–Tropsch synthesis are presented.

In 1998, the European Parliament and the Council adopted Directive 98/70/EC (RL 98/70/EG) concerning the quality of gasoline and diesel fuels and amending Directive 93/12 (93/12/EEG). This directive and the later amendments are intended to toughen the requirements for fuel quality and to reduce harmful gas emissions from engine fuel combustion. The Russian Federation State Standard *Motor Fuels: Non-ethylated Gasoline* (EN 228-99), issued on July 1, 2002, is adjusted to the EEC environmental programs and the Euro-2 and Euro-3 standards for automobile exhaust emissions.

Table 1 presents the main European and Russian specifications for gasoline. As can be seen, the main amendments in the European specifications are concerned with gasoline composition. Specifically, they require a reduction in the sulfur and aromatic hydrocarbon (particularly benzene) contents of fuel and impose a limitation on the olefin content. The allowable sulfur content of gasolines was reduced from 150 to 50 ppm in 2005 and will be further reduced to 10 ppm in 2009. The total aromatic hydrocarbon content should be lowered from 42 to 35% and the benzene content is limited to 1%.

The main amendments in the European specifications for diesel fuel, as in those for gasoline, are concerned with limitations on the sulfur and aromatic hydrocarbon contents (Table 2). The maximum allowable sulfur content is 350 ppm as from January 1, 2000, 50 ppm as from January 1, 2005, and 10 ppm as from 2009.

The decrease in octane number because of the reduced aromatic hydrocarbon and olefin contents of gasolines can be compensated for by raising the isoparaffin content and by using antiknock additions. Therefore, the role of isomerization, alkylation, and esterifi-

cation processes in the operation of current refineries is expected to increase. In our opinion, a better way of increasing the octane number of gasoline is by the isomerization of light hydrocarbons, since high-grade gasoline obtained by this method contains no sulfur, aromatics, or olefins. According to [1], the daily output of the isomerization plants in Europe increased from ~20000 m³ in 1980 to 80000 m³ in 2000.

Table 3 shows the total refinery capacities for the leading countries in 2000 [2]. In spite of the significant primary refinery capacity, Russia (second after the United States) is far behind the leading countries in secondary refining capacity, especially in hydrocracking, hydrotreatment, alkylation, and isomerization. Toughening the requirements for fuel composition will necessitate changes in the structure of oil refining in Russia, primarily an increase in the depth of refining, which is ~70% on the average in Russia and 86–94% in Europe and the United States [3].

The use of methyl *tert*-butyl ether (MTBE) as an antiknock additive to gasoline is not appropriate. In the United States, MTBE has been prohibited since the end of 2003. For instance, Alberta Envirofuels Inc. (AEF), which is a joint venture of Chevron Texaco and Fortum Oy for MTBE manufacture, was forced to switch to isooctane in late 2002 because of the ban imposed on the use of MTBE [4]. Now the future of MTBE is being debated in Europe on the basis of the experience accumulated in the United States.

To meet the current requirements for fuel quality, Russian refiners require significant capital investments for the restructuring of petroleum refining. The problems of increasing the refinement depth and of manufacturing environmentally friendly products cannot be solved without developing and implementing new technologies and a new generation of high-efficiency catalysts.

[†] Deceased.

Table 1. Main quality indices of gasoline

Index	EEC		Russia
	2000	2005	RF Standard GOST R 51866-2002 (EN 228-99)*
ON(IM)/ON(IM)**	≥95/85	≥95/85	≥95/85
Sulfur content, ppm***	≤150	≤50(10)	≤150
Content, %:			
aromatic hydrocarbons	≤42	≤35	≤42
olefins	≤18	≤18	≤18
benzene	≤1	≤1	≤1
oxygen	≤2.7	≤2.7	≤2.7
Saturation vapor pressure, kPa	≤60	≤60	≤45–60
Volume fraction of evaporated gasoline, %			
at temperature 100°C	≥46	≥46	≥46–71
150°C	≥75	≥75	≥75

* Premium gasolines.

** ON—octane number, IM—investigation method, and MM—motor method.

*** 10 ppm in 2009.

Table 2. Main quality indices of diesel fuels

Index	EEC		Russia (Soviet Standard GOST 305-82)
	2000	2005	
Cetane number	≥51	≥51	≥45
Density at 15°C, g/cm ³	≤0.845	≤0.845	≤0.86
Fractional composition: 95% is distilled at temperature, °C	≤360	≤360	≤360
Sulfur content*, ppm	≤350	≤50/10	≤2000(500**)
Aromatic hydrocarbon content, %	≤20	—	≤20**
Polycyclic aromatic hydrocarbon content, %	≤11	—	—

* In 2009, 10 ppm.

** For environmentally friendly diesel fuel (according to the Soviet Specifications TU 38.1011348–89).

Table 3. Total outputs of main refining processes in leading countries in 2000 (in million tons)

Process	Russia	The United States	The United Kingdom	Italy	France	Germany	Japan
Primary refining	333.65	827.05	89.23	117.03	95.01	113.77	249.88
Thermal processes	26.72	103.94	8.14	23.31	7.72	17.26	41.44
Catalytic cracking	19.05	278.08	22.47	15.01	17.62	17.00	37.02
Catalytic reforming	42.79	176.34	16.49	13.53	13.27	19.89	35.63
Hydrocracking	1.92	71.18	1.58	10.80	0.77	6.19	7.94
Hydrotreatment	0.43	88.95	13.31	18.02	9.69	34.03	123.77
Hydrosulfurization	117.93	448.02	40.35	38.06	40.70	50.15	87.54
Alkylation	0.50	54.46	4.66	1.82	0.92	1.21	2.34
Isomerization	0.71	31.79	4.46	4.44	3.43	3.06	1.02

Zeolites are active acidic components of catalysts in many refining processes. Many methods for the directed modification of the properties of zeolites are known. The basic ones are the following:

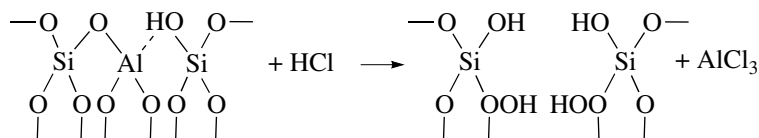
- control of the structure of zeolites;
- variation of zeolite cations;
- modification of the zeolite surface by reacting a modifying agent with zeolite hydroxyl groups;
- formation of active component–zeolite and support–zeolite phases.

The new generation of hydrocracking, hydrotreatment, catalytic cracking, and isomerization catalysts from leading companies (UOP, Engelhard, Grace, Union Carbide (Dow Chemical Co.), AKZO NOBEL, and Criterion) include the macroporous ultrastable zeolites Y (USY) [5–8]. The employment of these zeolites increases the yields of desired products and ensures the high and steady-state performance and selectivity of the catalyst, low carburization, a longer interval between regeneration runs, easy regeneration without activity loss, and the possibility of multiple regeneration.

The high thermal and thermal-steam stability of USY is due to the molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 > 6$ in the framework (which is 3–6 for zeolites Y prepared by direct synthesis) and the low Na_2O content. The high steady-state performance and selectivity of USY-based catalysts as well as their low carburization are due to the change in the acidic properties of the zeolites during the formation of their ultrastable form [9].

According to a theoretical model, when aluminum leaves the structure, the number of acid sites decreases but the number of isolated aluminum atoms increases and the strength of the acid sites also increases [10]. Depending on the dealumination mode, the aluminum that has left the lattice can appear as extra-framework aluminum compounds, for example, as compensating hydroxo cations possessing Lewis acidity. Aluminum atoms that contain AlO_4 tetrahedra in their second coordination sphere primarily undergo dealumination. The isolated aluminum atoms are bound to the structure most strongly, and the strongest acid sites form near such atoms. The acidity spectrum changes due to dealumination: the fraction of weak acid sites decreases and the numbers of strong and medium-strength acid sites increase. Furthermore, the strength of the strong acid sites increases.

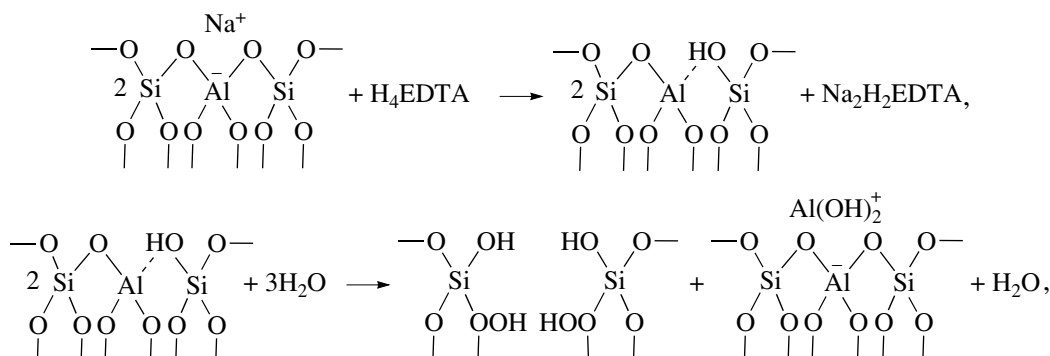
The main dealumination methods include treatment with inorganic acids [11, 12] and complexing agents (ethylenediaminetetraacetic acid (EDTA) and acetylacetone) [13, 14], heating under hydrothermal conditions [15–17], and dealumination with silicon-containing compounds (SiCl_4 [18, 19] and $(\text{NH}_4)_2\text{SiF}_6$ [20–23]). It is believed that two consecutive reactions occur during dealumination with dilute solutions of inorganic acids: decationation yielding a Brønsted acid site and aluminum outgo from the structure at the Brønsted acid site to form a structural defect called a “hydroxyl nest”:

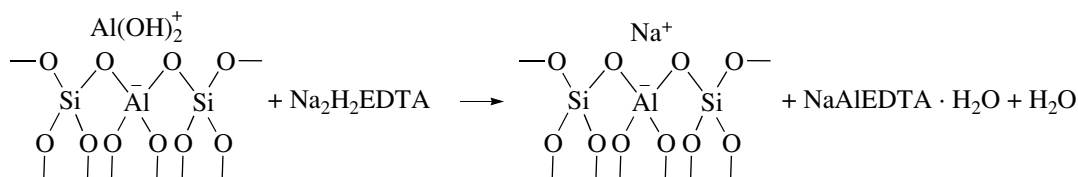


When the degree of dealumination and the degree of defectiveness are small, the extra-framework aluminum compounds do not reside in the zeolite because they are likely to pass into the solution.

When dealumination is carried out with EDTA, decationation also occurs, followed by the hydrolysis of aluminum and its elimination from the framework.

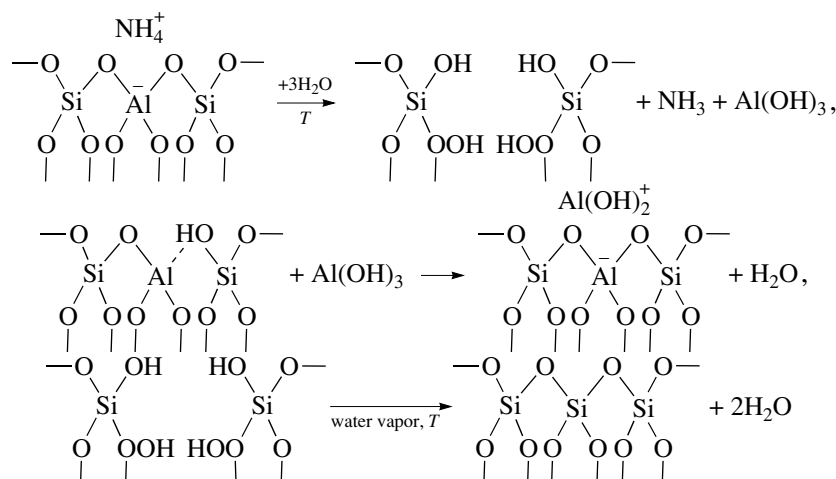
The aluminum lost from the structure appears as hydroxo cations compensating for the framework charge. When dealumination is carried out with EDTA, equivalent decationation and dealumination occur. In the dealumination with other acids, the degree of decationation is higher than the degree of dealumination.



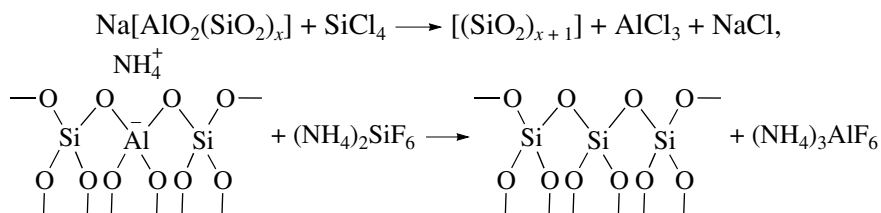


Upon thermal-vapor dealumination, aluminum leaves the lattice because of the hydrolysis of structural Al with water vapor. Extra-framework aluminum can

appear as hydroxo cations and/or polymeric neutral clusters. The aluminum vacancies can be "cured" by silicon migrating from the destructured regions:



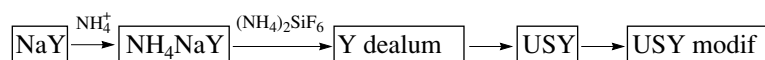
When the dealumination of zeolites is carried out with silicon-containing agents, Si atoms substitute for part of the Al atoms:



When dealumination is performed with SiCl_4 vapor or a $(\text{NH}_4)_2\text{SiF}_6$ solution, a higher degree of dealumination can be achieved without destroying the framework.

It is suggested to prepare USY zeolites with a con-

trollable degree of dealumination by treating deca- tionated zeolite Y with $(\text{NH}_4)_2\text{SiF}_6$ solutions combined with stepwise thermal treatments and cation exchanges without destroying the crystal structure [24–30]:

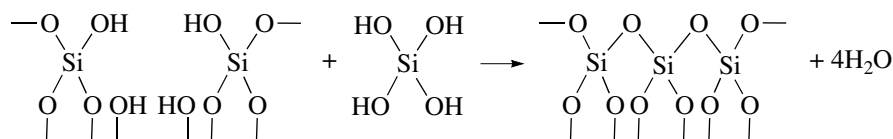
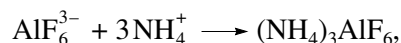
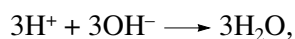
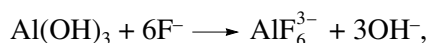
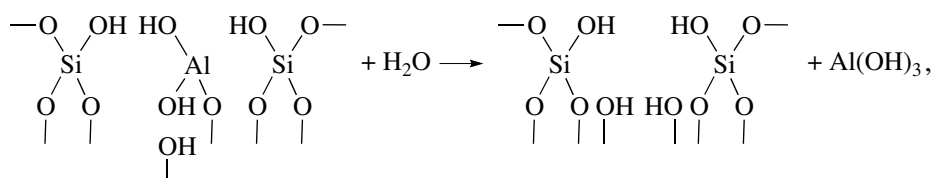
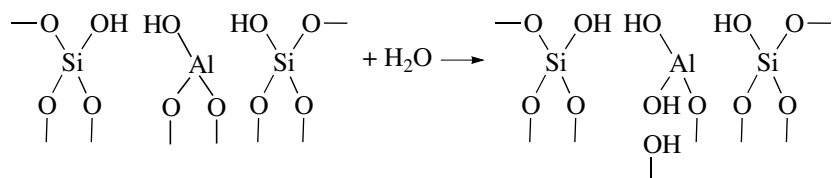
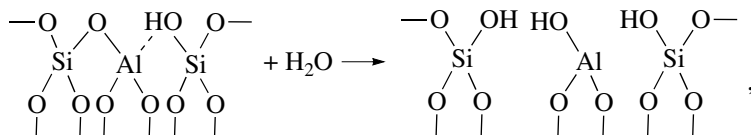
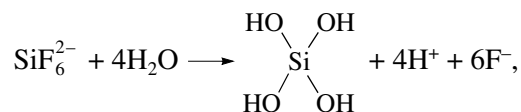
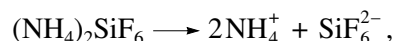


The effect of $(\text{NH}_4)_2\text{SiF}_6$ treatment conditions (the way in which the reagents are introduced, the concentrations of solutions, treatment time, the pH of the medium) on the properties of the dealumination products, the degrees of dealumination and deca- tionation, the phase composition, and the electron state of elements has been studied. A refined mechanism based on XRD, XPS, and IR spectroscopic data has been suggested for zeolite dealumination with an $(\text{NH}_4)_2\text{SiF}_6$ solution. $(\text{NH}_4)_2\text{SiF}_6$ dissociates in aqueous solution to

NH_4^+ and SiF_6^{2-} , and the latter is hydrolyzed in steps to form the free proton H^+ , the fluoride anion F^- , and the monomolecular silicon hydroxide Si(OH)_4 . According to previous views, a structural aluminum atom is bound by six free F^- ions and is then extracted as the AlF_6^{3-} complex into solution [31]. It was found that after NH_4^+ was exchanged for H^+ , tetrahedrally coordinated structural Al comes out because of the gradual hydrolytic cleavage of the bridging bond Si-O-Al , which yields

Si–OH and Al–OH nonacidic terminal groups. After all aluminum–framework bonds are ruptured, aluminum escapes to the solution as $\text{Al}(\text{OH})_3$ and forms the stable

complex $(\text{NH}_4)_3\text{AlF}_6$ through interaction with fluorine anions and ammonium cations. The monomer $\text{Si}(\text{OH})_4$ can occupy the resulting vacancy to form new Si–O–Si bonds:



A more complete dealumination yielding extra-framework aluminum compounds occurs at subsequent thermal treatment stages. The resulting ultrastable zeolite Y, with a low Na_2O content, can be further modified by various methods in order to control the activity and selectivity of the catalyst.

Ultrastable zeolites are used worldwide as components of hydrocracking catalysts. These catalysts are bifunctional systems manifesting both cleaving and hydrogenating activities. The acidic component performs the cleavage function, whereas Group VI and VIII metals fulfill the hydrogenating function. The presence of USY allows crude oil rich in tarry asphalt-

enes and metals to be processed without deactivating the catalyst to any considerable extent. To study the effect of various methods of USY modification on the activity and selectivity of catalysts, we studied the hydrocracking of vacuum gasoil. Figure 1 shows the effect of various methods of USY modification (ion exchange for rare-earth cations (RE^{3+}) and treatment with a dilute solution of HCl or NaOH) on the catalytic activity in hydrocracking of vacuum gasoil (with a final boiling point (FBP) of 520°C) at 10 MPa and $380\text{--}440^\circ\text{C}$ [32, 33]. The results of testing the hydrocracking catalyst HYC-642 (Technip) are shown for comparison.

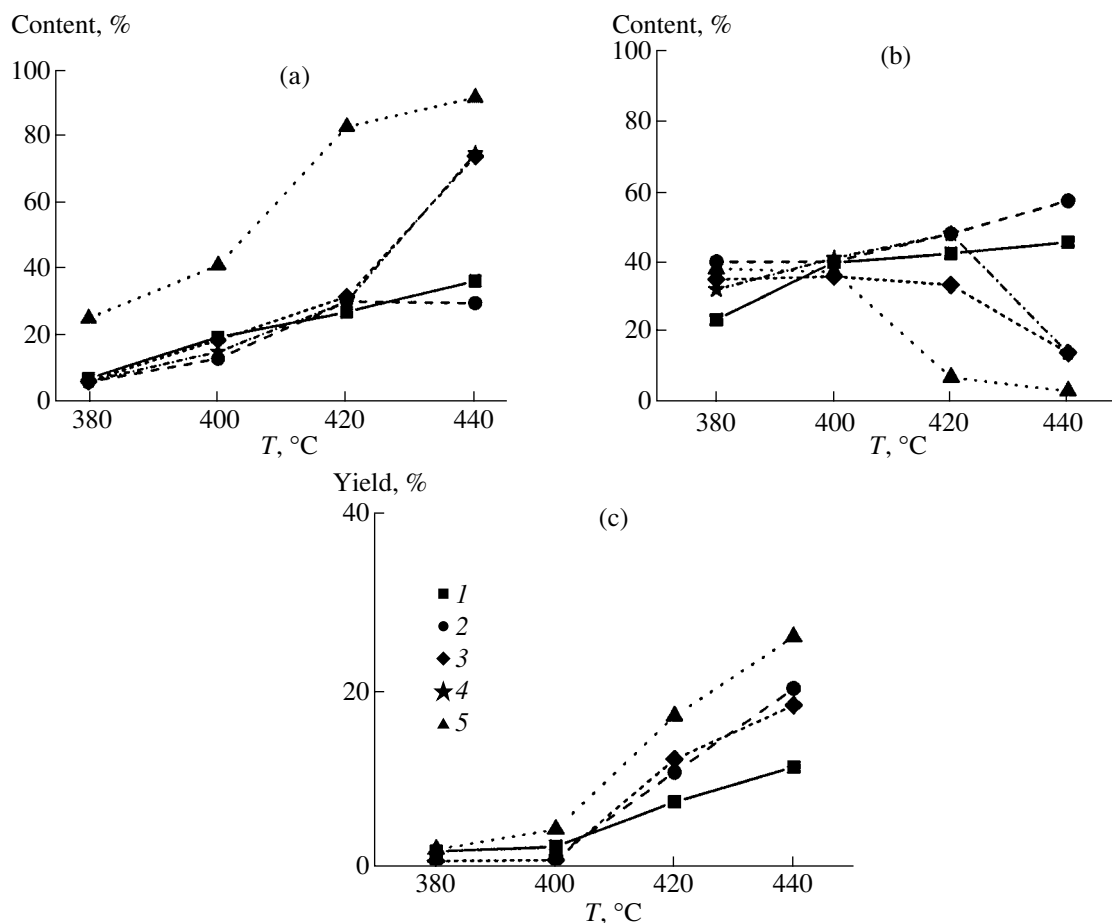


Fig. 1. (a) gasoline BP = 180°C and (b) diesel fraction (180–350°C) contents of the liquid distillate and (c) gas yield as a function of temperature in the hydrocracking of vacuum gasoil with FBP = 520°C over Ni–Mo/USY catalysts: (1) USY, (2) USY_{NaOH}, (3) USY_{HCl}, (4) USY_{REM}, and (5) Technip. $P = 10$ MPa, $v = 1$ h⁻¹, and H₂/raw material = 1000 : 1. BP = bubble point, and FBP = final boiling point.

For all catalysts, the proportion of the gasoline fraction in the hydrogenation product increases from 6–7% at 380°C to 27–30% at 420°C. The method of zeolite modification has no noticeable effect on the proportion of the gasoline fraction in this temperature range, which is typical of hydrocracking. Substantially different behaviors of the catalysts are observed starting at 440°C, when the contribution from cracking increases considerably. For instance, a much higher gasoline content (up to ~75%) is observed for USY specimens modified with dilute solutions of HCl and REM³⁺ because of the cracking of the diesel fraction as a secondary reaction. A slightly increased gasoline content of 30–36% is observed with unmodified USY and zeolite treated with an NaOH solution followed by decationation. For HYC-642 (Technip), the gasoline content of the hydrogenation product increases with increasing temperature and is significantly higher than the gasoline content attainable with any USY specimen

throughout the temperature range examined. This fact can be explained by HYC-642 having a higher cracking ability due to the enhanced acidity of its zeolite component.

A greater effect of zeolite modification is observed for the selectivity of the diesel fraction formation. At 380–400°C, the proportion of the diesel fraction slightly changes in the presence of USY modified with NaOH, HCl, and REM³⁺. The percentage of the diesel fraction at 380°C is lower for unmodified USY than for the other specimens. For unmodified USY and NaOH-modified zeolite, the proportion of the diesel fraction increases as the temperature is raised up to 440°C. Therefore, the hydrocarbons of the diesel fraction do not undergo secondary cracking. Over the specimens modified with HCl and RE³⁺, the percentage of the diesel fraction drops at 400°C due to an enhancement of the cracking activity. An enhancement of cracking on HYC-642 (Technip) is observed at >400°C. With an

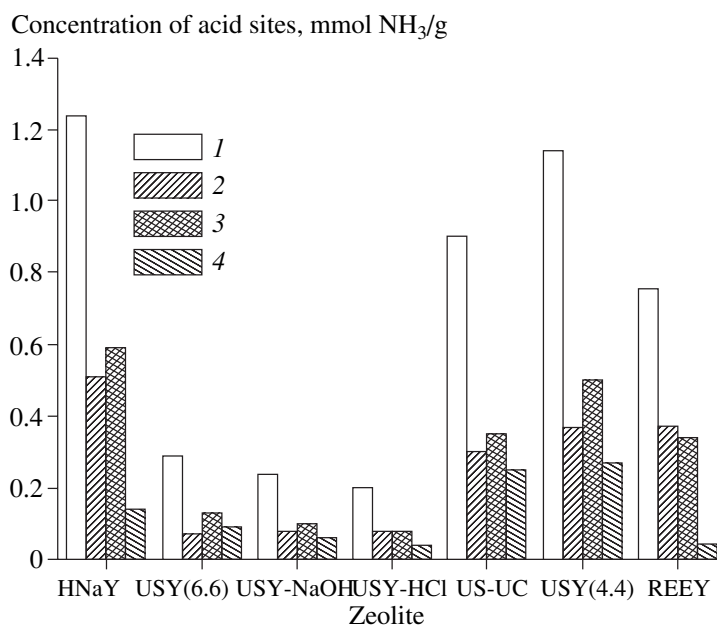


Fig. 2. Strength distribution of acid sites in ultrastable zeolites with various Si/Al ratios (according to chemical analysis), in catalysts modified with solutions of NaOH, HCl, and RE^{3+} , and in ultrastable zeolite from Union Carbide: (1) total acidity, (2) weak sites ($100^\circ\text{C} < T < 200^\circ\text{C}$), (3) medium-strength sites ($200^\circ\text{C} < T < 300^\circ\text{C}$), and (4) strong sites ($T > 300^\circ\text{C}$).

increase in temperature, the gas yield increases for all of the catalysts, especially for Technip's specimen.

Furthermore, catalysts based on ultrastable zeolites exhibit a high desulfurizing activity: only traces of sulfur are found in gasoline and at most 0.05% sulfur in the diesel fraction.

The change in catalytic activity caused by the modification of the ultrastable zeolites is due to the change in the nature and strength of the acid sites as well as to the increase in the accessibility of the active sites to reactant molecules. Upon the treatment of USY with a dilute HCl or NaOH solution followed by decationation, the extra-framework aluminum compounds formed during the preparation of the ultrastable form of zeolite Y are removed from the zeolite cavities and, as a consequence, the accessibility of the active sites to reactant molecules increases. It is also possible that the

imperfection of the structure decreases upon the treatment of the zeolite with an alkaline solution such as that used in the direct synthesis of zeolites because of the reduction of the T–O–T bridges (T = Si, Al) formed by terminal groups T–OH in the defect regions of the structure.

Modification changes the acidic properties of USY zeolites [24]. Figure 2 shows diagrams of the strength distribution of acid sites in ultrastable zeolites.¹

The acidity data obtained are highly consistent with the present view that dealumination causes a decrease in the total number of acid sites and a modification of the acidity spectrum. Once the degree of dealumination at which all aluminum atoms are isolated is reached, further strengthening of the acid sites caused by the decreasing proportion of structural Al cannot compensate for the decrease in the total acidity. The treatment of USY with a dilute solution of HCl or NaOH changes the acidity spectrum of USY only slightly. In the unmodified USY and in the NaOH-treated and decationated zeolites, the number of medium-strength acid sites is somewhat larger than the number of weak and strong acid sites. In USY modified with a dilute HCl solution and RE^{3+} cations, the proportion of weak acid sites is larger than or equal to the proportion of medium-strength acid sites. Furthermore, the modification of zeolites with RE^{3+} cations, which are Lewis acid sites, changes the nature of the acid sites.

Table 4. Catalytic properties of the phosphorus- and boron-modified ultrastable zeolites 0.5% Pt/USY in *n*-hexane isomerization ($P = 0.1$ MPa, $T = 350^\circ\text{C}$)

Specimen	Content P, %	Conversion, %	<i>iso</i> -C ₆ selectivity, %
USY in.	–	2.8	94.4
USY-P	0.2	54.7	98.0
USY-P	1.2	41.8	94.8
USY-B/P	0.8	46.8	93.8
USY-B/P	7.9	42.4	92.5

¹ The acidic properties of ultrastable zeolites were measured using the NH_3 TPD technique at the Laboratory of Kinetics and Catalysis, Department of Physical Chemistry, Faculty of Chemistry, Moscow State University.

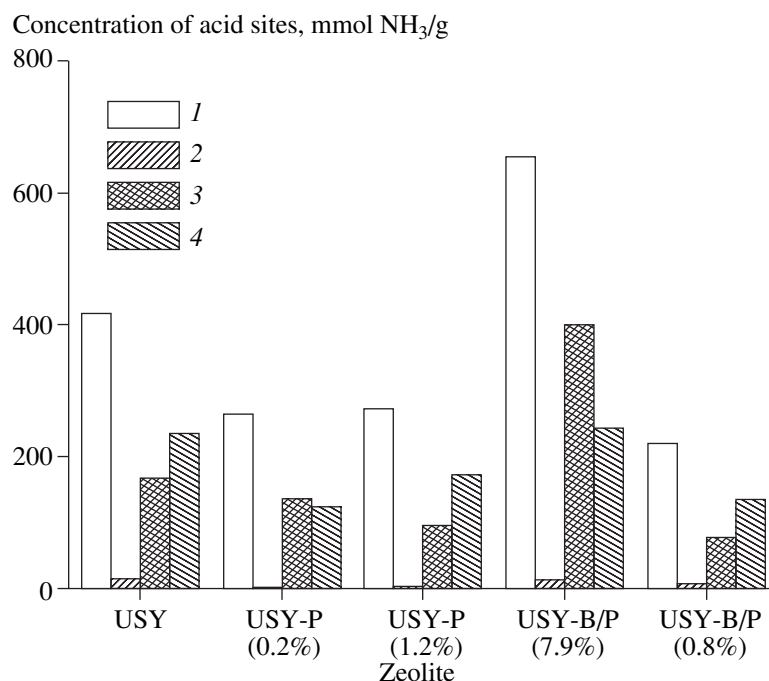
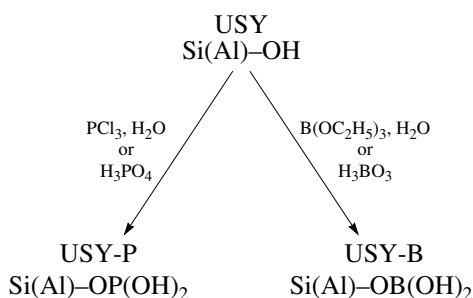


Fig. 3. Strength distribution of acid sites in ultrastable zeolites modified with phosphorus and boron. Phosphorus content is given in parenthesis: (1) total acidity, (2) weak sites, (3) medium-strength sites ($95 < E < 130$ kJ/mol), and (4) strong sites ($E > 130$ kJ/mol).

Therefore, the directed modification of USY zeolites with a dilute solution of HCl or NaOH and the introduction of rare-earth cations change the acidic properties of the zeolites and make it possible to efficiently control hydrocracking in order to obtain a product dominated by the gasoline and/or diesel fraction. Presumably, the medium-strength acid sites are to a greater extent responsible for the formation of the diesel fraction.

The catalytic properties of the modified zeolites were also studied in *n*-hexane isomerization. It was demonstrated that the modification of the ultrastable zeolites with phosphorus and boron enhances the isomerization activity of USY-based Pt catalysts [34–37] (Table 4). The modifying agents were PCl_3 and $\text{B}(\text{OC}_2\text{H}_5)_3$ vapors, which were then hydrolyzed, and H_3PO_4 and H_3BO_3 solutions. The amount of a modifying agent in the zeolite was varied by varying the number of treatment steps, and USY-B/P zeolites were produced by performing successive treatments with P and B.



The enhancement of isomerization activity of the phosphorus- and boron-modified USY zeolites is related to the change in their acidity (the strength and nature of the acid sites). The modification of USY diminishes the total number of acid sites and changes the strength distribution of acid sites (Fig. 3). The proportion of medium-strength acid sites and the isomerization activity increase due to the fact that the modifying agent preferentially blocks strong acid sites, on which hydrocarbon cracking primarily occurs.

The modification of ultrastable zeolites with small amounts of a modifying agent allows one to obtain active and high-selective catalysts for *n*-hexane isomerization.

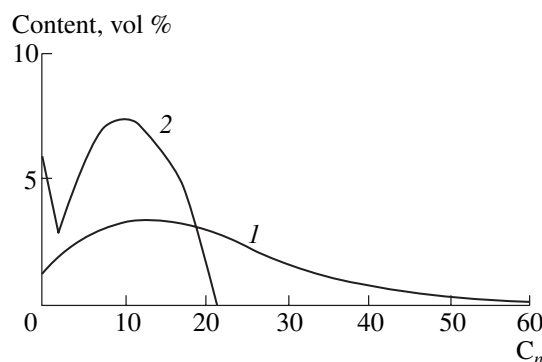


Fig. 4. Molecular-weight distribution of the hydrocarbon products of the Fischer-Tropsch synthesis: (1) Fe-fused catalyst and (2) zeolite-containing system.

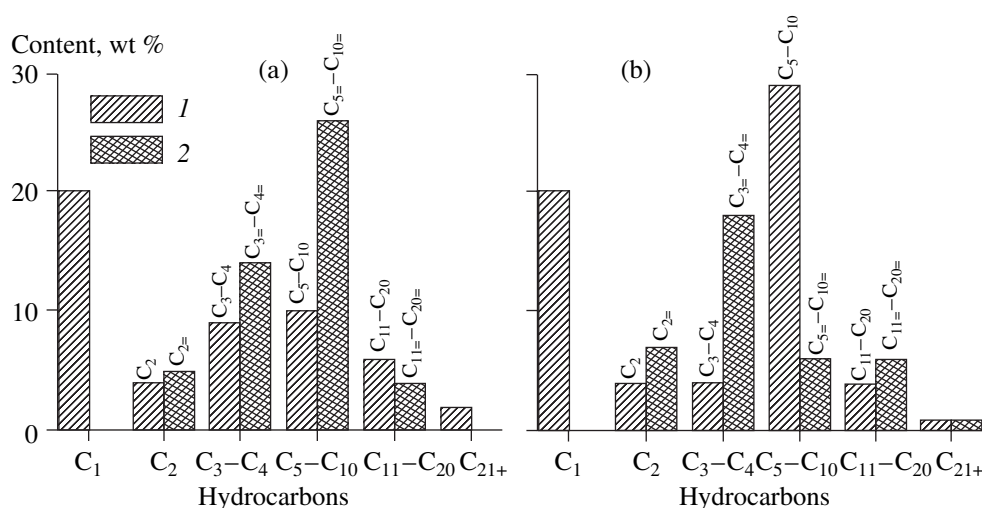


Fig. 5. Fractional composition of hydrocarbons (excluding methane) in the products of Fischer–Tropsch syntheses over (a) fused iron catalyst with a hydrocarbon efficiency of 80–100 kg m^{−3} h^{−1} and (b) a combination of the fused iron catalyst and a zeolite-containing catalyst with a hydrocarbon efficiency of 150–180 kg m^{−3} h^{−1}: (1) paraffins and (2) olefins.

An alternative to the production of motor fuel from oil is the two-stage methane conversion to synthesis gas followed by the formation of hydrocarbons via the CO + H₂ reaction (Fischer–Tropsch synthesis). The fuel thus obtained is environmentally friendly because it contains no sulfur compounds or aromatic hydrocarbons. Irrespective of the reaction conditions, the Fischer–Tropsch synthesis always yields a wide variety of products: olefins, paraffins, and oxygenated products (alcohols, aldehydes, acids, and ketones). The product-composition depends on reaction conditions (temperature, gas composition, and pressure) and on the nature of the catalyst and promoters. Hydrocarbons are formed by chain propagation through the successive addition of single-carbon species. The probability of chain propagation is determined by the total distribution of carbon atoms. Therefore, theoretical limitations are imposed on the yields of product fractions in the Fischer–Tropsch process [38–40]: the maximal yield of hydrocarbons of the gasoline fraction is ~45 wt %, that of the diesel fraction is about 25 wt %, and the yield of ethane and ethylene is at most 30 wt %. To increase the yield of the gasoline and diesel fractions, it is necessary to perform additional steps after the Fischer–Tropsch process. For instance, high-quality gasoline and diesel fuel can be produced by oligomerization of C₃–C₄ olefins. High-quality, sulfur-free, pure gasoline and diesel fuel (cetane number, ~65) can be obtained by hydrocracking of high-molecular-weight hydrocarbons (waxes).

The Fischer–Tropsch synthesis is carried out over an Fe- or Co-containing catalyst. As compared to the cobalt catalysts, the Fe-based catalysts typically afford lower molecular weight hydrocarbons (the probability of chain propagation is $\alpha = 0.6$ –0.8) and a higher percentage of olefins, show a slightly higher selectivity toward branched hydrocarbons (5–10 versus 2%), and

are characterized by a higher upper limit of the working temperature (up to 300–350°C). The cobalt-based catalysts are characterized by enhanced selectivity to C₂₀₊ high-molecular hydrocarbons (the probability of chain propagation is $\alpha = 0.8$ –0.9). The range of working temperatures for the Co catalysts is 200–240°C, because excess CH₄ forms at higher temperatures.

Figure 4 presents the molecular-weight distribution of the products of the Fischer–Tropsch synthesis over conventional fused iron catalysts and over zeolite-containing binary catalytic systems. A wide variety of hydrocarbons (C₁–C₆₀) is formed over the fused Fe catalyst and the corresponding curve has a fuzzy maximum extending up to C₃₀. The molecular-weight distribution curve for a combination of the conventional Fe catalyst and the zeolite-containing catalyst has peaks in the regions of methane and C₅–C₁₅ hydrocarbons, while paraffins with more than C₂₂–C₂₅ carbon atoms are absent from the synthesis product. This is due to the fact that the high-molecular-weight linear paraffins that form over the conventional iron catalyst undergo cracking over the zeolite component of the catalyst.

Figure 5 shows the fractional composition of the products of Fischer–Tropsch syntheses over the fused iron catalyst and over the two-component mixture of the fused iron catalyst and TsVM/Al₂O₃. The synthesis gas was nitrogen-diluted and had the following composition (vol %): N₂, 50; CO, 18–20; and H₂, 30–32. The syntheses were carried out in a fixed-bed flow reactor at a pressure of 3 MPa, a temperature of 270–310°C, and a feed VHSV of 2800–2900 h^{−1}. The CO conversion was at least 90%.² The presence of nitrogen in the syn-gas is explained by the fact that, when natural gas is

² These experiments were performed at the Bashkirov Laboratory of Catalytic Synthesis, Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences.

Table 5. Performance of binary catalytic systems in the Fischer–Tropsch synthesis

No.	Catalytic system	Operation time, h	T, °C	x _{CO} , %	Average volume of liquid products per day, ml l ⁻¹ Cat h ⁻¹		Average hydrocarbon yield per unit volume of the catalyst, g (l Cat) ⁻¹ h ⁻¹		Hydrocarbon yield per cubic meter of CO + H ₂ , g/m ³	Selectivity of CO conversion, %			Fractional composition, wt %				
					water	oil	total	liquid		to hydrocarbons	in CO ₂	to oxygen-containing compounds	CH ₄	C ₂ –C ₄	C ₅ –C ₁₀	C ₁₁ –C ₂₀	C ₂₁ +
1	Fe _m	48	290	75.9	65.0	55.6	271.4	126.7	116.5	52.2	45.8	1.9	20.3	33.1	31.8	12.5	2.4
2	Fe _m + γ-Al ₂ O ₃	47	275	96.5	92.2	78.9	147.1	72.7	116.1	55.4	42.8	1.8	17.4	33.2	32.9	12.9	3.5
3	Fe _m + KR-108*	48	270	96.1	96.7	70.6	152.5	68.9	113.8	52.9	45.2	1.9	19.3	35.5	31.3	10.9	3.0
4	Fe _m + OB-2**	45	275	96.0	100	77.8	174.5	83.9	123.4	56.5	42.4	1.1	18.6	33.3	34.7	10.8	2.7
5	Fe _m + TsVM/γ-Al ₂ O ₃	48	280	98.4	110.6	88.3	196.2	97.9	139.9	59.5	39.8	0.7	18.3	31.8	37.2	10.9	1.8

Note: $P = 3$ MPa; syngas composition: 18 vol % CO, 32 vol % H₂, and 50 vol % N₂; $v_{\text{gas}} = 2800$ l (g Cat)⁻¹ h⁻¹.

*KP-108 (commercial reforming catalyst): 0.36% Pt; 0.36% Re/Al₂O₃.

**OB-2 (commercial zeolite-containing catalyst for treatment of olefin-containing exhaust gases), based on TsVM/A₂O₃.

partially oxidized with air rather than pure oxygen, the resulting syngas contains ~50–60 vol % nitrogen. For example, in the Syntroleum technology [41, 42], methane undergoes reforming at low pressures in reactors purged with air and, therefore, an oxygen plant is unnecessary. CO conversion per pass in this technology should be high, because recycling the unreacted gas is not economically efficient.

A significant amount of olefins is formed over the conventional fused iron catalyst. When the Fischer–Tropsch synthesis is performed over a mixture of the fused iron catalyst and the zeolite-containing catalyst, the olefin composition of the hydrocarbon fractions changes: the proportion of C₂–C₄ olefins much increases due to the secondary cracking of high-molecular-weight hydrocarbons over the zeolite-containing component of the catalyst. At a total CO conversion of ~90% and a CO-to-CO₂ conversion of ~40%, the efficiency of the combination of the fused iron catalyst and the zeolite-containing catalyst is 180–200 g (l Cat)⁻¹ h⁻¹. The reaction product has the following composition (wt %): CH₄, ~20; C₂, 11; C₃–C₄, 24; gasoline fraction C₅–C₁₀, 36; diesel fraction C₁₁–C₂₀, 8; high-molecular-weight hydrocarbons C₂₁+, 1. The catalysts were tested for the steady-state activity over ~1500 h.

Table 5 presents the data obtained for various Fe catalysts. In the presence of a binary catalyst (samples 2–5), the CO conversion reaches 96–98%, while it is ~76% over the fused catalyst. The yield of hydrocarbons with the zeolite-containing catalysts (samples 4, 5) is substantially higher (up to ~140 g per cubic meter of syngas)

than the hydrocarbon yields attainable with the fused catalyst and the binary alumina systems (samples 1–3). With the zeolite-containing catalysts, the percentage of gasoline hydrocarbons, C₅–C₁₀, is also higher. This effect is likely to be due to the cracking of high-molecular-weight (C₂₀+) hydrocarbons.

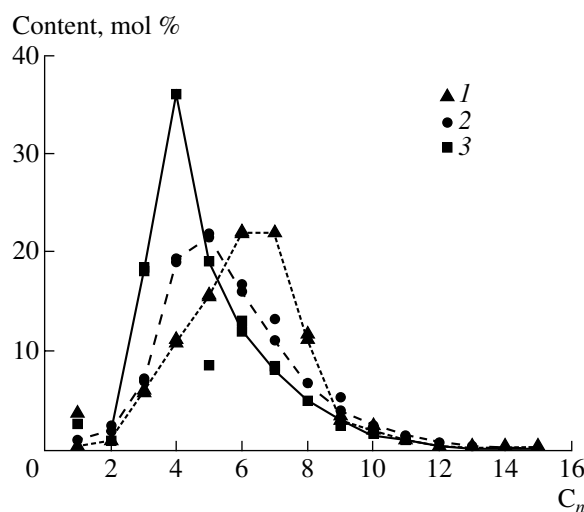


Fig. 6. Molecular-weight distribution of the products of hexadecane cracking over the catalyst TsVM/Al₂O₃ under the conditions of Fischer–Tropsch synthesis: $P = 3$ MPa; $T = (1)$ 230, (2) 250, and (3) 265°C; $v_{\text{gas}} = 3600$ – 3800 h⁻¹; $v_{\text{C}_{16}\text{H}_{34}} = 0.08$ – 0.10 h⁻¹, $v_{\text{H}_2\text{O}} = 0.25$ – 0.30 h⁻¹. Gas composition, vol %: N₂, 50; CO, 16; H₂, 33.

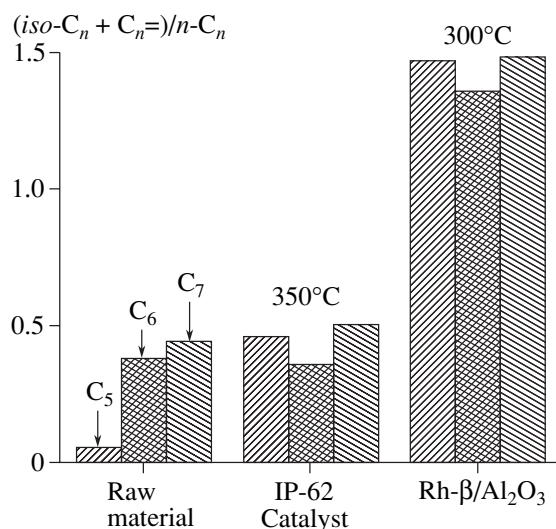


Fig. 7. Isomerization activity of the IP-62 and Rh/β/Al₂O₃ catalysts in the hydroisomerization of a product fraction of the Fischer–Tropsch synthesis at $P_{H_2} = 3$ MPa and $T = 300$ and 350°C .

The Fischer–Tropsch reaction is exothermic, and the average heat evolved per carbon atom of the “structural unit” $-\text{CH}_2-$ is ~ 35 kcal [38]. The main problem in reactor engineering is heat removal. The increase in catalyst-bed temperature should be minimized. The undesirable increase in temperature during the Fischer–Tropsch reaction reduces the selectivity of the process because of the enhanced methane formation and accelerated catalyst deactivation. A zeolite-containing component added to the fused iron catalyst stabilizes the catalyst performance likely by reducing or eliminating the catalyst overheating in the reaction zone. This is due to the fact that the heat evolved during the Fischer–Tropsch synthesis is consumed by the cracking of high-molecular-weight hydrocarbons over the zeolite-containing component of the binary catalytic system.

The secondary cracking on the acid sites of zeolites under Fischer–Tropsch synthesis conditions has repeatedly been debated [43, 44]. As shown in [45], the cracking of hexadecane occurs under these conditions (Fig. 6). The cracking activity of zeolite and the proportion of secondary cracking reactions increase with increasing temperature. The main cracking products are C_6 – C_8 hydrocarbons at 230°C and C_3 and C_4 hydrocarbons at 265°C .

The gasoline fraction of the Fischer–Tropsch synthesis product has an insufficiently high octane number and contains considerable amounts of olefins. To produce commercial fuels, it is necessary to carry out the hydrorefining of the Fischer–Tropsch products, including the isomerization of n -paraffins and the hydrogenation of unsaturated hydrocarbons. Preliminary experiments showed that the isomerization of the gasoline hydrocarbons C_5 – C_{10} occurs over zeolite-containing

catalysts (Fig. 7), whereas the commercial catalyst IP-62 mainly performs pentane isomerization, and the zeolite-containing catalyst is more active than IP-62. At present, the Topchiev Institute of Petrochemical Synthesis is performing research aimed at the development of catalysts for the hydrodesulfurization of fuel fractions.

ACKNOWLEDGMENTS

The authors are grateful to Dr. A.A. Kubasov, Dr. L.E. Kitaev, and V.V. Yushchenko (Laboratory of Kinetics and Catalysis, Department of Physical Chemistry, Faculty of Chemistry, Moscow State University) for the NH_3 TPD investigation of the acidic properties of zeolites; to Dr. O.P. Tkachenko (Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences) and E.A. Skryleva (Moscow State Institute of Steel and Alloys) for the XPS study of the composition and state of elements in zeolites; to Dr. Z.M. Bukina (Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences) for the investigation of the catalytic properties of ultrastable zeolites in n -hexane isomerization; and to Dr. E.I. Bogolepova, Dr. A.N. Shuikin, Dr. V.I. Kurkin, and E.V. Marchevskaya (Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences) for the investigation of the catalytic properties of the binary catalytic systems in Fischer–Tropsch syntheses.

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