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Development and study of zeolite catalytic systems for the transformation of lower hydrocarbons into valuable chemicals*

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The results of studies aimed at the development of highly efficient catalysts based on zeolites of the pentasil family for synthesis of aliphatic and aromatic hydrocarbons from C_2—C_5 olefins and paraffins are summarized.

Key words: zeolites, pentasil, catalysts; C_2—C_5 olefins, C_2—C_5 paraffins, aromatic hydrocarbons, aliphatic hydrocarbons.

Introduction

The problem of efficient use of gaseous hydrocarbon raw materials still remains topical, despite the fact that, in recent years, oil and gas production in Russia has diminished. Natural and casing-head gas and exhaust gases from oil refinement plants can serve as sources of gaseous hydrocarbons. Natural gas consists of more than 90% methane; however, natural gas from some deposits contains substantial quantities of ethane and C_3—C_5 hydrocarbons. For the current level of gas production, the potential resources of ethane in natural gas are estimated to be 15—16 million tons annually.[1,2] The proportion of C_3—C_5 hydrocarbons is approximately the same. The petroleum casing-head gases contain (on the average) 35% ethane, 7% propane, 23% butanes, and 35% pentanes. The refinery exhaust gases contain up to 40% C_3—C_4 olefins.

According to forecasts, based on the projected more extensive oil processing (and, hence, intensification of destructive technological processes such as catalytic cracking, *etc.*), the resources of exhaust gases are going to continuously increase.[3—5] In world practice, the main routes for the use of lower hydrocarbons in petrochemistry and petroleum refinement, in addition to the large-scale processes of ethylene and propylene polymerization, include pyrolysis of ethane and propane, dehydrogenation of C_3—C_4 paraffins, partial oxidation of C_2—C_4 olefins and paraffins, alkylation of aromatic hydrocarbons with olefins, and also manufacture of synthesis gas (from methane) and preparation of various chemical compounds from it. However, the proportion of light hydrocarbons consumed in petrochemical and other syntheses does not exceed 30% of the overall quantity of gaseous hydrocarbon raw materials produced.[1] The qualified use of these important energy-storing materials is still unsatisfactory. The transportation and primary processing of light hydrocarbons is accompanied by substantial losses; in addition, in some cases, these compounds are used inefficiently (in particular, as technological and household fuel) or directly destroyed by flaming. Consequently, not only is the valuable chemical raw material irrevocably lost but also the environmental conditions in the regions of oil and gas production and processing are constantly degraded.

Optimum solution of the above problems is associated with comprehensive processing of all the hydrocarbon components of natural, casing-head, and refinery gases and the gas condensate based on low-waste and, hence, environmentally clean, industrial technologies for the manufacture of valuable chemicals from C_2—C_5 hydrocarbons. The development of these highly efficient petrochemical processes requires the use of catalysts; therefore, progress in this field is mostly determined by progress in studies dealing with catalysis by zeolites. Zeolites, which are crystalline aluminosilicates possessing specific acidic and molecular-sieve properties, proved to be much more active and selective catalysts for a number of important chemical reactions than the catalytic systems used for this purpose until recently (amorphous metal oxides and supported metal-oxide catalysts).

Zeolites of the pentasil family occupy a special place among crystalline aluminosilicates; they differ from other types of zeolites in the structure and composition of the framework in which silicon predominates. During the past 15 years, the catalytic and physicochemical properties of these unique materials have been studied in a number of scientific centers both in Russia and abroad. In this review, we survey the results of our studies dealing with the development of highly efficient catalysts based on pentasils for the synthesis of aliphatic and

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* Dedicated to the memory of Academician M. E. Vol'pin timed to his 75th birthday.

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aromatic hydrocarbons from C_2—C_5 olefins and paraffins.*

Synthesis and modification of pentasils

The main feature of the synthesis of zeolites of the pentasil family is that hydrothermal crystallization of aluminosilica gel is carried out in an alkaline medium in the presence of various organic compounds (templates.)[6,7] The size and shape of template molecules predetermine the formation of a particular structure in the resulting particles. During the synthesis of pentasils, as the crystals grow, the molecules of organic templates insert themselves in the solid phase and ensure stabilization of the zeolite structure and formation of a system of channels consisting of ten-membered rings and intersecting at right angles.[8,9] The porous structure of the ZSM-5 pentasil incorporates both straight (0.54×0.56 nm) channels with elliptic cross-sections and sinusoida-shaped (0.51×0.55 nm) round channels. The system of pores in the ZSM-11 pentasil consists of straight channels with elliptic cross-sections.

At the early stage of studies, quaternary ammonium salts, mostly bromides, have been used as templates in the synthesis of pentasils.[9—11] The synthesis of ZSM-5 occurs in the presence of tetrapropylammonium bromide, while ZSM-11 crystallizes in the presence of tetrabutylammonium bromide.[6,11] By now, the main regularities of hydrothermal crystallization of pentasils in the presence of these templates have been studied in detail, and the factors that influence the phase purity of the resulting crystalline aluminosilicates and the structure of their channels have been elucidated.[7—12] The subsequent development of the methods of synthesis of pentasils has substantially extended the range of organic templates used; in particular, the zeolites have been crystallized in the presence of alcohols,[13] amino alcohols,[14] ethers,[15] and diamines.[16,17] All the templates used to prepare pentasils can be divided conventionally into three groups: organic cations, organic anions, and neutral molecules (Table 1).

Table 1. Organic templates used for hydrothermal synthesis of zeolites of the pentasil family

Type of organic compound	Template	Reference
Cations	Tetraalkylammonium, tetraalkylphosphonium	7—10
Anions	Alkylbenzenesulfonate, polymeric anions	16
Molecules	Alcohols	13
	Amino alcohols	14
	Ethers	15
	Diamines	16, 17

The procedure of hydrothermal synthesis has also been somewhat changed. The fast crystallization method[18] and the vapor-phase synthesis[19] have been proposed. The main specific feature of fast crystallization is that an amorphous gel and a solvent are prepared separately using centrifugation. In the case of vapor-phase synthesis, the amorphous gel prepared beforehand is treated with the vapor of an aqueous solution of an organic compound. Yet another promising version of the synthesis, which is vigorously developed now, is preparation of molecular sieves, in whose framework the Al atoms have been replaced partially or entirely by Fe, Ga, Ge, B, Cr, Ti, Zr, or V atoms.[20,21] However, it should be noted that the occurrence of isomorphous replacement has been confirmed reliably only for Fe, B, and Ga silicates with the pentasil structure.

The methods for the synthesis of pentasils involving no organic templates (crystallization in an alkaline medium)[22] and the preparation of materials with high phase purities in a weakly alkaline medium in the presence of organic templates[17,23,24] appear to be the most promising from the practical viewpoint. The pentasils produced in Russia without the use of organic compounds have been called zeolites of the ZVM series.[22] The main advantage of these materials is that the technology of their production is markedly cheaper, because expensive organic templates are no longer needed. The pentasils obtained by hydrothermal crystallization in a weakly alkaline medium (the ZVN series)[17,24] possess another significant advantage: using them as catalysts does not require removal of the Na^+ ions, because the content of Na_2O in the synthesized material does not exceed 0.1—0.2% (w/w).

The procedure for the preparation of the ZVN pentasils served as the basis for the development of a method for the preparation of metal-containing zeolites, in particular, galloaluminosilicates with the pentasil structure.[24,25] The use of this method makes it possible to exclude some stages from the scheme of the synthesis of the catalytically active material, namely, decationization of the zeolite, impregnation (or ion exchange), and subsequent washing of the catalyst. Thus, the manufacture of the catalysts becomes simpler, the amount of harmful sewage markedly decreases, and the possibility of developing a one-stage low-waste cycle for the production of metal-containing pentasils arises.

In addition to synthesis in a weakly alkaline medium, some other procedures have also been used and improved to prepare metal-containing pentasils, namely, impregnation of zeolites with aqueous solutions of the corresponding salts under conditions modeling ion exchange, hydrothermal synthesis in strongly alkaline media in the presence of iron and gallium salts to give ferrosilicates, gallosilicates, and galloaluminosilicates,

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and also mechanical mixing of the oxides (ZnO or Ga_2O_3) with the zeolite matrix. In addition, Ga-containing pentasils have been obtained by treatment of decationized pentasils with a solution of sodium gallate (gallation); Pt-containing pentasils have been prepared by ion exchange of the H-form of a zeolite with an aqueous solution of platinum ammoniate.

The properties of the surface of decationized and metal-containing pentasils

The properties of the pentasil surface have been studied using a set of modern physicochemical methods such as adsorption microcalorimetry, IR spectroscopy, X-ray photoelectron spectroscopy (XPS), ESR, NMR, and electron microscopy.

It is known that acid sites of zeolites play the crucial role in adsorption and catalysis.[26–28] Numerous studies on the chemistry of the surface showed that the acidic function of zeolites is associated with Brønsted (hydroxyl groups) and Lewis (low-coordinated lattice and extralattice ions or exchange cations) acid sites. The ratio of the concentrations of Brønsted (B) and Lewis (L) acid sites depends on the structure of the zeolite, the composition of its framework, thermal stability of the hydroxyl coverage, and the chemical nature of the substances used to modify the zeolite surface.[26,28,29]

The number and strength of the acid sites of pentasils were estimated quantitatively by measuring differential heats of adsorption of ammonia (q_{NH_3}). For comparison, Table 2 presents the results of a study of the acidity of dealuminized mordenite with a similar framework composition. It can be seen that pentasils contain much more L-sites and B-sites with q_{NH_3} = 130±10 kJ mol^{-1}. Unlike pentasil, mordenite was found to contain stronger B-sites (q_{NH_3} = 150±10 kJ mol^{-1}). The acid sites of pentasils possess high thermal stability: even after calcination at 800 °C, approximately 30% of the strong B-sites (q_{NH_3} = 130±10 kJ mol^{-1}) is retained.[30] These results are in agreement with those obtained in studies of the adsorption of pyridine on pentasil samples, calcined at 600—1000 °C, carried out by IR spectroscopy.[31,32]

IR-spectroscopic studies of the adsorption of various molecular probes and analysis of the spectra in the region of the stretching vibrations of the hydroxyl groups in pentasils made it possible to reveal the specific character of their acidic properties and to obtain new data about the distribution of B- and L-sites in their structure. Quantum-chemical calculations[33] of the force constants of the OH bonds in the $H_2Si_2O_7$ and $HSiAlO_7$ clusters have shown that the stretching frequencies of hydroxyl groups in zeolites (ν(OH)) can vary from 3400 to 3800 cm^{-1}. According to numerous experimental data,[26,27,34–36] zeolites of various structural types exhibit three main absorption bands at 3740, 3610, and 3640—3660 cm^{-1}, which correspond to three types of OH groups. The highest-frequency band was assigned to weakly acidic silanol OH groups, while the two other bands were attributed to isolated bridging hydroxyl groups possessing strong Brønsted acidity. In addition to the isolated OH groups, pentasils, unlike other zeolites, contain B-sites that are responsible for a broad absorption band at 3250 cm^{-1} in the IR spectra (see Refs. 36, 37). This band refers to the hydroxyl groups that form a strained intramolecular bond with the neighboring lattice O atom incorporated in an AlO_4 tetrahedron. In the IR spectra of pyridine adsorbed on H-pentasils, B-sites are responsible for a band at 1550 cm^{-1} (pyridinium ion), while L-sites account for a band at 1449 cm^{-1} (coordinately unsaturated Al atoms). The band at 1491 cm^{-1} corresponds to the adsorption of pyridine on both B- and L-sites; however, the major contribution to its intensity is also made by B-sites.[38]

Table 2. Concentrations of Lewis (L) and Brønsted (B)* acid sites in zeolites of the pentasil and mordenite types

Zeolite	Si/Al	L/mmol g^{-1}	B/mmol g^{-1}	
		(q = 170—180)	q = 130±10	q = 150±10
H-Pentasil	30	0.20	0.34	0.0
Dealuminized mordenite	34	0.05	0.23	0.07

* With different q_{NH_3}/kJ mol^{-1}.

The effect of modification with metals on the acidity and the distribution of active sites of pentasils has been studied most extensively for samples of the ZVN series. Metals (Ni, Co, Zn, Cd, Ga) were introduced into these zeolites using the traditional impregnation method or during hydrothermal synthesis in a weakly alkaline medium. The change of the acidic properties of pentasils upon isomorphous replacement of aluminum by gallium (gallosilicates, galloaluminosilicates) has also been studied.

Based on spectral data, we found that modification of pentasils with nickel, cobalt, zinc, cadmium, or gallium results in the formation of new aprotic acid sites, which adsorb pyridine much more efficiently than the L-sites of the initial zeolite, which are Al^{3+} cations. The L-sites containing the modifying atoms are responsible for the bands at 1453—1462 cm^{-1} in the IR spectra of adsorbed pyridine (see Refs. 25, 39—41). The strength of these sites depends on the nature of the modifying cation, and their stability is determined by the possibility of changing the charge of this cation in a reducing medium. If the cation can be reduced (like, for example, Ni^{2+}), then after treatment with hydrogen, the aprotic cationic site disappears. In the case of cations that are difficult to reduce (Co^{2+}, Zn^{2+}), this treatment does not lead to any spectral changes and, evidently, it does not have any effect on the structure and concentration of the L-sites formed. Moreover, in some cases, treatment with hydrogen is necessary for the formation of strong aprotic acid sites. This is true for catalysts prepared by mechanical mixing of a zeolite matrix with ZnO [42] or Ga_2O_3,[39,43] as well as for gallosilicates and galloaluminosilicates with the pentasil structure.

The stages of formation of L-sites in Ga-pentasils have been studied by IR spectroscopy; in addition, the surface properties have been studied by XPS and ESR and NMR spectroscopy. The gallium-containing aprotic sites are responsible for the band at 1462 cm^{-1} in the IR spectra of adsorbed pyridine.[39,44,45] These sites incorporate extralattice Ga atoms; the mechanism of their formation depends on the methods used to prepare and modify the catalysts. When the catalysts are prepared by impregnating the zeolite matrix with a solution of $Ga(NO_3)_3$, the bulk of gallium does not penetrate the channels but is mostly located on the outer surface of the zeolite crystals. Evidently, this is due to the large radius of the solvation shell of Ga^{3+} cations and to the electrostatic hindrance arising when isolated negative charges in the lattice are counterbalanced by polyvalent cations. After keeping these catalysts in a reducing medium, some of the gallium atoms migrate from the outer surface deep in the crystals.[39,45,46]

The active sites of the Ga-pentasils produced as a result of isomorphous replacement are formed by a different mechanism. The main step of this process is the removal of Ga atoms from the framework giving aprotic acid sites in the zeolite channels. The ability of the lattice Ga atoms to migrate was detected for the first time in our study of the physicochemical properties of gallosilicates with the pentasil structure.[47,48] Later, the use of IR spectroscopy made it possible to elucidate the nature of the acid sites in Ga-pentasils of various origin, to estimate their strength, and to identify the L-sites associated with the extralattice gallium.[39,45]

The removal of the Ga atoms from the gallosilicate framework was observed after treatment of the catalysts with hydrogen or water vapor, or after "reaction—regeneration" cycles repeated many times. The galloaluminosilicates that crystallized during hydrothermal syntheses both in a weakly alkaline medium (Ga/ZVN zeolites) and in excess alkali contained extralattice gallium, in addition to the Ga atoms in the lattice. The results of studies of thermal desorption of pyridine showed that the strength of aprotic Ga-containing sites of galloaluminosilicates increases with an increase in the concentration of the framework aluminum. The difference between the strengths of the aprotic sites in gallosilicates and galloaluminosilicates can be due to the different compositions of their coordination spheres. The coordination sphere of galloaluminosilicates contains adjacent or fairly closely spaced Ga, Al, and Si atoms, whereas the framework in gallosilicates is formed only by Ga and Si atoms. The number and the strength of B-sites in galloaluminosilicates are determined by the concentration of aluminum in the framework and, hence, by the number of bridging OH groups containing active protons and linked to the lattice Al atoms. The carriers of the Brønsted acidity in gallosilicates are bridging groups like $\equiv Si-(H)O \rightarrow Ga \equiv$, which are much less acidic than the OH groups in the aluminosilicate pentasils.[47,48]

The aprotic gallium-containing sites characterized by the absorption band at 1462 cm^{-1} in the IR spectra of adsorbed pyridine have also been found in the catalysts prepared by mechanical mixing of H-pentasil with Ga_2O_3 powder and in those prepared by gallation, *i.e.*, by treatment of the zeolite matrix with a low content of aluminum (Si/Al > 100) with sodium gallate. Figure 1 shows the IR spectra of pyridine adsorbed on Ga-pentasils prepared by mechanical mixing of Ga_2O_3 with the ZVN zeolite (Si/Al = 26) and subjected to various types of treatment. The spectrum of a freshly prepared sample of Ga_2O_3+ZVN recorded after desorption of pyridine at 200 °C does not differ from the spectrum of the initial

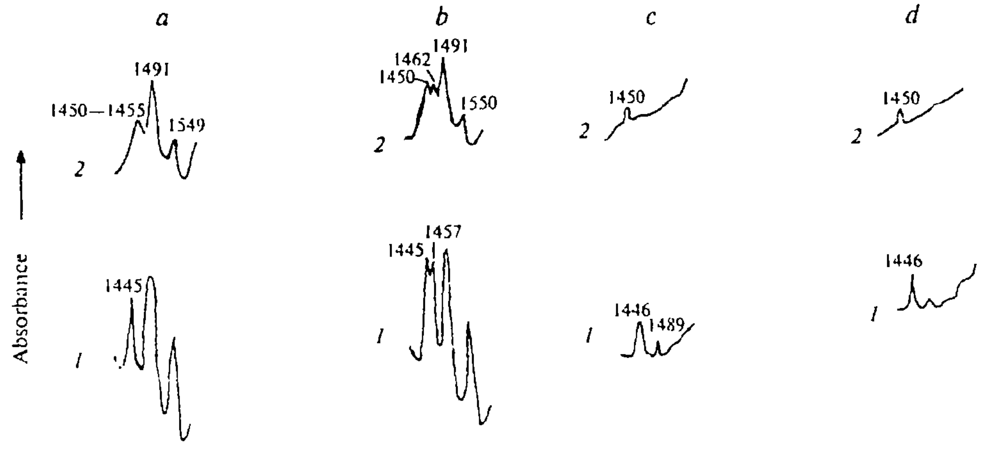

Fig. 1. IR spectra of the pyridine adsorbed on Ga_2O_3+ZVN and Ga_2O_3 samples: *a*, Ga_2O_3+ZVN (starting), T_{des}/°C = 230 (*1*), 530 (*2*); *b*, Ga_2O_3+ZVN treated with H_2, T_{des}/°C = 230 (*1*), 530 (*2*); *c*, Ga_2O_3 (starting), T_{des}/°C = 230 (*1*), 410 (*2*); *d*, Ga_2O_3 treated with H_2, T_{des}/°C = 230 (*1*), 410 (*2*).

zeolite matrix. However, when the desorption temperature (T_{des}) is increased to 530 °C, broadened absorption bands in the 1450—1455 cm^{-1} region appear in the spectrum (spectrum *a*), and after treatment with hydrogen, two peaks with maxima at 1450 and 1462 cm^{-1} appear (spectrum *b*). The spectra of pure Ga_2O_3 (spectrum *c*) and Ga_2O_3 treated with H_2 (spectrum *d*) exhibit weak bands at 1446—1450 cm^{-1}. The thermodesorption measurements showed that most of the pyridine, bound to the sites that are responsible for these bands, is desorbed at T_{des} < 400 °C. Hence, regarding the intensity and positions of the absorption bands of the coordinated pyridine, the aprotic sites of Ga_2O_3 do not differ much from the L-sites of nonmodified pentasil. Evidently, treatment of a mechanical mixture of Ga_2O_3 and pentasil with hydrogen facilitates the dispersion of Ga particles and accelerates the topochemical reaction between gallium oxide and the zeolite matrix.

To elucidate the specific features of the formation of aprotic acid sites in gallated pentasils, the composition of their surface was studied by XPS, and their acidic properties were studied by IR spectroscopy. It follows from the data listed in Table 3 that the outer surface of the freshly prepared gallated pentasil is much more enriched in gallium than the surface of a sample prepared by impregnation; in the former case, the Ga/Si ratio is 5—6 times larger. After treatment of a gallated sample with air at 550 °C, the surface concentration of Ga decreases, whereas for the catalyst prepared by impregnation, the Ga/Si surface ratio increases. This is due to the different degrees of dispersion of gallium particles in these two cases. The impregnation of H-pentasil with gallium nitrate yields a coarsely dispersed Ga_2O_3 phase ($d \approx$ 1—5 μm),[49] and the majority of the aggregates is inaccessible for XPS measurements; conversely, gallation is accompanied by dispersion of gallium oxide particles. It is quite probable that sodium gallate is occluded by the zeolite in a dispersed form, which favors its migration into the channels as early as at the calcination stage. After "reaction—regeneration" cycles, the difference between the surface concentrations of Ga in these two samples becomes less pronounced.

Table 3. Composition of the surface of Ga-pentasils according to the data of XPS and atomic absorption spectrophotometry (AAS)

Treatment conditions[a]	$\frac{O1s}{Si2p}$	$\frac{Ga2p_{3/2}}{Si2p}$	Contents of Ga (%, w/w)		
			XPS[b]		AAS
			I	II	
		Gallated pentasil[c]			
A	2.041	0.316	26.6	30.0	1.7
B	2.237	0.097	9.4	10.4	1.7
C	2.060	0.056	5.9	4.5	1.7
		Ga-pentasil prepared by impregnation[d]			
A	1.950	0.057	6.6	7.2	1.5
B	2.031	0.082	8.7	7.4	1.5
C	1.824	0.034	3.4	2.9	1.5

[a] *A*, the starting sample; *B*, treatment with air at 550 °C; *C*, treatment with air at 550 °C + 5 "reaction—regeneration" cycles.

[b] The content of gallium was calculated from the ratio of the intensities of $Ga2p_{3/2}$: Si2p (I) and Ga3d : Si2p (II).

[c] Si/Al = 115; |Ga| = 1.7% (w/w).

[d] Si/Al = 115; |Ga| = 1.5% (w/w).

In the IR spectra of pyridine adsorbed on gallated pentasil, the absorption band at 1462 cm^{-1} was detected after conduction of "reaction—regeneration" cycles;[50] this points to the formation of extralattice Ga atoms, which possess electron-accepting properties. These results were confirmed by analysis of the IR spectra of adsorbed hydrogen.[50,51] Thus, the acidic properties and the surface composition of the gallated pentasil substantially differ from those of a catalyst with a close composition prepared by impregnation. The most significant stage in the formation of the active sites of gallated pentasils is the migration of gallium into the channels, which occurs apparently according to the following scheme. A part of the Ga atoms isomorphically replace the Al atoms in the framework of the H-form of pentasil during its treatment with sodium gallate. Some gallium is dispersed on the outer surface of the crystallites and migrates into the channels already at the stage of calcination. The process of migration occurs even more efficiently after repeated "reaction—regeneration" cycles or after treatment with hydrogen. The results obtained make it possible to assume that gallated pentasils can incorporate gallium in various forms: as finely dispersed oxide on the outer surface, as gallium atoms in the channels, and as extralattice and lattice Ga atoms linked to hydroxyl groups. A similar distribution of gallium has also been found in the structure of gallosilicates.[47]

The introduction of platinum into Ga-containing pentasils substantially changes the electronic properties of aprotic sites. From a comparison of the XPS data obtained for gallated pentasils, it follows that the electronic state of gallium depends on the conditions of treatment of the catalysts (Table 4). According to published data,[52] the binding energy (E_b) for the Ga3d line is 21.6 eV, which corresponds to trivalent gallium. After treatment of gallated pentasil containing no platinum with hydrogen at 550 °C, an additional peak with E_b = −0.8 eV appears in the spectrum. This peak corresponds to the reduced state of gallium, Ga^{1+} (see Refs. 50, 51). The relative concentration of these ions amounts to 32%. In a sample of platinum-containing gallated pentasil, the proportion of the reduced Ga^{1+} ions increases to 82%, *i.e.*, platinum promotes the reduction of gallium. Treatment with hydrogen results in the reduction of 70% of platinum to the zero-valent state. Platinum in gallated pentasils tends to occur as coarsely dispersed particles located on the outer surface of zeolite crystals.

Analysis of the X-ray photoelectron spectra of a gallosilicate and a sample of Pt-gallosilicate has shown

Table 4. Influence of treatment conditions on the electronic states of gallium and platinum in the Ga-pentasil and Pt/Ga-pentasil catalysts prepared by gallation (XPS data)

Treatment conditions[a]	$Ga2p_{3/2}$	Ga3d	$Pt4f_{7/2}$/eV	
	eV		Pt^{2+}	Pt^0
		Ga-pentasil[b]		
A	1118.1	21.7	—	—
B	1118.1	21.7	—	—
C	1118.0	21.7 (68%) + + 20.9 (32%)	—	—
		Pt/Ga-pentasil[b]		
A	1117.9	21.8	73.4	—
B	1117.6	21.6	73.6 (55%)	72.1 (45%)
C	1117.5	21.8 (18%) + + 20.9 (82%)	74.0 (30%)	71.4 (70%)

[a] *A*, the starting sample; *B*, treatment with air at 450 °C; *C*, treatment with air at 450 °C + treatment with hydrogen at 550 °C.

[b] The proportions of Ga^{3+}, Ga^{1+}, Pt^{2+}, and Pt^0 calculated from the intensities of the corresponding lines are given in parentheses.

Table 5. Influence of pretreatment conditions on the XPS parameters of the gallosilicate and Pt-gallosilicate catalysts

Treatment conditions[a]	Ga3d /eV	$Pt4f_{7/2}$/eV	
		Pt^{2+}	Pt^0
	Gallosilicate		
A	21.7	—	—
B	21.4	—	—
	Pt-gallosilicate[b]		
A	21.2	73.4	—
B	21.3	73.1 (57%)	71.8 (43%)
C	21.6 (68%) + + 20.7 (37%)	73.2 (35%)	71.6 (65%)

[a] *A*, the starting sample; *B*, treatment with air at 450 °C; *C*, successive treatment with air at 450 °C and with hydrogen at 500 °C.

[b] The proportions of Ga^{3+}, Ga^{1+}, Pt^{2+}, and Pt^0 calculated from the intensities of the corresponding lines are given in parentheses.

that in this case, too, the rate and degree of reduction of gallium increase in the presence of platinum (Table 5). The additional peak with E_b = −0.9 eV corresponding to Ga^{1+} was detected in the spectrum of Pt-gallosilicate that had been heated in a hydrogen atmosphere at 500 °C. In addition, during calcination and subsequent treatment with hydrogen, the electronic state of platinum changes: some of the Pt^{2+} is reduced to Pt^0. The set of data obtained by XPS and by electron microscopy made it possible to conclude that the Pt-gallosilicate catalyst contains platinum particles of different sizes, namely, large crystallites ($d \approx$ 10 nm), which contain a relatively small fraction of the total amount of platinum, a relatively small number of finely dispersed clusters ($d \approx$ 1 nm) and, finally, a large number of platinum particles shaped as hemispheres with $d \approx$ 2—3 nm with a height of ~2 nm. These particles of the "island" morphology are located on the outer surface of the gallosilicate.

The fact that platinum promotes the reduction of gallium to Ga^{1+} can be due to two reasons; both of them assume the participation of highly reactive mobile atomic hydrogen (hydrogen spillover) formed upon the dissociative adsorption of molecular H_2 on platinum.[53,54] First, it cannot be ruled out that under the action of atomic hydrogen activated on platinum, the removal of Ga atoms from the gallosilicate lattice and the reduction of extralattice ions to the monovalent state can occur simultaneously. However, detailed analysis of the X-ray photoelectron spectra (in particular, the absence of substantial changes in the Ga/Si surface ratio) indicates that this process is relatively unlikely. Apparently, Ga^{1+} ions result from the reduction of extralattice gallium atoms, formed upon various kinds of treatment, with the spillover hydrogen.

Thus, it follows from the spectroscopic data considered above that the main characteristic feature of the formation of aprotic acid sites in Ga-pentasils is the high ability of gallium to migrate. In the case of catalysts prepared by impregnation, this ability is manifested as the migration of a part of gallium from the outer surface deep in the crystallites. For samples of Ga_2O_3+H-pentasil, the formation of electron-accepting Ga-sites is associated with the high-temperature treatment with hydrogen, which initiates migration of gallium into the channels. In the case of gallated pentasils, it is assumed that some of the framework Al atoms are isomorphically replaced by gallium during the reaction of sodium gallate with the zeolite matrix and then gallium emerges from the lattice as a result of various types of treatment. Finally, gallosilicates and galloaluminosilicates are characterized by the appearance of extralattice Ga atoms upon the "reaction—regeneration" cycles and also upon treatment of the catalysts with hydrogen or water vapor. The effect of platinum on the formation of active sites in Pt—Ga-pentasils is manifested as an increase in the rate and degree of reduction of gallium to Ga^{1+}.

The above-described study of the surface properties of modified pentasils demonstrated that a significant role in the formation of active sites in these systems is played by the nature of the modifying metal, the method of introducing the metal into zeolites, pretreatment of the catalyst, and promotion with platinum. A set of physicochemical methods has been used to study the acidic properties of pentasils in detail and to test the electronic state, dispersity, and location of the modifying elements in the zeolite structure. This makes it possible to control all the above-listed surface properties in order to develop the most efficient catalytic systems,

Table 6. Transformation of C_2—C_4 olefins at 320 °C on decationized pentasil (Si/Al = 30)

Starting hydrocarbon	Degree of conversion (%)	Yield of hydrocarbons (%, w/w)	
		C_1—C_5	C_6—C_{10}
Ethylene	99.2	30.9	68.3
Propylene	97.4	19.6	78.8
n-Butene	98.5	6.3	92.2
Isobutene	99.1	7.0	92.1

active in the synthesis of aliphatic and aromatic hydrocarbons from lower olefins and paraffins. Some examples of the use of the developed catalysts in the oligomerization and aromatization of C_3—C_4 olefins and aromatization of C_2—C_5 paraffins are presented below.

Synthesis of aliphatic and aromatic hydrocarbons from C_2—C_4 olefins in the presence of pentasils

In the presence of pentasils, lower olefins are converted, depending on the reaction conditions (temperature, residence time, pressure), either into a mixture of aliphatic hydrocarbons of the composition C_6—C_{10} (T = 320 to 350 °C) or into a concentrate of aromatic hydrocarbons (T = 400 to 550 °C) containing toluene and xylenes as the major components. At 320 °C, the yield of aliphatic hydrocarbons, which are mostly branched, reaches 92% (Table 6). The selectivity of formation of liquid products increases with an increase in the residence time; it does not depend on the content of aluminum in the pentasil framework (for Si/Al ratios ranging from 18 to 140) and sharply decreases upon a decrease in the partial pressure of the initial olefins.[39,55] For example, in the experiments with ethylene under atmospheric pressure, it was shown that reasonable yields of liquid products can be obtained only when the concentration of C_2H_4 is larger than 10% (v/v) (Fig. 2). The conversion of dilute ethylene-containing mixtures into liquid products can be accomplished at pressures >0.3 MPa. It should be noted that mixtures containing ~10% (v/v) ethylene are formed in the oxidative condensation of methane.[56] Thus, the use of zeolites of the pentasil type offers the way for preparation of valuable chemical products from natural gas by converting it first into ethylene and then into liquid hydrocarbons without intermediate fractionation of the olefin.

The optimum temperature range for aromatization of lower olefins in the presence of pentasils is 450—550 °C, although the formation of aromatic hydrocarbons is observable even at 350 °C.[55] The modification of pentasils with metals increases the selectivity of aromatization (S_{arom}). The S_{arom} values for the transformations of isobutene at 350 °C in the presence of H-pentasil with Si/Al = 20 and in the presence of metal-containing pentasils prepared by impregnation of this zeolite with the corresponding salts are given below:

Modifier	None	V	Zn	Ga
S_{arom} (%)	35.7	40.0	48.1	63.1

Of metal-containing silicates with the pentasil structure prepared by isomorphous replacement, gallosilicates were found to be the most selective catalysts of aromatization of lower olefins (Table 7).

Aromatization of lower paraffins

Decationized pentasils transform C_2—C_5 paraffins into aromatic hydrocarbons with $S_{arom} \approx 30\%$ (see Refs. 57, 58). Aromatization is accompanied by substantial cracking; consequently, the ratio of the rate of the

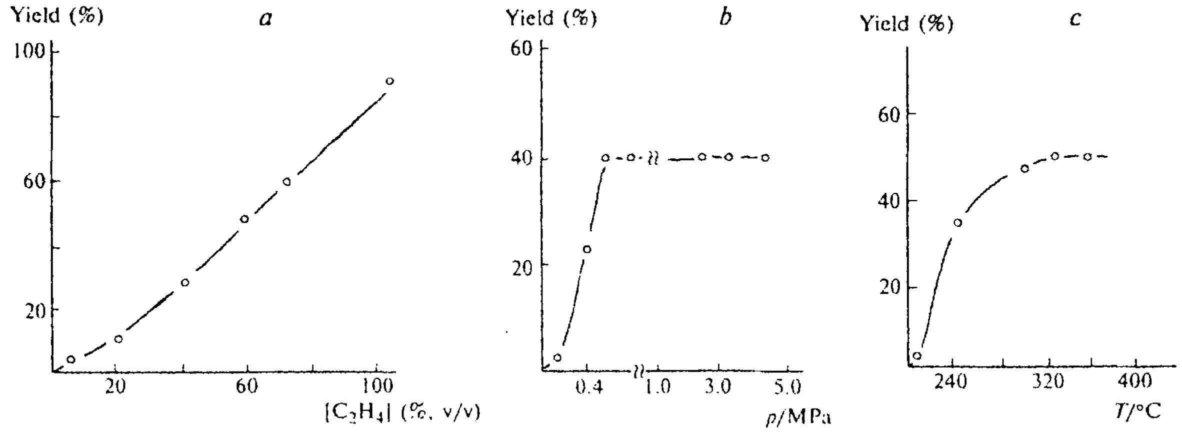

Fig. 2. Dependence of the yield of liquid products of the transformation of ethylene: *a*, on the content of C_2H_4 in its mixture with N_2 (T = 350 °C, p = 0.1 MPa, V = 4 L h^{-1}); *b*, on the overall pressure of the gas mixture (T = 350 °C, $[C_2H_4]$ = 9% (v/v)); *c*, on the temperature ($[C_2H_4]$ = 9% (v/v)).

Table 7. Selectivity of aromatization of propylene on Fe, Al, and Ga silicates with the pentasil structure

Catalyst	Composition (%, w/w)			T/°C	S_{arom} (%)
	Al_2O_3	Fe_2O_3	Ga_2O_3		
Ferrosilicate	1.4	3.4	—	350	28.7
				500	46.3
Aluminosilicate	3.0	—	—	350	35.7
				500	43.0
Gallosilicate	—	—	6.5	350	45.0
				500	55.1

Table 8. Aromatization of ethane on Pt-containing gallosilicates and galloaluminosilicates at 600 °C

Catalyst	Conversion of C_2H_6	S_{arom}	S_{crack}
		(%)	
Gallosilicate (Si/Ga = 23)	3.7	—	27.0
0.5% Pt-gallosilicate	36.0	58.1	16.5
Galloaluminosilicate (Si/Ga = 140; Si/Al = 55)	36.4	45.6	34.8
0.5% Pt-galloaluminosilicate	35.5	64.2	17.0

Note. Reaction conditions: $U = 0.6 \cdot 10^{-5}$ mol (s g)$^{-1}$.

desired reaction to the rate of destruction of the starting hydrocarbons does not exceed 0.3. To increase the yield of the desired products and, hence, to increase the selectivity of aromatization, we used chemical and thermal modification of pentasils. The chemical modification consisted of the introduction of metal ions into the zeolite matrix, while the thermal modification involved high-temperature treatment of decationized and metal-containing zeolites with air, hydrogen, and water vapor, which made it possible to control the ratio of the concentrations of the B- and L-sites.

The most pronounced increase in S_{arom} was attained in the presence of Pt-, Zn-, and Ga-containing pentasils. Thus the selectivity of Zn-pentasil (Si/Al = 20) in the aromatization of propane at 550 °C was 1.3 times higher than that of the corresponding H-form, and after the introduction of the second modifying element, S_{arom} increased to even a greater extent, while the selectivity of the formation of cracking products (S_{crack}) simultaneously decreased:

Modifier	Zn	Zn+Cu	Zn+Sn	Zn+Cr
S_{arom} (%)	42.0	44.6	49.9	54.7
S_{crack} (%)	54.4	49.9	41.7	35.6

Among modified pentasils, Ga-containing pentasils were found to be the most selective catalysts for the aromatization of C_2—C_5 paraffins. Detailed study of the dependence of the catalytic activity of Ga- and Pt/Ga-pentasils on the composition of the zeolite framework, concentration of the promoter, the method of preparation of the catalyst, and the conditions of its pretreatment resulted in the development of efficient catalytic systems for aromatization of not only C_4—C_5 paraffins but also substantially less reactive propane and ethane. The highest selectivity in the aromatization of ethane was observed in the case of Pt-containing gallosilicates and galloaluminosilicates (Table 8). The selectivity of aromatization of C_4 paraffins also markedly increased after modification with platinum. The results obtained for the transformations of *n*-butane (Table 9) indicate that the S_{arom} value observed in the presence of Pt-gallosilicate is fairly high and reaches ~75% at 550 °C. Attention is attracted to the distribution of the aromatic products obtained from *n*-butane in the presence of this catalyst (Table 10), in particular, by an increased content of xylenes.

Mechanism of the catalytic action of pentasils and the role of acid sites of various natures in the transformations of lower hydrocarbons

The major contribution to the transformations of lower olefins on decationized pentasils is made by the

Table 9. Temperature dependence of the catalytic properties of gallosilicate and Pt-gallosilicate in the aromatization of *n*-butane

T/°C	Gallosilicate			0.5% Pt-gallosilicate		
	Conversion of *n*-butane	Yield of aromatic hydrocarbons	S_{arom}	Conversion of *n*-butane	Yield of aromatic hydrocarbons	S_{arom}
		(%)			(%)	
300	12.4	—	—	28.6	0.5	1.7
350	18.0	—	—	49.4	7.7	15.6
400	36.7	4.6	12.5	66.7	20.3	30.4
450	50.9	18.2	35.8	80.9	46.9	58.0
500	71.2	37.4	52.5	86.9	59.5	68.5
550	82.1	47.4	57.7	88.3	66.6	75.4

Note. Reaction conditions: $U = 3 \cdot 10^{-5}$ mol (s g)$^{-1}$; *n*-C_4H_{10} : He = 1 : 3.

Table 10. Distribution of the products of aromatization of *n*-butane at 400 °C on gallosilicate and Pt-gallosilicate

Catalyst	Conversion of *n*-butane (%)	Composition of aromatic hydrocarbons (%)				
		Benzene	Toluene	Ethylbenzene	Xylenes	C_9—C_{10}
Gallosilicate	49.6	30.0	41.2	2.8	22.1	3.9
Pt-gallosilicate	50.9	8.0	44.0	3.0	42.5	2.5

B-sites, which participate in the adsorption, protonation, and dimerization (oligomerization) of unsaturated molecules.[28,39,59] The transformation of dimers (oligomers) into aromatic hydrocarbons can follow two competing pathways. The first of them is consecutive abstraction of hydrogen from the molecules of oligomers and thermal cyclization of the resulting polyunsaturated structures. The second route includes partial cracking of oligomers to give fairly reactive allylic carbenium ions, which are easily converted into di- and trienyl cations and then into aromatic hydrocarbons. This sequence of transformations of lower olefins on pentasils is consistent with the mechanism suggested[60,61] for the high-temperature transformations of oligomers of C_2—C_4 olefins preliminarily chemisorbed on these zeolites. This mechanism is based on the suggestion that high-temperature aromatization of lower olefins on pentasils is preceded by the cracking of chemisorbed oligomers and formation of allylic carbenium ions acting as reactive intermediates.

The aromatization of lower paraffins is a multi-route process consisting of a number of consecutive and parallel stages, the first of which is formation of unsaturated hydrocarbons. In the presence of H-pentasils, olefins are mostly formed upon cracking of the starting paraffins, whereas in the case of modified pentasils, unsaturated compounds are mostly formed *via* dehydrogenation of alkanes, and only a small portion of olefins is produced by cracking.

The ability of decationized pentasils to activate molecules of lower alkanes and to accomplish the subsequent dehydrocyclization of the resulting intermediates is directly related to the acidity of zeolites and, most of all, to the presence of strong B-sites. These sites are responsible for cracking of the starting alkanes, oligomerization of olefins, and their partial cleavage as well as for the cyclization of intermediate unsaturated compounds. The subsequent deprotonation and redistribution of hydrogen afford aromatic hydrocarbons and alkanes in a ratio of 1 : 3, and the yield of the aromatization products is restricted by this ratio.

Unlike decationized materials, modified pentasils are bifunctional catalytic systems with activity and selectivity depending on contributions of both protic acid sites of the zeolite matrix and the metal-containing L-sites. The strong L-sites are capable of dehydrating molecules of lower alkanes to give the corresponding olefins. Oligomerization of these olefins occurs on the B-sites. In addition, the aprotic acid sites participate in the abstraction of hydride ions from unsaturated molecules, which yields highly reactive allylic intermediates. Aromatic hydrocarbons can be obtained both *via* consecutive elimination of hydride ions from olefin molecules containing not less than six carbon atoms and upon direct interaction of two allylic cations accompanied by elimination of hydrogen. This pathway to aromatic structures does not need simultaneous formation of alkanes; therefore, in this case, the yield of aromatic hydrocarbons is not restricted by a stoichiometric ratio (one molecule of aromatics per three molecules of an alkane). Evidently, it is this fact that accounts for the higher yields of the products of aromatization of lower alkanes achieved in the presence of modified pentasils.

Our studies as well as the results obtained by other researchers[39,45,58,62] have shown that aromatization of lower alkanes occurs most selectively on Ga-pentasils. This is due to some specific features of these catalysts and, first of all, to the fact that the promoters are localized in the units of the pentasil structure. The crucial factor that determines the selectivity of aromatizaton on Ga-pentasils is the method of their preparation. Gallosilicates and galloaluminosilicates containing extralattice gallium in the zeolite channels are the most selective catalysts. Apparently, the electron-accepting properties of the L-sites incorporating extralattice Ga atoms differ from these properties of both the gallium sites concentrated on the outer surface (for example, in the Ga-pentasils prepared by impregnation) and the Zn-, Cd-, Co-, and Ni-containing aprotic sites localized in the channels of pentasils.

* * *

Thus, the use of a set of physicochemical methods provided new data on the nature of the active sites of pentasils, the mechanism of their formation, and the evolution of the protic and aprotic acid sites during catalysis and high-temperature treatment with hydrogen, air, or water vapor. Thus the IR-spectroscopy studies of adsorption of molecular probes made it possible to identify for the first time strong Lewis acid sites in pentasils modified with metals and to characterize their properties (strength, thermal stability). The structure of the surface of pentasils was studied in detail for the first time by XPS; this method was also used to determine the areas of localization of the active centers and to demonstrate the ability of the modifying metal atoms to migrate from the outer surface deep in the zeolite crystals and to change (in the case of gallium and nickel) the electronic state under the action of a reducing medium. Based on the results of physicochemical studies, it was shown that the strong aprotic acid sites play the crucial role in the acceleration of the key stage of the aromatization of lower hydrocarbons, *viz.*, the abstraction of hydrogen from saturated and unsaturated molecules, in the presence of metal-modified pentasils.

Systematic investigation of the transformations of lower olefins and paraffins on decationized and modified pentasils made it possible to elucidate the main factors that influence their activity and selectivity (the ratio of the concentrations of the lattice atoms, the nature of the modifying element and its concentration and localization in the zeolite matrix, reaction conditions, and pretreatment of the catalyst).

The results of the studies described above were used to formulate the principles of selecting effective catalysts for the synthesis of aliphatic and aromatic hydrocarbons from lower olefins and paraffins. These principles include the use of zeolites of the pentasil family with the optimum Si/Al ratio as the matrix; creation of conditions ensuring the formation of strong aprotic acid sites; the use of Zn-pentasils prepared by the solid-phase interaction of the zeolite with zinc oxide and pentasils obtained by isomorphous replacement and containing extralattice Ga atoms.

As a result, a number of new catalytic systems based on zeolites of the pentasil family manufactured in Russia have been developed and tested in pilot plants using real raw materials (hydrocarbon components of natural gas, casing-head gas, and refinery exhaust gases). These catalysts are capable of transforming C_2—C_4 olefins into high-octane engine fuels with a selectivity of up to 95% and permit the preparation of a concentrate of aromatic hydrocarbons from ethane and propane with a selectivity of up to 60%, or from C_3—C_4 olefins, butanes, and pentanes with a selectivity of 65—70%.

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