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Aromatisation of low-molecular-weight paraffins on pentasil group zeolites

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ABSTRACT. Experimental data on the application of pentasil group zeolites in the aromatisation of low-molecular-weight paraffins are surveyed. Modern ideas concerning the mechanism of the aromatisation and the nature of the active centres in pentasil are examined. Examples of the application of pentasil-containing catalysts in technological processing of gaseous hydrocarbons are presented.

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I. Introduction

Low-molecular-weight hydrocarbons are a readily available and cheap raw material for the synthesis of polymeric materials, high-octane components of motor fuel (C_6-C_8 isoalkanes and aromatic hydrocarbons), as well as various intermediates in fine organic synthesis.[1–3] Among the principal sources of lower paraffins, one should distinguish in the first place the byproduct petroleum gas (C_2-C_5 alkane content up to 70%) and natural gas (overall content of ethane, propane, and butanes up to 25%),[4,5] the scale of the extraction of which runs into tens and hundreds of billions of cubic metres per year respectively. A tendency has arisen recently towards a more complete utilisation of petroleum by processing also its heavy fractions and towards an increase of the output of apparatus for thermal and catalytic cracking—the principal degradative processes used in modern petrochemical and petroleum processing industry. This has resulted in a considerable increase in the evolution of waste gases in which C_2-C_4 paraffins predominate and which contain an appreciable amount of the corresponding alkenes. The processes based on CO and H_2—the gaseous coal processing products—also occupy a fairly important place in the manufacture of lower hydrocarbons.[6,7] Until recently, a considerable proportion of the components of natural, byproduct, and petroleum industrial gases have been used merely as industrial fuels and have not found applications in the synthesis of chemical products.

The task involving the effective utilisation of hydrocarbon gases has stimulated the search for new catalysts, among which synthetic zeolites occupy a special place.[8,9] The first generation zeolites (faujasites, mordenite, erionite, etc.) are replacing traditional catalysts based on amorphous aluminosilicates in petroleum cracking processes, in the alkylation of paraffins and aromatic hydrocarbons, and in the oligomerisation of lower alkenes. A new stage in the development of zeolite catalysis involves the synthesis of high-silica pentasil group zeolites.[1–3,10] Zeolites of this structural type, which have no natural analogues, were first synthesised by the Mobil Oil Company at the beginning of the 1970's. They were given the abbreviated designations ZSM-5 and ZSM-11.[11–17] In the Soviet Union, analogues of these zeolites are referred to as pentasils of the TsVK and TsVM types and ultrasil.[15] New methods of synthesis of pentasils, in the lattices of which aluminium atoms have been replaced by boron, iron, gallium, germanium, zinc, and chromium atoms as well as atoms of other elements, have been developed recently.[18–20]

Pentasil-based catalysts have found applications in many large-scale petroleum processes such as isomerisation, disproportionation, and alkylation of aromatic hydrocarbons,[21–23] the cracking of gas oil fractions,[3,24] deparaffinisation of petroleum fractions,[24] the conversion of methanol into hydrocarbons,[25–27] etc. In these processes, pentasils proved to be more effective as selective catalysts than the previously employed first generation zeolites or non-zeolitic systems of various compositions. In addition, pentasils possess the unique ability to convert lower paraffins and alkenes into higher-molecular-weight products.[3,27–32] C_2-C_4 alkenes are almost quantitatively converted into high-octane components of motor fuel on pentasils at atmospheric pressure and at temperatures in the range 300–350 °C.[11–13,28–30] During the last 4–5 years, there has been a growth of interest in pentasils as catalysts of the aromatisation of lower paraffins. The modification of pentasils by the addition of various transition elements made it possible to obtain catalytic systems for the conversion of propane and butanes into C_6-C_{10} aromatic hydrocarbons with a selectivity of 60–70%.[31–34]

The results of the study of the catalytic properties of zeolites, including pentasils, in various reactions have been treated systematically in a number of reviews[1–3,16,22–27,35,36] published at the beginning of the 1980's. The aim of the present review is to survey and analyse the information accumulated during the last 5–6 years about the reactions of low-molecular-weight paraffins in the presence of pentasils of various compositions, to discuss the possible mechanisms of these reactions, and to consider certain technological aspects of the use of pentasil-based catalysts in the processing of hydrocarbon gases.

II. Structure and active centres of pentasils

The skeleton of zeolites—crystalline aluminosilicates—consists of aluminium–oxygen and silicon–oxygen tetrahedra, which have common vertices and form the structural elements of the lattice—tetrahedral and hexahedral prisms, cancrinite and sodalite cells, cubooctahedra, etc.[37,38] Without going into details, which have been described in a number of reviews and monographs,[8,9,16,37,38] we shall note only the principal features of the structure of pentasils. The pentasil skeleton is based on five-membered rings formed predominantly by silicon–oxygen tetrahedra, since the concentration of aluminium in these zeolites is low (not more than 5 atoms per unit cell, which corresponds to the ratio Si/Al ranging from about fifteen to tens of thousands).[3,14,38] The five-membered rings are joined up into cells consisting of eight such rings and form chains which are combined into layers, each chain in the layer representing the mirror image of the neighbouring chain (Fig. 1). In the skeleton of pentasils of type ZSM-5 and ZSM-11 there exists a system of pores consisting of channels intersecting at right angles, which are produced by ten-membered rings. The porous structure of the ZSM-5 zeolite includes both straight (0.54 × 0.56 nm) channels with an elliptical cross-section and sinusoidal (0.51 × 0.55 nm) channels with a circular cross-section. The pore system of the ZSM-11 pentasil consists of straight channels with an elliptical cross-section.

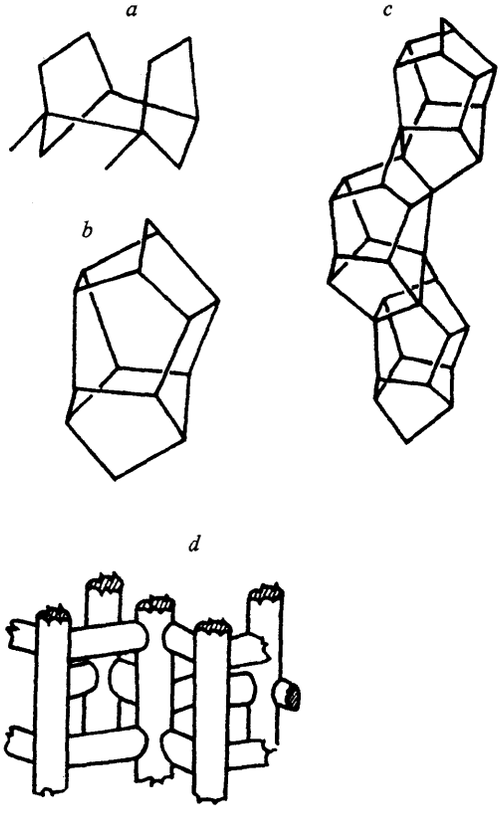
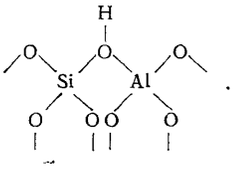
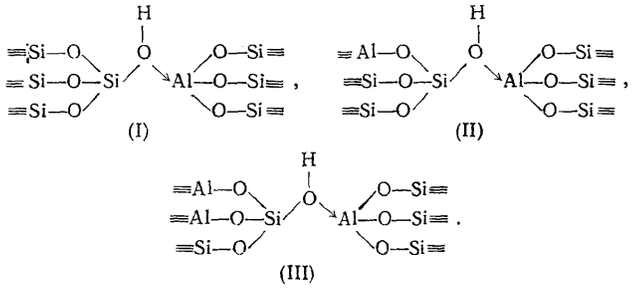


Figure 1. The structure of pentasil: *a*, structural element; *b*, cell made up of eight five-membered rings; *c*, chain made up of cells; *d*, schematic representation of the channel structure of pentasil.[3]

It must be emphasised that the aluminium atoms occupy a special position in the crystal lattice of zeolites. They substitute isomorphously the silicon atoms in the structural skeleton but are involved in tetrahedral coordination with respect to oxygen atoms. As a result of this, the coordination number and valence of aluminium are not the same, which leads to the appearance of an excess negative charge on the aluminium–oxygen tetrahedron AlO_4^-. This charge may be compensated either by a metal cation or by a proton (in the decationated forms of the zeolite). The compensating proton forms a covalent bond with one of the four oxygen atoms in the AlO_4^- tetrahedron, which creates isolated structural hydroxy-groups of the bridging type:



An IR spectroscopic study of the interaction of the OH bridging groups with the molecules of adsorbed bases[39–49] established that they are strong Brønsted acid centres (B-centres). According to modern ideas[42,47–52] based on quantum-chemical calculations and experimental IR data, the entire wide variety of the acid hydroxy-groups reduces to three principal types with different numbers of aluminium atoms in the immediate structural environment of the hydroxyl.



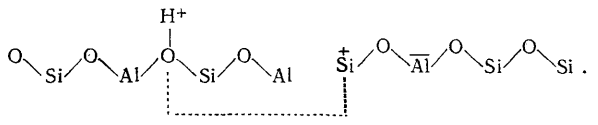
The acid properties of the hydroxyls are weakened on passing from (I) to (III) and further to silanol groups Si–OH, which have no proton-donating capacity. High-silica pentasils and mordenites contain type (I) OH groups and terminal silanol hydroxyls similar to the surface hydroxy-groups on silica gel.[46,49,50] Apart from the isolated bridging hydroxyls, pentasils include bridging OH groups forming fairly strong hydrogen bonds with the lattice oxygen atoms.[46,53] The concentration of such hydroxyls can reach 20% of the total number of OH groups.[46] According to Medin et al.,[53] these groups have unusual properties. For example, at room temperature they are capable of interacting with adsorbed paraffin molecules, while at elevated temperatures they undergo a transition to an isolated state. According to quantum-chemical calculations,[54] hydroxyls of this type should have stronger electron-donating properties than isolated bridging OH groups.

Apart from B-centres, zeolites contain aprotic (Lewis) acid centres (L-centres) possessing electron-accepting properties. Various coordinatively unsaturated lattice atoms or ions having an unoccupied *p* orbital as well as exchange cations with a positive charge constitute the zeolite L-centres. In the structure of dehydroxylated hydrogen-forms of zeolites, AlO_4^- tetrahedra lacking

a proton compensating their charge and having the properties of a Lewis base, are also present.

The results of IR spectroscopic studies[46–53] have shown that, on dehydroxylation of decationated pentasils and mordenites obtained by direct hydrothermal synthesis, aprotic acid centres of three types are formed: one of them consists of coordinatively unsaturated lattice aluminium atoms, others consist of silicon ions, and finally the third group comprises aluminium atoms outside the lattice. In the dealuminated mordenites, L-centres of only one type—tricoordinate lattice silicon ions—are formed after the removal of OH groups.

According to the results of a number of studies,[17,55,56] high-silica zeolites of the type of pentasil and mordenite contain also a smaller amount of very acid ("superacid") centres. These are protic centres whose acidity has been enhanced as a result of the inductive effect of a neighbouring Lewis centre.[57]



Thus acid centres of different nature have been identified in zeolites by the IR spectroscopy of adsorbed molecules. The ratio of the concentrations of the L- and B-centres depends on the structure of the zeolite, the composition of the skeleton, the thermal stability of the hydroxyl coating, and the chemical nature of the substances used to modify the inner and outer surfaces of the catalyst.[8,9,34]

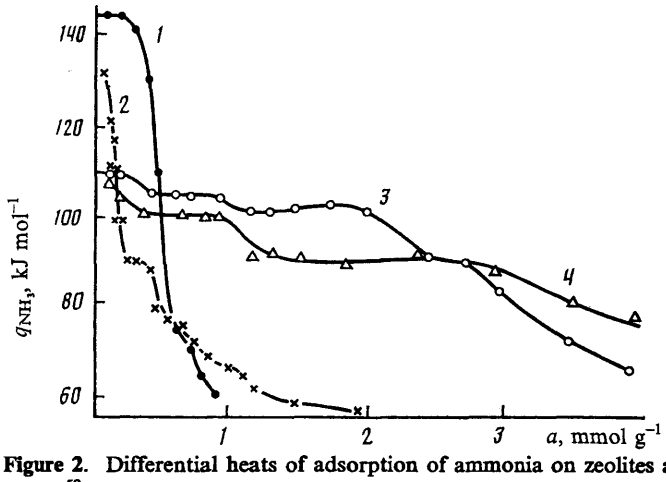


Figure 2. Differential heats of adsorption of ammonia on zeolites at 30 °C:[59] *1*, dealuminated mordenite with Si/Al = 24; *2*, pentasil of the type H-TsVK with Si/Al = 40; *3*, HNaY (degree of decationation α = 80%); *4*, HNaX (degree of decationation α = 80%).

Apart from IR spectroscopy, adsorption microcalorimetry,[40,58–66] heterophase isotope exchange between deuterium and hydroxy-groups,[67–71] programmed thermal desorption of ammonia and organic nitrogen-containing bases,[72,73] etc. have been used to investigate the acidity of zeolites of different structure, including pentasils. Adsorption microcalorimetry, based on the direct measurement of the differential heats of adsorption of nitrogen-containing bases and especially of ammonia, is most suitable for the quantitative estimation of the concentration and strength of the acid centres. The stepwise character of the curves reflecting the dependence of the differential heat of adsorption of ammonia q_{NH_3} on the amount of adsorbed ammonia Q shows that the inhomogeneity of the adsorption centres of zeolites is discrete in nature (Fig. 2). The acidity spectra of certain zeolites having different compositions and structures (Fig. 3) contain bands with the same q_{NH_3}. These indicate the presence of centres of identical strength in different zeolites but at different concentrations. With increase in Si/Al, a trend is observed towards an increase in the strength of the acid centres and a decrease in their number.[63–66] Comparison of the acidity spectra has shown that both pentasils and mordenites contain strong acid centres with $q_{NH_3} > 120$ kJ mol^{-1}.[61–63] However, in contrast to mordenites, pentasils contain no centres adsorbing ammonia with $q_{NH_3} > 130$ kJ mol^{-1}.

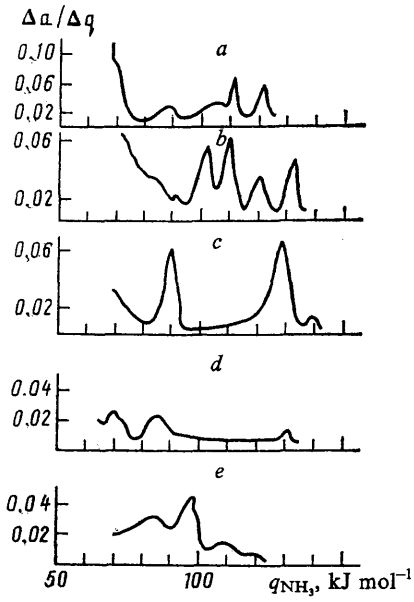
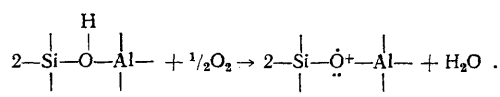


Figure 3. Distribution of acid centres of different structure with respect to energy:[63] *a*, zeolite L (α = 82%); *b*, mordenite (α = 90%); *c*, dealuminated mordenite with Si/Al = 9; *d*, pentasil of type H-TsVK with Si/Al = 30; *e*, pentasil of type H-TsVM with Si/Al = 20 ($\Delta a/\Delta q$ = fraction of acid centres with a specific q_{NH_3}).

The acid centres of pentasils are distinguished by a high thermal stability. The results of measurements of the concentration of hydroxy-groups by heterophase isotope exchange and adsorption microcalorimetric methods[63,71] showed that the protic centres of pentasils begin to decompose above 700 °C and that, even after heat treatment at 800 °C, about 40% of the hydroxyls persist on the surface. Pentasil vacuum heat-treated at 800 °C contains strong acid centres which adsorb ammonia with q_{NH_3} = 110–130 kJ mol^{-1}.[63] The number of these centres is approximately three times smaller than for the specimen heated at 500 °C.

Together with acid centres of different nature, the zeolites contain oxidation-reduction centres, which were identified by the EPR method.[74] The Brønsted acid centres of pentasils can be converted into centres of another type—solid state defects—as a result of high-temperature heat treatment (> 500 °C):[75]



When these centres interact with ionisable organic molecules, radical-cations can be produced.

III. Aromatisation of low-molecular-weight paraffins

The first communications about the catalytic conversion of low-molecular-weight paraffins into aromatic hydrocarbons appeared at the beginning of the 1970's.[76–79] According to thermodynamic calculations,[79] at 627 °C the equilibrium constant of the reaction $3C_2H_6 \rightleftarrows C_6H_6 + 6H_2$ is ~21, which corresponds to 78% of benzene in the equilibrium mixture at atmospheric pressure. The equilibrium constant of the reaction 2 iso-$C_4H_{10} \rightleftarrows C_6H_4(CH_3)_2 + 5H_2$ is 16.2 at 427 °C and 1.2×10^4 at 527 °C.[76] Table 1 presents the calculated temperatures at which the free energies ($\Delta G°$) of the alkane aromatisation and dehydrogenation reactions become zero. The conversion of ethane, propane, and hexane into benzene requires much lower temperatures than their dehydrogenation.[80]

Table 1. Temperature (°C) at which benzene and olefins are formed from various alkanes with $\Delta G° = 0$.[80]

Alkane	Benzene	Alkenes
Methane	1075	1350 (C_2H_4)
Ethane	575	774 (C_2H_4)
Propane	450	655 (C_3H_6)
n-Hexane	320	575 (C_6H_{12})*

*2-Methylpentene.

By analogy with the dehydrocyclisation of paraffins containing six and more carbon atoms, bifunctional deposited metallic reforming catalysts, which exhibit a dehydrogenating activity, were used initially for the conversion of light alkanes.[76–79,81–89]

Ethane may be aromatised in the presence of an M/Al_2O_3 catalyst, where M = Pt, Pd, Ru, Rh, or Ir.[79,81–83] Aluminoplatinum catalysts exhibited an appreciable activity in the aromatisation reactions of propane,[77,84,85] butanes,[76,86] and pentane.[77] Aromatic hydrocarbons have also been obtained from n-butane in the presence of Mo, W, Cr, V, and Mn oxides deposited on Al_2O_3.[78] The aromatisation reactions of lower paraffins on non-zeolitic catalysts have been examined in detail in a number of reviews.[87–89] We may note that, in the presence of the M/Al_2O_3 catalysts the selectivity in the formation of aromatic hydrocarbons S_{arom}, defined as the ratio of the yield of the aromatisation products to the overall degree of conversion, does not exceed 20%. Most of the initial hydrocarbon is converted into cracking and condensation products. As a result of the deposition of these products on the surface, the activity of the catalyst falls rapidly during the reaction.

A new stage in the study of the conversion of lower paraffins with less than six carbon atoms into aromatic hydrocarbons is associated with the use of zeolites of the pentasil group. In the decationated form, these zeolites are capable of aromatising saturated hydrocarbons even in the absence of dehydrogenating components. Modification of pentasils by various metals made it possible to increase significantly the degree of conversion of paraffins and S_{arom}.

All the promoting elements can be divided arbitrarily into two groups. The first includes noble metals (Pt, Rh, Pd), which increase the degree of conversion and the yield of aromatic hydrocarbons, while the second group includes certain Group II and III elements (Zn, Cd, Ga), in the presence of which S_{arom} increases sharply. Examples of the aromatisation of C_2-C_5 paraffins in the presence of pentasils in the hydrogen-form and modified catalysts are examined below.

1. Decationated pentasils

Pentasils of the type H-TsVM exhibit an appreciable activity in the aromatisation of ethane.[90–96] At 600 °C and for a contact time $\tau \simeq 30$ s, the yield of aromatic hydrocarbons relative to the paraffin passed through the system ($A_{C_2H_6}$) was 10% on a specimen Si/Al = 18. Under the same conditions, the degree of conversion of propane was appreciably higher. In the range 500–600 °C, the degree of conversion of propane ($x_{C_3H_8}$) varied from 72 to 98%, while $A_{C_3H_8}$ varied from 14 to 37%. At $T \geqslant 600$ °C and for $\tau \geqslant 20$ s, propane undergoes a thermal transformation: $x_{C_3H_8} = 40-80\%$.[97,98] In the presence of a pentasil of the type of ultrasil with Si/Al = 22 for $x_{C_3H_8} = 93\%$ and $A_{C_3H_8} = 24\%$ (600 °C, $\tau = 30$ s), most of the propane was converted into methane (37%), ethane (21%), and C_2-C_4 alkenes (14%).[99,100] On silicalite containing less than 0.03 wt.% Al, the main reaction pathway at 630 °C and for $\tau \simeq 5$ s was the formation of C_1-C_3 hydrocarbons (88%), while $A_{C_3H_8}$ did not exceed 3%.[101] On type H-TsVK pentasil (Si/Al = 30), at 600 °C and for $\tau = 8$ s, $S_{arom} \simeq 10\%$ for $x_{C_3H_8} = 67\%$.[102] Under these conditions, ethane was not converted into aromatic hydrocarbons, while in the reaction with isobutane A reached 23%.

The aromatisation of propane has also been studied under relatively mild conditions (500–550 °C, $\tau \leqslant 10$ s, $p_{C_3H_8} = 0.01-0.1$ MPa) where the contribution of the thermal process is insignificant.[101–104] The liquid catalytic reaction mixture consisted, as at 600 °C, only of aromatic hydrocarbons, among which benzene, toluene, and xylenes predominated. Despite the fact that the reaction conditions and the compositions of the catalyst in a number of studies were different,[101–103] S_{arom} and the proportions of the aromatic C_6-C_8 hydrocarbons at 500–550 °C proved to be almost identical: 25–30% of benzene, 46–50% of toluene, and 20–26% of xylenes plus ethylbenzene with $S_{arom} = 25-30\%$. Only in some instances[104,105] did S_{arom} reach ~50% at 500–650 °C.

Apart from temperature and contact time, an important factor influencing the degree and nature of the transformation of lower paraffins in the presence of pentasils is the ratio of the concentrations of silicon and aluminium in their lattices. The role of the composition of the skeleton of decationated pentasils in the aromatisation of propane and isobutane has been studied.[100,106–111]

An increase in the Si/Al ratio in ultrasils from 22 to 95 led to a decrease in $x_{C_3H_8}$ from almost 100 to 42% (at 600 °C and for $\tau \simeq 30$ s).[106] Simultaneously with the falling degree of conversion, the activity of the catalyst fell in the aromatisation, cracking, and coke formation reactions and to a lesser extent in the dehydrogenation of propane.[100]

The activity of pentasils of type H-TsVK and H-TsVM with Si/Al = 15–140 in the transformations of propane and isobutane[108–110] also increased appreciably with increase in the content of aluminium [Al] in the skeleton (Fig. 4). The quantity $x_{C_3H_8}$, which increases monotonically with increase in [Al], reaches ~80% at 600 °C and for $V = 450$ h^{-1} on specimens with Si/Al = 15–24. The dependence of $A_{C_3H_8}$ on the composition of pentasils has a somewhat different character (Fig. 4, curve *2*). The plot shows clearly two sections, one of which corresponds to the variation of A with increase in [Al] from 0.3 to 1.4 wt.% and the other corresponds to the variation of A as [Al] increases from 1.4 to 3.2 wt.%. On zeolites containing ≤1.4 wt.% Al, $A_{C_3H_8}$ ranges from 5 to 8%, which is almost identical with the yield of aromatic hydrocarbons on quartz, i.e. under the conditions of the thermal conversion of propane. The aromatisation of the more reactive isobutane does not require as much Al in the skeleton as for the transformation of propane,[109] but the maximum value of $A_{C_4H_{10}}$ (42% at 600 °C and for $V = 450$ h^{-1}) was obtained on the catalyst with Si/Al = 20.

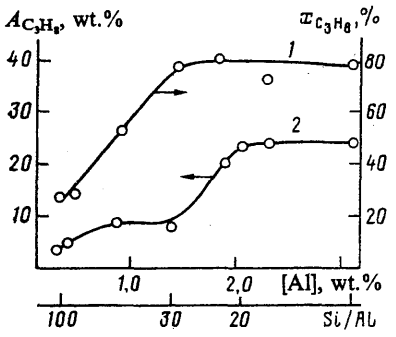


Figure 4. Dependence of the degree of conversion of propane (curve *1*) and of the yield of aromatic hydrocarbons at 600 °C (curve *2*) on the aluminium concentration in the pentasil skeletons.[109]

The composition of the skeleton influences significantly not only the activity of pentasils but also the selectivity of their action. Fig. 5 presents the dependence of $A_{C_3H_8}$ on $x_{C_3H_8}$. The degree of conversion was varied by varying the temperature for constant τ. The principal characteristic feature of the relations obtained is the linear variation of A, the straight lines on the plot starting from the origin of coordinates. This indicates the constancy of S_{arom} within the limits of each series of catalysts. All the pentasils in the H-form investigated can be divided into two groups. The first contains specimens with Si/Al ranging from 49 to 140; in their presence, propane is converted into aromatic hydrocarbons with the lowest selectivity (S_{arom} = 15%). The second group comprises pentasils with a comparatively high [Al] (Si/Al = 18–24), on which S_{arom} = 28%.

It is noteworthy that the principal pathway followed in the conversion of C_3–C_5 paraffins on decationated pentasils is the cleavage of the molecules of the initial hydrocarbons and reactions involving the resulting C_2–C_3 unsaturated products. For example, on a specimen of the H-TsVK pentasil with Si/Al = 140, the degree of conversion of isobutane at 600 °C reached 60%, whereas $A_{C_4H_{10}}$ did not exceed 13%.[109] The principal isobutane conversion products under these conditions were methane, ethane, and propene, whose overall yield was 40%. Pentane is cracked on pentasils at lower temperatures than propane and isobutane.[112,113] At 450 °C on an H-ZSM-5 specimen with Si/Al = 26, ~50% of pentane is converted into propane with $S_{arom} \simeq 15\%$.[112] As for the transformations of the C_3–C_4 paraffins, the activity of the decationated pentasils in the aromatisation of pentane depends on the composition of the skeleton and increases sharply with increase in [Al]. However, there is a simultaneous increase in the overall degree of conversion, so that S_{arom}, measured for constant x, changes little as Si/Al is varied from 26 to 450.[112]

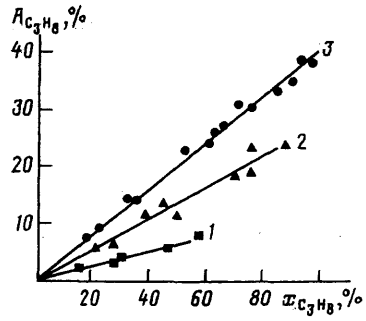


Figure 5. Dependence of the yield of aromatic hydrocarbons on the degree of conversion of propane in the presence of H-pentasils (curves *1* and *2*) and Zn-pentasils (curve *3*) with different Si/Al ratios:[110] *1*, 49–140; *2*, 18–24; *3*, 20–140.

Thus decationated pentasils of different composition are capable of converting C_2–C_5 paraffins into aromatic hydrocarbons, but the ratio of the rates of the target dehydrocyclisation reaction and the cracking side reaction is always appreciably less than unity.

2. Pentasils containing group VIII metals

As mentioned above, catalysts with bifunctional activity, which are active in dehydrogenation and are capable of converting the resulting alkenes into aromatic hydrocarbons, are most suitable for the aromatisation of C_2–C_4 alkanes.

Since decationated pentasils exhibit a high activity in the aromatisation of low-molecular-weight alkenes[3,28,114–124] (and to some extent even paraffins), one might expect that the introduction of a dehydrogenating component into their composition would promote the aromatisation of saturated hydrocarbons. Such bifunctional catalysts should also retain the principal advantages of pentasils—molecular sieve properties[16,17,125] and high resistance to coke formation.

According to patent data,[126] on Pt/H-ZSM-5 at 600 °C ethane is converted to a slight extent into a mixture of benzene, toluene, and xylenes. Detailed study of the catalytic properties of pentasils of the

H-TsVM type, containing Pt, Rh, or Pd, in the aromatisation of ethane and propane[90–97,127–130] led to the discovery of the specific features of the catalytic effect of each element, determined by its nature, in particular the unequal capacities of the M^{n+} cations for undergoing a change in the oxidation state in the oxidation-reduction treatment, and also by the possible differences in the degree of dispersion and in the distribution of the metallic phase within the channels and on the surface of the zeolite component of the catalyst.

It follows from Table 2 that $A_{C_2H_6}$ on Pt/H-TsVM is approximately twice as high as on the initial H-form. On metal-containing pentasils, the reaction proceeds at a lower temperature than on H-TsVM. Comparison with the results obtained on a Pt/Na-TsVM specimen showed that protic acid centres play an important role in the conversion of lower paraffins. If such centres are absent, then the reaction pathway changes radically—the principal ethane conversion products become ethylene and methane, while aromatic hydrocarbons are not formed. It was observed similarly that the main propane conversion product at 300 °C on Pt/Na-ZSM-5 is propene.[131] Catalysts modified by Pd and Rh exhibit a lower activity in the aromatisation of ethane than Pt/H-TsVM.[96,129,130] On raising the temperature to 600 °C, the degree of formation of methane increases and $A_{C_2H_6}$ falls sharply on Rh/H-TsVM.

Table 2. The transformations of C_2H_6 on modified pentasils *.[94]

Catalyst	T, °C	Yield of liquid products, %	Composition of liquid products, %		Composition of gas, %			
			C_5–C_8	C_9–C_{12}	CH_4	C_2H_4	C_2H_6	C_3, C_4
Na-TsVM	600**	0	—	—	2,5	7,5	90	traces
H-TsVM	600	10	95	5	3	1	96	»
0.5% Pt/Na-TsVM	600	traces	—	—	6,5	11,5	82	»
0.5% Pt/H-TsVM	500	10	74	26	18	4	75	3
	600	20	83	17	19	3	78	traces
0.5% Rh/H-TsVM	500	10	85	15	6	2	92	»
	600	2,5	—	—	29	4	67	»
0.5% Pd/H-TsVM	600	2,5	—	—	12	3	85	»
	600**	12,5	54	46	7.5	2,5	90	»

*Flow system, space velocity 120 h^{-1}, treatment of the catalyst with air at 550 °C for 5 h.

**Treatment of the catalyst with air (5 h, 550 °C) and hydrogen (5 h and 550 °C).

Metal–pentasil catalytic systems possess a number of characteristic features. In the first place, the activity of the catalysts depends to a large extent on the conditions in their preliminary treatment. Specimens treated with air or with air and hydrogen in succession are much more active than catalysts reduced directly with hydrogen without preliminary heating in a stream of air (Table 3). The study of the catalyst by X-ray photoelectron spectroscopy (XPES) and electron microscopy made it possible to explain the results of the catalytic experiments.[94,96,97,127–130] Direct treatment with hydrogen leads to the complete reduction of platinum to the zerovalent state and induces the migration of metal particles to the outer surface. Large crystallites, approximately 10 mm in size, are then formed. On heat treatment in air without reduction, approximately 60% of platinum is present as Pt^{2+} ions. Oxidative treatment at 350–500 °C promotes the migration of cations into the interior of the channels. An appreciable proportion of the Pt^{2+} cations then remain in an isolated state. Heat treatment in air is accompanied by the reduction of some of the metal cations to an intermediate or zerovalent state.[130] The Si/Al ratio in the surface layer also increases on heat treatment. This may be caused by the migration of the aluminium outside the skeleton or by the "shielding" of the aluminium as a consequence of the localisation of the cations near the aluminium–oxygen tetrahedra. If the catalysts are treated with air before reduction, it is possible to obtain extremely finely dispersed particles (< 1 nm) with a very narrow distribution with respect to size.[127–130,132] The platinum particle size in the Pt/H-TsVM catalyst was estimated by electron microscopy[127,130,131] and by H_2–O_2 titration,[133] similar results being obtained in both cases. According to the present authors' data,[129] fine metal particles are more active in aromatisation and hydrogenolysis reactions.

Table 3. The influence of the state of the metal and of the degree of its dispersion on the catalytic properties of the M/H-ZSM systems in ethane aromatisation and hydrogenolysis reactions.[129]

M	Treatment of catalyst**	State of metal (%)	Particle size, nm	Aromatisation*		Hydrogenolysis
				yield of AH***, %	S_{arom}	turnover number, s^{-1}
Pt	1	Pt^{2+} (60) Pt^0 (40)	1–2	18	18–20	—
	2	Pt^0 (100)	0,8	15	13–17	9,6
	3	Pt^0 (100)	10	1,5	4,5	0,55
Rh	2	Rh^0 (65) Rh^+ (35)	1–2	13	25	0,54
	3	Rh^0 (75)	3–5	0,9	7,5	0,05

*The aromatisation temperatures for Pt and Rh were 550 and 450 °C; the corresponding temperatures for hydrogenolysis were 420 and 250 °C.

** *1*, At 550 °C in air; *2*, at 550 °C in air and at 450–520 °C in H_2; *3*, at 450–520 °C in H_2.

*** AH = aromatic hydrocarbons.

The influence of the conditions in the preliminary treatment of Pt/H-ZSM-5 on the degree of dispersion of the metallic phase has also been observed in other studies.[134–136] According to the data of Engelin et al.,[134] finely dispersed platinum particles (1–2 mm) are formed on slow heating (1 K min^{-1}) of the catalyst in a stream of oxygen diluted with helium. Appreciably larger crystals (⩾10 nm) are formed at a heating rate up to 10 K min^{-1} and only a small proportion of the platinum is localised within the channels. In order to obtain platinum crystallites whose size is less than 1 nm, preliminary stepwise heating of the catalyst in a stream of air (180–300 °C) at a rate of 1 K min^{-1} followed by reduction by

hydrogen and subsequent flushing with nitrogen at 530 °C necessary.[135]

The data examined have shown that the reduction of platinum in pentasils leads, as in faujasites,[137,138] to the localisation of metal atoms or clusters in the zeolite structure and to their partial migration to the outer surface. Such behaviour is also characteristic of the Rh/H-TsVM catalyst.[130]

Another characteristic feature of the catalytic effect of metal-containing pentasils consists in the so-called "running in" of the catalyst during the reaction. This effect is strikingly manifested when aromatisation is carried out under pulse conditions, "running in" not being observed on hydrogen-forms without the metal. One of the possible causes of this phenomenon may be a change in the oxidation state of the metal during the reaction owing to its interaction with the carrier and the catalytic reaction products. The influence of the reaction medium on the formation of the active state of the metal has been investigated in relation to the aromatisation of ethane in the presence of platinum- and rhodium-containing pentasils of the type H-TsVM.[96,97,127,129,130] In order to elucidate the causes of the "running in" phenomenon, a study was made, simultaneously with the study of the catalytic activity of Pt/H-TsVM, of the electronic state of platinum during aromatisation by comparing the X-ray photoelectron spectra of the specimens transferred from the catalytic reactor to the spectrometer. In a specimen heat-treated in a stream of air (Fig. 6, curve *1*), platinum was readily reduced with increase in the number of ethane pulses and the yield of the aromatic hydrocarbons rose and reached a maximum. At this point, the platinum has a positive charge $\delta+$. On a catalyst reduced in a stream of H_2, the nature of the dependence of the yield on the number of pulses remain the same and the maximum yield also corresponded to the appearance of a charge $\delta+$. According to X-ray photoelectron spectroscopic data, the Pt4*f* parameters changed appreciably during the "running in" of the catalyst.[96,127,129,130] Analysis of the photoelectron spectra made it possible to differentiate two types of platinum centres differing in their spectroscopic characteristics: (1) platinum particles whose X-ray photoelectron spectra have been appreciably displaced (by 1.2 eV) relative to the spectrum of the metal; (2) platinum particles in the spectra of which there is no positive shift or a slight negative shift is observed (for example, after ten ethane pulses). It has been suggested[127,129,130] that the positive shift is at least partly due to the transfer of electron density from platinum to the electron-accepting sections of the carrier. During the "running in" of the catalyst, the positive charge on the platinum increases (Fig. 6) and then, after the attainment of the maximum activity, diminishes somewhat, although some of the metallic centres carry a more positive charge both in the initial and in the deactivated specimens.

Large platinum crystallites localised on the outer surface of the zeolite belong to centres of the second type. On the basis of modern ideas concerning the strong interaction of the metal with the carrier,[139] it has been suggested[127,129,130] that under severe reaction conditions (550–600 °C, hydrocarbons, hydrogen), oxygen vacancies may be formed in the pentasil lattice and Al^{3+} ions located in the vicinity of the platinum particles may be reduced. The interaction of platinum atoms or clusters with such electron-donating centres should lead to the appearance of an excess electron density on platinum, which has in fact been observed experimentally by X-ray photoelectron photoscopy.

Summarising data on the state of platinum in Pt/H-TsVM catalysts and taking into account at the same time the change in catalytic properties, one may postulate that there exists a special form of platinum ($Pt^{\delta+}$ with a shift of approximately 1.2 eV) which in fact determines the activity of the catalysts in the aromatisation of ethane.

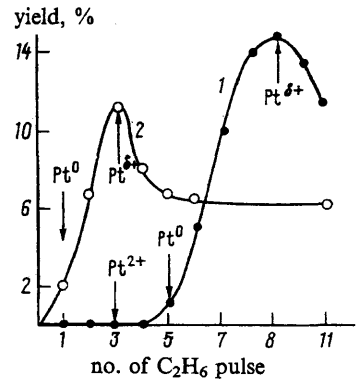


Figure 6. Dependence of the yield of the ethane aromatisation products in the presence of Pt/H-TsVM on the number of pulses:[129] *1*, treatment with air; *2*, treatment with hydrogen.

The Rh-form of the H-TsVM pentasil behaves similarly to the platinum-form.[129,130] After treatment with hydrogen at 400–450 °C, an appreciable portion of rhodium (~40%) in the zeolite remains unreduced. Analysis of the X-ray photoelectron spectra during the aromatisation of ethane demonstrated the presence of two states of rhodium: a state close to the metallic state and one formally corresponding to Rh^+. The change of their relative contributions with increase in the number of ethane pulses is caused by the additional reduction of rhodium and the interaction of the zerovalent metal with the reaction mixture. A similar interaction had been observed earlier for aluminorhodium catalysts of the cyclotrimerisation of ethylene.[130] During the reaction, a significant change in the activity of the catalyst and in the electronic state of the metal occurred. A positive charge arose on rhodium clusters [the maximum shift was $\Delta E_b Rh3d_{5/2} \simeq 0.7$ eV].

A combined study of the catalytic properties of metal-containing pentasils and of the physicochemical properties of the platinum, rhodium, and palladium surfaces[90,92,94–97,127–130] made it possible to elucidate the role of the oxidation state and of the degree of dispersion of metals in the aromatisation of ethane. Evidently the same factors should determine the activity of similar catalysts also in reactions involving C_3-C_4 paraffins. It has been established that the method used to prepare the Pt/H-ZSM-5 catalysts has an appreciable influence on the degree of conversion of propane.[140,141] The specimen obtained by the ion exchange method proved appreciably more active than that in which platinum was introduced by impregnation with a $[Pt(NH_3)_4]Cl_2$ solution. These data were confirmed in other studies.[131,134,135] If part of the platinum is on the outer surface of the zeolite (which is characteristic of catalysts obtained by the impregnation method), then during the first 30–60 min of the experiment these particular metal particles are deactivated and the activity then varies during a long period, since the platinum surface centres located near the structural OH groups are very resistant to coke formation by virtue of the molecular sieve properties of pentasils.[134]

Thus the introduction of noble metals, in the first place platinum, leads to a significant increase in the yield of the products of the aromatisation of lower paraffins and in the selectivity of this process.

3. Pentasils modified by Group II and III elements in the periodic system

As mentioned in the preceding section, pentasils modified by platinum and other noble metals exhibit a high activity in the reactions of lower alkanes, but the selectivity of the aromatisation in their presence does not exceed 30%. In order to increase S_{arom}, pentasils modified by different elements (Ni, Co, Mo, W, Cd, Zn, Ga) were used, but the best results were obtained with the aid of zinc, cadmium, and gallium.[142–152] The modifying elements are introduced in different ways: by ion exchange, by impregnation, by the mechanical mixing of powders, and finally by the isomorphous substitution of aluminium in the lattice with formation of gallosilicates or zinc-silicates.[18,19,80,153–155]

The catalytic properties of Zn/H-ZSM-5 specimens prepared by ion exchange and of the initial decationated form of pentasil have been compared[101,103,156] in propane conversion processes at 450–550 °C and atmospheric pressure. The introduction of Zn^{2+} cations increases $x_{C_3H_8}$ by a factor of 1.5 and S_{arom} by a factor of 2. In aromatic products of the reaction of Zn/H-ZSM-5, the fraction of benzene and toluene is higher, while the content of C_8-C_9 alkylbenzenes is lower than on the unmodified zeolite.[102,103] The proportions of the gaseous hydrocarbons also change appreciably. Modification with zinc leads to a sharp decrease in the degree of conversion of propane into methane and to an increase in the ethane concentration.[101,102,109]

Higher temperature and longer contact times τ are required for the aromatisation of ethane on Zn-pentasils than for the aromatisation of propane. Zinc has an appreciable promoting effect in the aromatisation of ethane on H-TsVM and H-TsVK pentasils with different compositions.[98,157] With decrease in the Si/Al ratio from 32 to 15, $x_{C_2H_6}$ increased at 600 °C and τ = 30 s from 27 to 57%.[157] The maximum value S_{arom} = 35% was obtained on a specimen with Si/Al = 23 at 650 °C. With increase in the aluminium concentration in the zeolite skeleton, the yield of methane and naphthalenes increased and that of hydrogen and C_8 alkylbenzenes fell. On a type H-TsVM (Si/Al = 15) pentasil containing 0.5 wt.% of zinc, $x_{C_2H_6}$ = 32% and $S_{arom} \simeq$ 60% at 600 °C.[98]

Catalysts prepared by the ion exchange method have been used in some studies.[98,101,103] However, the ion exchange capacity of pentasils is low,[158] which precludes the variation of the concentration of the promoting agent within wide limits. According to calculations,[80] the maximum zinc content in pentasil cannot exceed 2 wt.% when the metal is introduced by ion exchange with Na^+ or NH_4^+ ions. Nevertheless the activity of the catalyst should evidently depend on the concentration of the modifying element.[80,117,118,159] A larger amount of the metal can be introduced by the impregnation method into pentasil than by ion exchange. Comparison of the H-TsVK pentasil specimens (Si/Al = 30), containing 0.5, 1.4, and 10 wt.% ZnO showed that the quantities $x_{C_2H_6}$ and $A_{C_2H_6}$ in their presence are greater the higher the zinc content, while in the propane and isobutane conversion reactions the specimens with 1.4 and 10 wt.% ZnO have similar activities.[102]

As in the case of the H-forms, the composition of the skeleton influences the catalytic activity of the Zn-containing pentasils.[103,108–111] On pentasils with Si/Al = 20, 49, 100, and 140, containing 1.5 wt.% Zn, the quantities $A_{C_3H_8}$ and $A_{C_4H_{10}}$ increase appreciably with increase in [Al].[109,110] At the same time, the composition of the skeleton does not affect S_{arom} for catalysts modified with zinc. It follows from Fig. 5 that all the points corresponding to the zinc-containing catalysts with different aluminium contents in the lattice lie on a single straight line starting from the origin of coordinates. The slope of this line corresponds to $S_{arom} \simeq$ 42%, which is greater by 1.5 than on similar unmodified pentasils.

The independence of S_{arom} of x indicates the simultaneous conversion of lower alkanes into aromatisation and cracking products. The increase in S_{arom} as a result of the modification with zinc is caused by the increase in the rate of aromatisation. This relation is evidently independent of the composition of the skeleton of Zn-pentasils and is determined solely by the content of the promoting element in the catalyst.

The composition of the skeleton of Zn-pentasils affects not only the overall catalytic activity but also the ratios of the individual aromatisation products. This is manifested particularly clearly when one examines the isobutane conversion products on pentasils with Si/Al = 20 and 140.[109] The ratios of the concentrations of C_8-C_{10} alkylbenzenes change most significantly. The relative yield of xylenes and ethylbenzenes increases with decrease in [Al]. An important feature of the conversion of lower alkanes on pentasils is the formation of condensed aromatic hydrocarbons, principally naphthalene and its alkyl derivatives. An increase in [Al] in the skeletons of Zn-pentasils favours the formation of naphthalene: the yield of these products at 600 °C is approximately 7 times greater on the specimen with Si/Al = 20 than on the catalyst with Si/Al = 140.

It is known[62,63] that the concentration of the acid centres of pentasils is proportional to [Al] and that their strength is independent of the ratio Si/Al. Consequently the catalytic activity of pentasils of different composition in aromatisation is determined by the number of acid centres, which is consistent with experimental data (see Figs. 4 and 5).

In order to elucidate the role of the acidity of the zeolite carrier in the aromatisation of propane, the catalytic properties of Zn/H-ZSM-5 and Zn/borosilicate specimens were compared.[103] It is known[160–162] that the acidity of borosilicates is significantly lower than that of H-ZSM-5 pentasils. At 550 °C and $P_{C_3H_8}$ = 101 kPa, neither the H-form of the borosilicate nor the borosilicate modified with zinc showed an appreciable activity ($x_{C_3H_8} \simeq$ 1.2–2.0%). The authors explained the inactivity of the H-form by the fact that the weak acid centres of the borosilicate are incapable of activating the propane molecules. However, Zn/borosilicate also proved to be inactive. The aromatisation of propane apparently requires the presence of not only zinc but also of a certain number of acid centres, such as, for example, those in the H-TsVK pentasil with Si/Al = 140.[108–110]

The introduction of another Group II element, namely cadmium, leads to an appreciable rise in activity and S_{arom}. The available information about the promoting effect of cadmium is contained principally in the patent literature.[163–165] A number of studies have been devoted to the systematic investigation of the role of cadmium in the aromatisation of lower paraffins on pentasils.[113,166,167] An almost twofold increase in $A_{C_4H_{10}}$ and S_{arom} has been observed after the introduction of even extremely small (~0.7 wt.%) amounts of cadmium. The degree of conversion of the initial paraffins did not increase after the introduction of cadmium. It is quite likely that the increase in S_{arom} as a result of the modification is associated with the decrease in the cracking activity due to the blocking of the strong protic centres of pentasil by cadmium.

Yet another extremely effective promoting agent for the catalysts of the aromatisation of lower paraffins is gallium.[80,103–105,112,143,144,168–171] According to patent data,[143,144,168] the selectivity of the aromatisation of ethane on Ga/H-ZSM-5 is $S_{arom} \sim 30\%$. An appreciably higher value of S_{arom} (60%) has been observed on the 2% Ga/H-TsVM catalyst at 600 °C and for $\tau \sim 30$ s.[171]

Gallium-containing pentasils, prepared by the ion exchange method, acquire an increased capacity for aromatising lower alkanes after heat treatment in the range 400–700 °C.[80] The influence of the method of preparation of Ga-pentasils on their activity in the aromatisation of C_2-C_4 alkanes has been investigated.[171] Catalysts based on the H-TsVM pentasil (Si/Al = 15) have been prepared in three different ways: by combining the ion exchange of the NH_4^+ cations for Ga^{3+} with subsequent impregnation of the zeolite with the mother liquor (method A); by impregnating the H-form of the zeolite with a solution of gallium nitrate (method B); by the dry mixing of pentasil and gallium oxide powders with subsequent heat treatment in a stream of air at 550 °C by a procedure similar to that of Kucherov and Slinkin[172,173] (method C). Specimen A proved to be the most active, with specimen C showing an appreciably lower activity. A 1:1 mechanical mixture of H-ZSM-5 and Ga_2O_3 has an appreciably higher activity in the aromatisation of propane than pure H-ZSM-5.[174,175]

The catalytic properties of pentasils containing different amounts of gallium in the reactions of C_2-C_5 paraffins have been studied in detail.[103–105,112,170,171,176,177] The introduction of even 0.5 wt.% of gallium appreciably accelerates the aromatisation of ethane and propane and increases A by a factor of 1.3–1.5 compared with the H-form.[171] A gallium concentration of approximately 2 wt.% appears optimal. In the presence of the 2% Ga/H-TsVM catalyst, the quantity A ranges from 30% for ethane to 55–60% for propane and isobutane. In another study,[176] the 6% Ga/H-ZSM-5 catalyst proved to be most active in the conversion of propane. According to Kitagawa et al.,[104] S_{arom} for propane increases sharply after the introduction of ~1 wt.% of gallium and reaches the maximum value (70%) on the 1.6% Ga/H-ZSM-5 (Si/Al = 31) specimen at 500 °C. An even higher selectivity in the aromatisation of propane (up to 85%) on Ga-pentasils was achieved by Tan et al.,[105] S_{arom} being somewhat higher on the Ga/Na-ZSM-5 specimen than on Ga/H-ZSM-5. However, these results do not agree with the data of other investigators[80,103,104,112,170] and are apparently too high.

Ga-pentasils also exhibit a much higher efficiency in the aromatisation of pentane than the decationated specimens.[112] Whereas the maximum value S_{arom} = 38% on H-ZSM-5 (Si/Al = 26) at 600 °C, on the Ga-pentasil with the same composition of the skeleton more than 50% of pentane is converted into aromatisation products. For low degrees of conversion of pentane ($x < 20\%$), the yields of the reaction products on Ga- and H-pentasils are approximately the same. The formation of aromatic hydrocarbons becomes appreciable only for $x_{C_5H_{12}} > 20\%$ and on Ga/H-ZSM-5 the quantities $A_{C_5H_{12}}$ and S_{arom} are significantly higher than on the unmodified catalyst and cracking takes place to an appreciably smaller extent.

The activity of gallium-modified pentasils depends significantly on the composition of the carrier skeleton.[170,177] Active and selective catalysts are obtained only when pentasils with a comparatively high aluminium content (Si/Al = 20) are used. In this case, the values of S_{arom} for isobutane and propane are respectively 60 and 50%. When a carrier with a low aluminium content (Si/Al = 140) is used, S_{arom} diminishes by a factor of approximately 1.5. Similar changes in A and S_{arom} as a function of the Si/Al ratio have been observed also in the aromatisation of pentane.[112] This relation is characteristic only of Ga-pentasils. As mentioned above, on Zn-pentasils with different compositions of the skeleton the aromatisation of propane occurred with identical selectivities.[109,110] The formation of highly active aromatising centres in Ga-pentasils probably requires a combination of a large number of strong B-centres of the carrier and gallium atoms.

The capacity for the activation and aromatisation of lower paraffins is possessed also by certain elementosilicates with the pentasil structure.[18,19,34,153–155,178–187] The modifying element is introduced into such systems in the stage involving hydrothermal synthesis.[37,38] There is then a possibility of obtaining crystalline silicates with a pentasil structure containing skeletal atoms of other elements instead of aluminium. We may note that proof of the isomorphous substitution of silicon atoms in the lattice is frequently either lacking or is inadequate. Gallosilicate, where the presence of Ga atoms in the skeleton has been reliably established by different physical methods, is an exception.[188] These questions have been discussed in detail in a number of communications.[18,19,38] Among the elementosilicates containing Mn, V, Co, Cr, Ti, Ni, Ga, and Zn[179] which have been investigated, the greatest selectivity in relation to aromatisation is shown by zinc-silicates and gallium-silicates.[34,180,181,185–187] On Zn-silicates, where Si/Zn = 140 at 600 °C, $V = 2000\ h^{-1}$, and $N_2/C_3H_8 = 4$, we have $x_{C_3H_8} = 62-64\%$ with $S_{arom} = 43-44\%$.[179,186,187] In contrast to this, the activity and selectivity of Ga-silicates depends to a large extent on the composition of the skeleton. With decrease in Si/Ga from 40 to 15, the quantity $x_{C_3H_8}$ rises from 26 to 84% and S_{arom} increases from 38 to 67%.[34,156,179,186] On the H-ZSM-5 pentasil (Si/Al = 24), S_{arom} did not exceed 30% under similar conditions.[103] Comparison of the results obtained on Ga-silicates and Ga/H-ZSM-5 shows that the isomorphous substitution of silicon by gallium leads to an appreciably greater increase in S_{arom} than treatment with gallium aluminosilicate salts having the pentasil structure.

An important feature of Ga-silicates is the dependence of the activity and selectivity of the conditions on the duration of the reaction and the preliminary activation. With increase in the number of "reaction–regeneration" cycles, both A and S_{arom} in the propane aromatisation reaction on the Ga-silicate increased.[182] According to IR spectroscopic data, such a change in catalytic properties is associated with the emergence of gallium atoms from the skeleton.[182] The increase in the activity of Ga-silicate in the cracking of n-butane after the hydrothermal treatment of the catalyst has been explained by the appearance of extra-skeletal gallium in the form of amorphous Ga_2O_3.[183]

The data presented above referred to Zn- and Ga-silicates synthesised under hydrothermal conditions from reaction mixture in which the aluminium-containing component had been replaced by zinc or gallium salts in the gel-formation stage.[180,181,185,189] Another method of synthesis of gallosilicates has been proposed.[178] It consists in the isomorphous substitution of Si^{4+} ions in the silicalite II lattice (its structure is identical with that of the ZnSM-11 pentasil) by Ga^{3+} cations by treating the silicalite with an aqueous sodium gallate solution at 100 °C. According to X-ray diffraction and NMR spectroscopic data, the material thus obtained is a pentasil containing Ga^{3+} cations in its skeleton. The introduction of gallium into the silicate lattice leads to the manifestation by the latter of an appreciable catalytic activity in the n-butane aromatisation reaction (at 550 °C, $A_{C_4H_{10}} = 29\%$). We may note, however, that the conclusion that silicon ions are substituted by gallium ions[178] was not confirmed in a later investigation.[190]

The use of bimetallic catalysts with the pentasil structure—Pt/Zn-silicates and Pt/Ga-silicates—for the aromatisation of lower paraffins is of great interest.[34,179,180,185] The characteristic features of the catalytic action are determined by the combination of the striking dehydrogenating properties of platinum with the unusual molecular sieve and acid properties of elementosilicates, which are capable of converting C_3-C_5 paraffins and alkenes into aromatic hydrocarbons with a high selectivity. Fig. 7 illustrates the temperature dependence of the degree of conversion of ethane, propane, n-butane, and n-pentane on a Pt/Ga-silicate.[19] Other conditions being equal, the degree of conversion is higher the higher the molecular weight of the paraffin. The quantities S_{arom} are 41.5% for C_2H_6, 57.6% for C_3H_8, 31.9% for n-C_4H_{10}, and 35.8% for n-C_5H_{12}. These results were obtained at 500 °C and $V = 2000\ h^{-1}$ and for a paraffin : carrier gas (nitrogen) concentration ratio of 1 : 4. In the propane conversion reaction, Pt/Ga-silicates are more active than the initial carriers with Si/Ga = 15–40; the quantities S_{arom} for these systems are similar and are much higher than for the Pt/H-ZSM-5 catalysts.

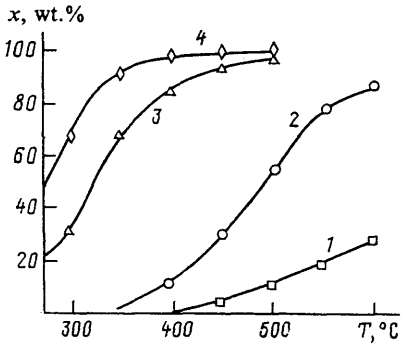


Figure 7. Temperature dependence of the degree of conversion of C_2-C_5 paraffins on the Pt/Ga-silicate catalyst (Si/Ga = 21):[19] *1*, C_2H_6; *2*, C_3H_8; *3*, C_4H_{10}; *4*, C_5H_{12}.

The introduction of platinum into Ga- and Zn-silicates retards the deactivation of the catalysts.[34,178,180] Whereas $x_{C_3H_8}$ fell from 80 to 40% in 10 h on the initial decationated specimens, on platinum-containing catalysts it remained above 50% even after 24 h. Such increase in stability has been attributed[179,180] to the hydrogen spill-over effect.[191–193] The hydrogen activated on platinum can interact with condensed aromatic structures and can "clean" the surface by removing adsorbed condensation products. This hypothesis has been confirmed by the results of a number of studies[133,194,195] in which the role of the hydrogen spill-over in adsorption processes on platinum-, palladium-, and nickel-containing pentasils was investigated. For example, activated hydrogen ("spill-over hydrogen") is capable of displacing chemisorbed CO and CH_4 molecules from the platinum surface.[133,194]

Bifunctional Pt/elementosilicate catalysts are extremely promising for practical use, because they retain their activity in the aromatisation of lower alkanes much longer than other modified pentasils. According to a number of workers,[34,179,196] the activity of the Pt/Ga-silicate catalyst, estimated from $x_{C_3H_8}$, remained unchanged for 1000 h in the "reaction (25 h)–regeneration (0.5 h)" regime at 550 °C and $V = 2000\ h^{-1}$ and for the ratio $C_3H_8 : N_2 = 1 : 4$.

4. The mechanism of the aromatisation of lower paraffins on pentasils

As shown above, the H-forms of pentasils exhibit an appreciable activity in the reactions of C_2-C_5 paraffins. The ability of these catalysts to activate saturated molecules is due to the presence of strong B-centres on which the degradation and conversion of alkenes takes place. Analysis of the dependence of the proportions of the lower paraffin conversion products on the degree of conversion makes it possible to discuss the possible routes to the formation of aromatic and aliphatic hydrocarbons with participation of acid protic centres of pentasils. Fig. 8 presents the dependence of the yields of certain pentane,[112] isobutane,[177] and propane[104] conversion products on x. The character of these curves shows that aromatic hydrocarbons are not the primary reaction products. For low degrees of conversion ($x \leqslant 20\%$), pentane and isobutane are converted into propane with a selectivity in excess of 60%.[113,167]

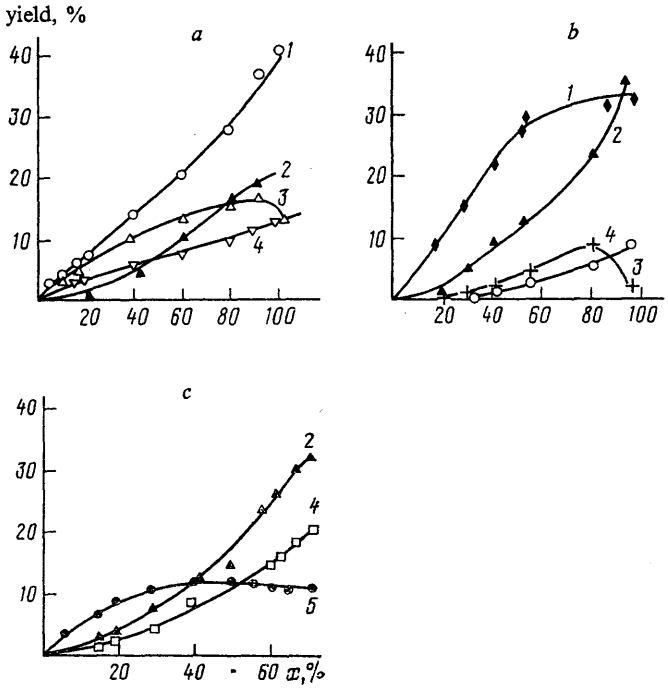


Figure 8. Dependence of the yield of the pentane (*a*), isobutane (*b*), and propane (*c*) conversion products in the presence of H-pentasils on the degree of conversion:[104,112,177] *1*, yield of propane; *2*, overall yield of aromatic hydrocarbons: *3*, overall yield of propene and butenes; *4*, overall yield of ethane and ethylene; *5*, overall yield of ethylene and propene.

Small amounts of propene and butenes are formed simultaneously. The yield of C_3-C_4 alkenes passes through a maximum, which indicates the participation of unsaturated hydrocarbons in subsequent reactions. For $x \leqslant 20-30\%$, propane is converted

mainly into ethylene and methane. These hydrocarbons can be formed via a stage in which propane decomposes to methane and the $C_2H_5^+$ cation with participation of protons in accordance with the scheme

$$C_3H_8 + H^+ \rightarrow \left[\begin{matrix} H_3C \\ \diagdown \\ H \end{matrix} \cdots\cdots CH_2CH_3\right]^+ \rightarrow CH_4 + \overset{+}{C}H_2{-}CH_3.$$

The possibility of the occurrence of this reaction has been demonstrated for the conversion of propane in a strongly acid medium[197] and of C_4 alkanes in the presence of solid superacids.[198]

The question of the contribution of the cracking reaction to the overall conversion of lower alkanes on zeolite active centres is of fundamental importance for the understanding of the mechanism of the catalytic action of decationated pentasils. For low conversions, n-butanes and isobutanes undergo the following transformations:[199]

$$\text{n-}C_4H_{10} \swarrow \searrow \quad C_2H_6 + C_2H_4 \quad CH_4 + C_3H_6, \qquad \text{iso-}C_4H_{10} \rightarrow CH_4 + C_3H_6.$$

Two mechanisms of the cracking of lower alkenes are known: the carbenium ion and radical mechanisms. A scheme taking into account the participation of protic centres in the formation of carbenium ions was presented above. On Lewis acid centres, a hydride ion may be abstracted from the alkane molecule:

$$CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2\overset{+}{C}HCH_3 + H^- .$$

According to the results of two investigations,[199,200] the radical reactions of lower alkanes make a considerable contribution on solid amorphous superacids—HU and H-ZSM-5 zeolites. In this case, the initial stage in the cracking process involves the appearance of radical-cations, which are subsequently converted into alkenes. For example, the formation of isobutene from isobutane can proceed via a stage involving the formation and subsequent decomposition of a surface radical-cation with participation of electron-accepting (EA) centres:

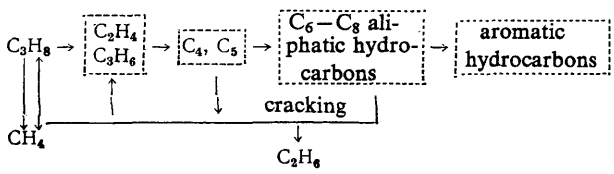
$$\text{iso-}C_4H_{10} + EA \xrightarrow{k_1} [\text{iso-}C_4H_{10}^+][EA^-]$$

$$\text{iso-}C_4H_{10}^+ \xrightarrow{k_1} \text{iso-}C_4H_8 + H_2 + EA \qquad \xrightarrow{k_2} C_3H_6 + CH_4 + EA .$$

It is believed[104] that under the conditions of high conversion, propane molecules are activated as a result of the abstraction of a hydride ion by the carbenium ion R^+:

$$C_3H_8 + R^+ \rightarrow RH + \overset{+}{C}H_3CHCH_3.$$

The $C_3H_7^+$ ion formed is converted either into propene or into a carbonium ion with a larger number of carbon atoms. The overall mechanism of the propane conversion reaction on H-ZSM-5 assumes the following form:



Thus the capacity of the decationated forms of pentasils for the deactivation and subsequent dehydrocyclisation of lower paraffin molecules is determined by the presence of strong acid centres on which protonation, hydride ion abstraction, and cracking reactions take place and lead to the formation of unsaturated structures. The reactions of lower paraffins on the acid centres of pentasils apparently proceed with participation of both carbenium ions and radical-cations. The important role of the acidity of the H-forms of pentasils in the aromatisation of lower paraffins is indicated, in particular, by data[104] according to which the dependence of $x_{C_3H_8}$ on the activation temperature in the presence of NH_4-ZSM-5 passes through an extremum. The catalyst heated in a stream of dry air at 580 °C shows the maximum activity. The decrease in the degree of conversion on further increase in the activation temperature is induced directly by the decrease in the concentration of acid hydroxy-groups owing to dehydroxylation.

In contrast to the decationated forms, pentasils modified by Group (II), (III), and (VIII) metals are bifunctional catalysts to the activities of which both the protic acid centres of the carrier and the centres containing metal atoms contribute.

It follows from the data presented that pentasils containing platinum or other Group (VIII) metals are effective catalysts of the aromatisation of lower paraffins and that in terms of activity and selectivity they are superior to the M/Al_2O_3 catalysts. In the first studies on the aromatisation of C_3-C_5 paraffins in the presence of Pt/Al_2O_3, a possible mechanism of this reaction taking into account the bifunctional nature of the deposited metallic catalysts was already proposed.[86,87] We shall examine certain principal conclusions arising from these studies, because the characteristic features of the conversion of lower paraffins on metal-containing pentasils and Al_2O_3-based catalysts are undoubtedly similar.

A consecutive mechanism of the dehydrocyclodimerisation of alkanes includes three stages: (1) the dehydrogenation of alkanes to alkenes and alkadienes; (2) the dimerisation of the alkenes formed—mainly on acid centres and to some extent by a thermal pathway via conjugated dienes; (3) the aromatisation of unsaturated hydrocarbons on the metallic component and on the acid centres. The side reactions are the isomerisation and disproportionation of the aromatic alkyl-substituted products as well as the cracking of the aliphatic hydrocarbons and coke formation. The selectivity in the conversion of lower paraffins into various products must be determined by the relative rates of the individual stages. The set of reactions of n-butane is presented below:[86]

$$C_4H_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_4H_8 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C_8H_{16} \xrightarrow{k_3} C_6H_4(CH_3)_2 .$$

$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow k_5$$

$$H_4C + C_3C_3 \qquad + C_5$$

According to Csicsery's ideas,[86] on the optimum aromatisation catalyst the rate of dehydrogenation should be higher than the rate of dimerisation ($k_1 > k_2$). In addition, the condition $k_3 > k_2$ should hold and it is most important that the aromatisation should occur much faster than cracking ($k_5 \ll k_3 \geqslant k_2$).

We shall now compare data for the aromatisation of lower paraffins on Pt/Al_2O_3 with the results of kinetic studies[135] on Pt/H-ZSM-5. Analysis of the dependence of the proportions of the isobutane conversion products on the contact time in the presence of 0.8% Pt/Al_2O_3 [76,87] and of the dependence of the yield of propane conversion products on the degree of conversion in the presence of 0.5% Pt/H-ZSM-5 (Fig. 9) shows that in both cases the

aromatisation consists of a set of consecutive and parallel reactions, where the key reaction is the dehydrogenation of the initial paraffin. The presence of an extremum in the variation of the content of the corresponding alkenes (butenes and propene) shows that they are the primary products of the conversion of the alkanes. Both catalysts are extremely active in cracking: the content of C_1-C_2 hydrocarbons exceeds the content of aromatic products, especially on Pt/Al_2O_3. On Pt/H-ZSM-5, S_{arom} can reach very large values, although a considerable proportion of the initial propane is also converted into methane and ethane. The nature of the carrier plays an important role in the aromatisation of saturated hydrocarbons. Whereas alumina is inactive in the reactions of lower paraffins and its activity is low in the aromatisation of alkenes,[201–203] the decationated pentasils readily convert propane and isobutane into aromatic hydrocarbons (see above). Thus both the metallic component and the carrier contribute to the activity of the Pt/H-ZSM-5 catalyst. Another cause of the increased aromatising capacity of Pt/H-ZSM-5 compared with Pt/Al_2O_3 is resistance to coke formation. Whereas Pt/Al_2O_3 is deactivated 15–20 min after the start of the experiment,[76,87] the stable operation of Pt/H-ZSM-5 continues for about 6 h.[134,135]

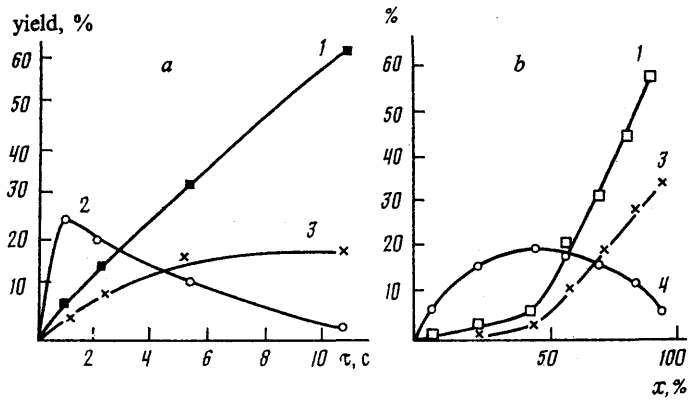


Figure 9. The proportions of the isobutane conversion products on Pt/Al_2O_3 (*a*) at 550 °C and of propane conversion products on Pt/H-ZSM-5 (*b*) at 530 °C:[76,135] *1*, overall yield of methane and C_2 hydrocarbons; *2*, yield of butenes; *3*, overall yield of aromatic hydrocarbons; *4*, yield of propene.

Judging from the data of Gnep et al.,[135] the rate of hydrogenolysis of the initial propane on Pt/H-ZSM-5 is clearly lower than the rate of hydrogenation of ethylene—one of the primary propane conversion products on H-ZSM-5. Thus platinum participates not only in the dissociation of C–C bonds but also in the formation of new C–H bonds as a result of hydrogenation and hydrogenolysis reactions. These two reactions always accompany the aromatisation of lower paraffins on platinum-containing pentasils and are the main cause of the decrease in S_{arom}.

The promoting effect of zinc, cadmium, and gallium as well as the cooperative effect of deposited Group VIII metals are due to the dehydrogenating properties of the M–pentasil systems. Kinetic data, which have been analysed in a number of studies,[104,167,176,177] lead to this conclusion.

Fig. 10 presents curves for the accumulation and consumption of the individual propane, isobutane, and n-pentane conversion products on Zn- and Ga-pentasils. An extremum in the dependence of the yield of C_3-C_5 alkenes on x or τ is characteristic of these catalysts as well as Group VIII metal–pentasil systems, which can be regarded as evidence for the intermediate formation of unsaturated structures from lower paraffins and their subsequent conversion into aromatic hydrocarbons. The principal unsaturated propane conversion product is propene. Apart from butenes, propene is formed from isobutane; olefinic pentane conversion products contain ethylene, propene, butenes, and pentenes.

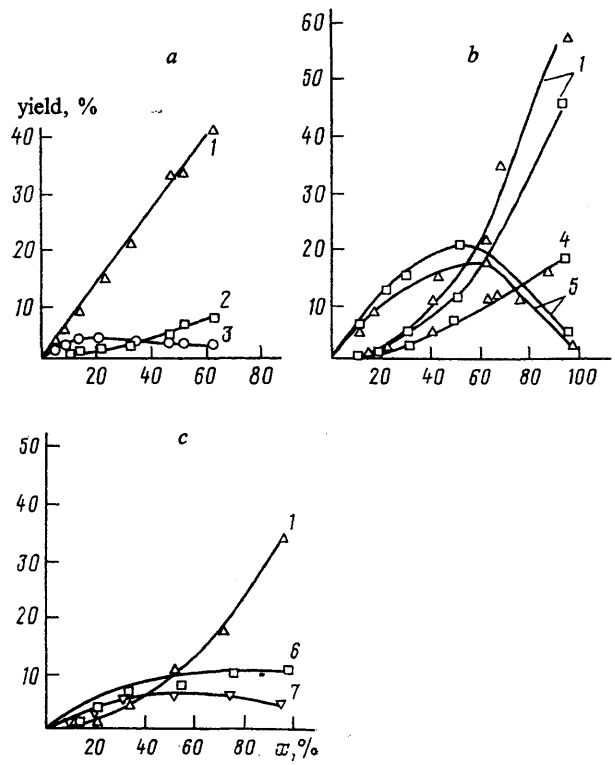


Figure 10. The proportions of the propane conversion products on Ga/ZSM-5 (*a*), the isobutane conversion products on Zn/ZSM-5 (squares) and Ga/ZSM-5 (triangles) (*b*), and the pentane conversion products on Ga/ZSM-5 (*c*) at 500 °C:[112,177] *1*, overall yield of aromatic hydrocarbons; *2*, overall yield of ethane and ethylene; *3*, overall yield of ethylene and propene; *4*, yield of propane; *5*, overall yield of propene and butenes; *6*, overall yield of butanes and butenes; *7*, yield of propene.

According to Bondarenko et al.,[177] under the conditions of low conversion the principal pathway in the reaction of isobutane on Zn- and Ga-pentasils is dehydrogenation, while on the H-form it is cracking. Appreciable amounts of aromatic hydrocarbons are formed only for comparatively high values of $x_{C_4H_{10}}$. Thus $A_{C_4H_{10}} \simeq 10\%$ is obtained for $x \simeq 50\%$ on Ga-pentasil, for 60% on Zn-pentasil, and for 85% on H-pentasil. The results of the calculation of the rate of accumulation of aromatic hydrocarbons for

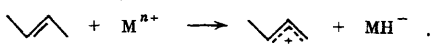
x = const. $\simeq$ 50% showed that the aromatisation of isobutane on Zn- and Ga-pentasils takes place 9 and 12.5 times faster respectively than on the H-form.[177] The activity of Cd-pentasils differs little from the activity of Ga-containing specimens.[166,167]

Thus the aromatisation of lower paraffins on pentasils modified with zinc, cadmium, and gallium includes an alkene formation stage, as happens in the presence of bifunctional platinum-containing catalysts based on pentasil or Al_2O_3. The abstraction of a hydride ion from the alkane molecule with participation of Zn^{2+} cations on the surface (s) may proceed in accordance with the following scheme:[101,108]

$$C_3H_8 + Zn^{2+}_{(s)} \rightarrow \text{iso-}C_3H^{+}_{7(s)} + [Zn-H]^{+}_{(s)}.$$

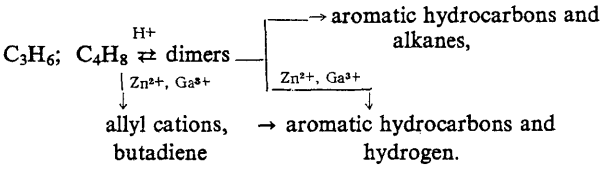
In this case, the zinc cation plays the role of a hydride ion acceptor. According to the result of Kokes and Dent,[204] zinc oxide is capable of effecting the heterolytic dissociation of the C–H bond with formation of intermediate $[Zn-H]^+$ structures. It is generally believed[101,103,105,108–110] that the composition of the paraffin dehydrogenation centres includes promoting elements and that subsequent reactions of the unsaturated compounds formed occur as a result of the interaction of these compounds with protic acid centres of the pentasils. The mechanism of the alkene conversion reactions on pentasils has been discussed in detail in a number of publications.[3,53,119,203,205]

Apart from the first stage (the dehydrogenation of saturated hydrocarbons), zinc and gallium introduced into pentasils participate also in the stage involving the abstraction of a hydride ion from alkene molecules with formation of intermediate allylic compounds.



This conclusion was reached from the analysis of kinetic data for the conversion of but-1-ene into aromatic hydrocarbons on Zn/H-ZSM-5.[206] The introduction of zinc into pentasil led to a sharp increase in S_{arom}. A similar effect has been observed on comparing the activities of H-, Zn-, and Ga-pentasils in the aromatisation of isobutene[170,177] as well as propene.[103] The dependence of the proportions of the but-1-ene conversion products on τ shows that, for low values of x, lower alkenes (ethylene and propene) as well as aliphatic hydrocarbons with a higher molecular weight predominate.[206] These data confirm that the formation of aromatic products is preceded by the oligomerisation of the initial alkene accompanied by the partial cracking of the oligomers. We may note that similar conclusions were reached previously[119,203,207] from the analysis of kinetic data for the conversion of isobutene and propene on type H-TsVK and H-TsVM pentasils. An appreciable amount of butadiene was observed in the but-1-ene conversion products on the Zn-borosilicate catalyst[206] (the selectivity in the formation of butadiene reached 77% for x = 10%), which indicates the dehydrogenation of the initial alkene. The participation of zinc cations in this reaction is confirmed by the finding that the molar ratio of the concentrations of alkanes and aromatic hydrocarbons in the but-1-ene conversion products on Zn-pentasils is 0.9, whereas on H-ZSM-5 it is 2.9. In the presence of Zn-pentasils, the first stage in the activation of but-1-ene may be one involving the formation of allylic (butenyl) structures. The dimerisation of these structures and the subsequent abstraction of hydrogen atoms led to the formation of aromatic hydrocarbons. The capacity of zinc oxides for the formation of allylic structures has been confirmed by spectroscopic methods.[204,208]

On the basis of experimental data, a scheme for the conversion of lower alkenes on pentasils modified with zinc or gallium has been put forward:[206]



Lower alkenes dimerise via the carbenium ion mechanism on the B-centres of decationated pentasils.[3,205,209–211] The dimers can subsequently isomerise and be cleaved to reform the lower alkenes or can be converted into carbenium ions. On subsequent deprotonation and redistribution of hydrogen, aromatic hydrocarbons and alkanes are produced. The formation of one molecule of the aromatic hydrocarbon is accompanied by the formation of three alkane molecules[205] and the yield of alkene aromatisation products is limited by these proportions.

As stated above, in the presence of Zn-pentasils a hydride ion can be abstracted from the molecules of the initial alkenes or converted into allylic intermediates. Aromatic hydrocarbons can be formed in their turn both as a result of the subsequent abstraction of hydride ions from the molecules of alkenes with higher molecular weights (in which the number of carbon atoms is not less than six) and via the direct interaction of two allylic structures with the simultaneous elimination of a hydrogen molecule. This pathway to the formation of aromatic structures does not require the obligatory simultaneous formation of alkanes and therefore in this case the yield of aromatic hydrocarbons is not limited by the stoichiometric relation. This explains the higher yield of the products of the aromatisation of lower alkenes on Zn-pentasils. A similar sequence of transformations of C_2-C_5 alkanes and alkenes is apparently characteristic also of Cd- and Ga-pentasils.

5. The nature of the active centres of the modified pentasils

The results examined in the previous Section show that the modified pentasils possess dehydrogenating properties. In the case of Pt/H-ZSM-5 and other deposited Group VIII metals, the abstraction of hydrogen from saturated molecules takes place with participation of metal clusters dispersed in the zeolite. The nature, structure, and location of the active centres of Zn-, Cd-, and Ga-pentasils are less clear.

As mentioned previously, the catalytic activity of pentasils is determined by the number of acid centres of different nature. Modification with zinc and cadmium alters significantly the acid properties of zeolites. The influence of these promoting agents on the concentration, strength, and nature of the acid centres active in the aromatisation of lower alkanes has been studied in detail.[108–111,166,167,177,212] For this purpose, the hydroxyl coating and the interaction of pyridine molecules with the L- and B-centres of H-, Cd-, and Zn-pentasils, differing in the ratio of the concentrations of aluminium and silicon in the lattice, were investigated by IR spectroscopy.

Three absorption bands with maxima at 3745, 3610, and 3330 cm^{-1} were recorded in the IR spectra of the H-forms of the pentasils in the region of the principal stretching vibrations of the hydroxy-groups.[48–50] They correspond respectively to non-acid silanol and

acid bridging hydroxyls in a free state (3610 cm^{-1}) and in the hydrogen-bonded state (3300 cm^{-1}).[48,50,52] The bands of the acid OH groups in pentasil with Si/Al = 20 are much more intense than in the specimen with Si/Al = 140.[170,177,212]

The introduction of zinc into pentasils leads to some decrease in the intensity of the 3610 and 3330 cm^{-1} bands as a result of the blocking of some of the aluminium–oxygen tetrahedra by zinc cations. Furthermore, an additional absorption band appears at 3520 cm^{-1}. It has been assigned to hydroxyls bound to the Zn^{2+} cations.[212]

Absorption bands referring to the generated pyridinium ions (1550 cm^{-1}, B-centres) and to coordinated pyridine (1448–1453 cm^{-1}, L-centres) have been observed in the range 1300–1600 cm^{-1} in the IR spectra of pyridine adsorbed on H-, Cd-, and Zn-pentasils of the TsVK and TsVM types.[108–111,113,166] By analogy with zeolites of other structural types (faujasites, mordenites, etc.), containing transition metal cations,[39] the band with a maximum at 1453 cm^{-1} in the spectra of all the specimens modified with zinc and cadmium was assigned to pyridine coordinated to the cations of the modifying element. The position of this band is determined by the nature of the cation and the hypsochromic shift (from 1448 to 1453 cm^{-1}) is induced by the increase in the electrostatic field strength and the strength of the aprotic centres.

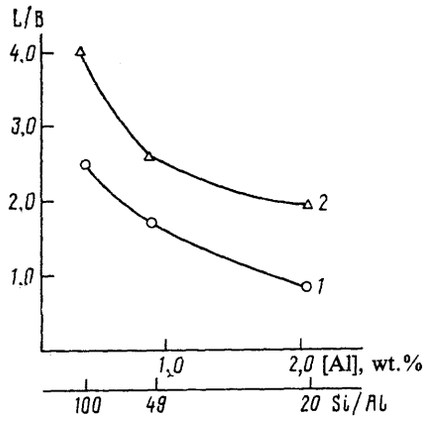


Figure 11. Variation of the L/B ratio with the Al concentration in the skeletons of H-pentasils (curve *1*) and Zn-pentasils (curve *2*).[110]

Fig. 11 illustrates the variation of the ratio of the intensities of these bands (L/B) as a function of [Al] in the lattices of the H- and Zn-forms of the pentasils. A common feature is characteristic of both series of catalysts—the increase in the L/B ratio with increase in Si/Al. This is due to the decrease in the number of B-centres, which is approximately proportional to the number of aluminium atoms in the unit cells of pentasils. As a result of the modification with zinc, the L/B ratio increased by a factor of ~1.5, which indicates the appearance of a large number of new L-centres. A similar picture was observed also for Cd-pentasils. The number of aprotic centres formed depends on the concentration of the promoting agent. Fig. 12 shows how the intensities of the absorption bands of the coordinated pyridine (L), the pyridinium ion (B), as well as the L/B ratio vary with the cadmium concentration. With increase in [Cd] to 2.5 wt.%, L and L/B increase monotonically, while B remains constant. This means that the ratio L/B increases only as a result of the appearance of new L-centres. Further increase in the cadmium content to 5 wt.% lowers the number of protic B-centres, which can be explained by the blocking of the bridging hydroxy-groups by cadmium.

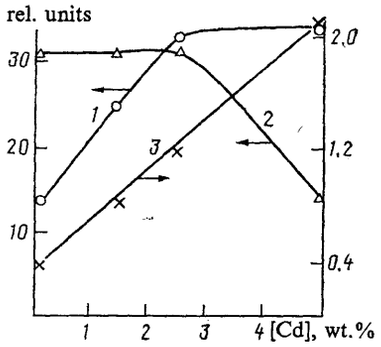


Figure 12. Dependence of L (curve *1*), B (curve *2*), and L/B (curve *3*) on the Cd concentration in type H-TsVM pentasil (Si/Al = 20).[166]

In order to estimate the strengths of the L- and B-centres, a study was made of the thermal desorption of pyridine from the surfaces of pentasils of different composition.[108,111,113] The "(I^t/I°)–desorption temperature" thermal desorption plots are illustrated in Fig. 13.

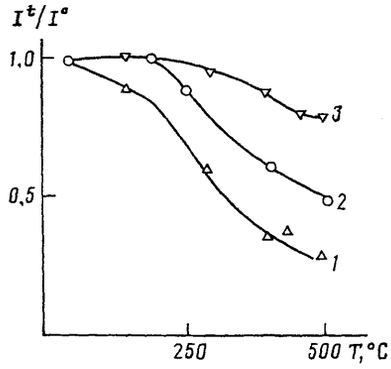


Figure 13. Variation of the relative intensities of the absorption bands of coordinated pyridine as a function of the desorption temperature:[113] *1*, H-TsVM; *2*, 1.5% Cd/H-TsVM; *3*, 1.5% Zn/H-TsVM.

Here I^t is the intensity of the 1448 (1453) cm^{-1} absorption band due to the coordinated pyridine after desorption at the corresponding temperature and I° is the maximum initial intensity of this band before desorption. In the case of unmodified zeolites, an

appreciable desorption of pyridine from the L-centres is observed even at $T < 300$ °C virtually without change in the intensity of the band corresponding to the pyridinium ion; on the other hand, even at 500 °C pyridine remains strongly bound to the B-centres. These data indicate the presence of strong B-centres on the surfaces of the decationated forms of pentasils, which agrees with the result obtained by adsorption microcalorimetry.[61–66] A different picture is observed in the case of pentasils modified with zinc and cadmium. The strength of the coordinate bonds between pyridine and the zinc and cadmium cations is much greater than the strength of the bond with the L-centres of the decationated specimens: more than half the molecules of the adsorbed base remain on the surface at 500 °C.

The properties of the aprotic acid centres of the Zn-pentasils have been investigated by diffuse scattering IR spectroscopy.[170,177,212] Hydrogen (adsorption temperature –196 °C) and carbon monoxide (adsorption temperature 25 °C) were used as probe molecules. The small size of the adsorbate molecules, the large shift of the stretching vibration frequency following polarisation on centres of different nature, the low desorption temperature, and at the same time the possibility of a quantitative determination of the concentration of the active centres impart certain advantages to this research technique.[48,50]

Absorption bands at 4105–4110 and 4125–4130 cm^{-1} have been observed in the IR spectra of hydrogen adsorbed on H- and Zn-pentasils (Fig. 14). They characterise the interaction of molecular hydrogen with bridging and silanol hydroxyls respectively.[46,48–50] Apart from these bands, additional lines appear in the spectra on Zn-pentasils at 3955, 4015, and 4075 cm^{-1}. They refer to complexes of hydrogen with aprotic acid centres of different types. The principal components of such centres are the $Zn^{2+}-O^{2-}$ acid–base pairs.[170,177,212] Since a single line is manifested at 4019 cm^{-1} in the IR spectra following the adsorption of hydrogen on massive zinc oxide,[213] presumably the properties of the ZnO deposited on the surfaces of pentasils differ from those of the massive oxide.

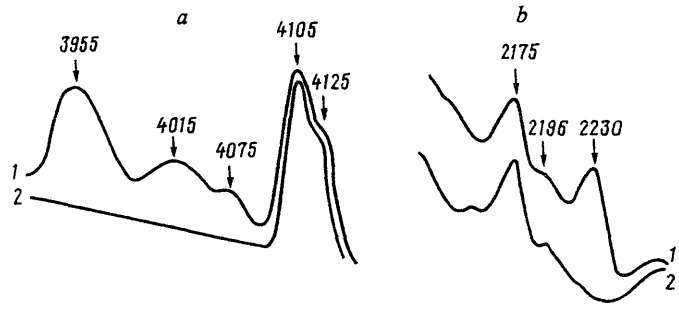


Figure 14. IR spectra of H_2 (*a*) and CO (*b*) adsorbed on Zn-pentasil (curves *1*) and the unmodified H-TsVM (curves *2*).[170,177]

The band at 3955 cm^{-1} undergoes the greatest shift ($\Delta\nu_{H-H}$ = 210 cm^{-1}) relative to the vibration frequency of gaseous hydrogen.[48] It has been shown[212] that at room temperature hydrogen is dissociatively adsorbed on these centres. Furthermore, the $Zn^{2+}-O^{2-}$ acid–base pairs are capable of strongly polarising the C–H bonds in the molecules of lower alkanes. Additional bands at 2805 cm^{-1} (for CH_4) and 2745 cm^{-1} (for C_2H_6), which have undergone bathochromic shifts by 200 and 250 cm^{-1} respectively, have been observed in the IR spectra of methane and ethane adsorbed on Zn-pentasils.[212]

Aprotic acid centres containing zinc cations can be formed on different sections of the pentasil structure. For example, centres to which the absorption bands at 3955 and 4015 cm^{-1} have been attributed are located directly on the aluminium–oxygen tetrahedra, while the band at 4075 cm^{-1} characterises the formation of the ZnO phase which is not linked to the pentasil lattice.

Analysis of the spectra of adsorbed carbon monoxide[177] also leads to the conclusion that new L-centres are formed as a result of the modification of pentasil with zinc (Fig. 14*b*). Bands at 2175, 2195, and 2230 cm^{-1} have been observed in the IR spectra of the modified specimens. The first two bands, present also in the spectra obtained for the H-form, refer respectively to complexes with bridging hydroxy-groups and weak aprotic centres. The band at 2230 cm^{-1} appears only after the introduction of zinc and refers to complexes of CO with fairly strong electron-accepting centres.[42] The preliminary adsorption of molecular hydrogen at room temperature, leading to its dissociation, prevents the appearance of the band at 2230 cm^{-1}, which means that CO is adsorbed on the L-centres responsible for the polarisation of the H–H and C–H bonds in the adsorbed hydrogen molecules and lower paraffins respectively.

Analysis of the IR spectra of adsorbed CO and H_2 demonstrated a fundamental difference in the character of the interaction of these molecules with the acid centres of Zn- and Ga-pentasils.[177,214] Modification with gallium does not lead to the appearance of absorption bands corresponding to aprotic acid centres: the spectra of the H- and Ga-pentasils are identical. The use of other adsorbates (CH_4, CH_3CN) also did not permit the detection of L-centres bound to gallium. It has been suggested[177,214] that one of the causes of the absence of the interaction of these probe molecules with the aprotic centres of Ga-pentasils may be the preferential localisation of gallium on the outer surfaces of the crystallites. It is known[215] that it is very difficult to introduce triply charged cations into pentasils by ion exchange because their solvation shell has a large radius. Furthermore, there is a possibility of electrostatic difficulties associated with the compensation of the isolated negative charges in the lattice by multicharged cations. If gallium is distributed on the outer surface of pentasil, which constitutes approximately 2.5–3.0% of the total surface,[37,38,216] the concentration of centres incorporating Ga^{3+} ions should be low. It is not easy to detect and record such centres by IR spectroscopy owing to the inadequate sensitivity of the method. The paramagnetic probe method,[216–218] based on the analysis of the EPR spectra of various stable radicals adsorbed on the surfaces of catalysts, is much more sensitive. On formation of complexes between radicals and metal ions involved in coordination with low coordination numbers, whose nuclear spin is non-zero, a characteristic EPR spectrum with a hyperfine structure due to the corresponding nuclei is observed. It has been established[177,214,218] that a large (~1.1 nm) stable nitroxyl radical—2,2,6,6-tetramethylpiperidin-1-yloxyl (tanane)—forms donor–acceptor complexes with coordinatively unsaturated Ga^{3+} ions introduced into pentasils. The interaction of the unpaired electron of tanane with the nuclei of the ^{69}Ga and ^{71}Ga isotopes, which have a nuclear spin $I = 3/2$, is characteristic of these complexes. This leads to the appearance of a well resolved quartet with a constant $B_{Ga} = 38$ Oe for splitting by the gallium nuclei. The results obtained by the paramagnetic probe method show that the coordinatively unsaturated Ga^{3+} cations are localised preferentially on the outer surface of the crystallites,

forming ion pairs of the $Ga^{3+}-O^{2-}$ type. Evidently these cations possess electron-accepting properties like the zinc and cadmium cations located within channels of pentasils.

The aprotic acid centres arising as a result of the introduction of gallium have been detected by the paramagnetic probe method on the outer surface of gallosilicates after they have been heated at 500–600 °C and after the propane aromatisation reaction has been carried out.[182] In this case, the appearance of L-centres is caused by the migration of the extraskeletal gallium onto the outer surface under the influence of the reaction medium.

Electron-accepting centres incorporating gallium ions possess certain specific features which distinguish them from the centres formed by zinc or cadmium cations. Thus, after the successive treatment of a Ga/H-ZSM-5 specimen with hydrogen and oxygen at 450 °C, the ability of the catalyst to adsorb hydrogen increases sharply and the reduction of Ga^{3+} to Ga^{+} is facilitated.[105] According to Guo's data,[169] after Ga-pentasils have been heated in hydrogen at 550 °C, the Ga $2p_{3/2}$ binding energy diminishes by approximately 5 eV, which indicates the partial reduction of gallium. In contrast to this, an appreciable decrease in the Ga $2p_{3/2}$ binding energy was not observed after treatment of the Ga/H-TsVM catalyst with hydrogen, although the composition of the surface layer changed significantly.[171] Under the influence of hydrogen, the surface concentration of gallium diminishes sharply, which may be due to its migration into the bulk phase.

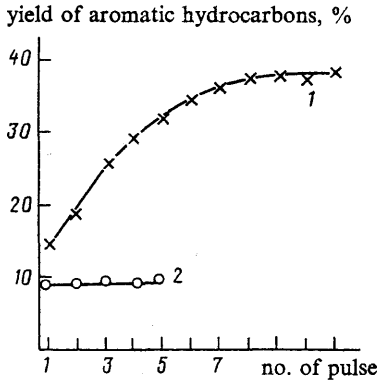


Figure 15. Dependence of the yield of aromatic hydrocarbons on the number of propane pulses:[171] *1*, 2% Ga/H-TsVM; *2*, H-TsVM.

The "running-in" of the Ga-pentasils in the course of the aromatisation of propane under pulse conditions constitutes indirect confirmation of the change in the oxidation state of gallium under the influence of reductants[169,171] (Fig. 15). It is believed[171] that one of the causes of this phenomenon may be the change in the electronic state of gallium resembling the situation arising with platinum and rhodium.[127,129,130] Furthermore, gallium can be redistributed in the zeolite matrix under the influence of the reaction medium. However, we may note that the mechanism of the formation of the active centres in the gallium-containing zeolites requires further study.

Thus one may conclude that, as a result of the introduction of zinc, cadmium or gallium into pentasils, strong L-centres are formed. By virtue of their electron-accepting properties, these are capable of activating the molecules of lower paraffins and of catalysing the dehydrogenation reaction—the key stage in the aromatisation of saturated hydrocarbons.

IV. Application of pentasil-based catalysts in technological processes for the preparation of valuable chemical products from hydrocarbon gases

The dynamics of the development of the manufacture and utilisation of low-molecular-weight hydrocarbons is such that at the beginning of the 1990's an excess of effluent gases from petrochemical industries should arise.[6,7,33] On the other hand, there is an acute problem as regards the rational employment of the components of natural and by-product gases. Such a situation has stimulated the development of new effective processes designed to utilise gaseous hydrocarbons.

Hitherto various foreign companies have suggested several catalytic processes for the conversion of gaseous hydrocarbon raw material in which pentasil-group zeolites are employed. Among them, the following three processes, which are at the introduction stage, may be regarded as the most promising.

(1) MOGD (Mobil Olefin to Gasoline and Distillate) designed to convert gaseous alkenes into high-octane petrol (gasoline) and middle distillates.

(2) "M2-forming" ensuring the formation of concentrates of aromatic hydrocarbons, predominantly the benzene–toluene–xylenes (BTX) fraction from low-boiling alkenes, paraffins, and naphthenes.

(3) "Cyclar"—designed to convert low-molecular-weight paraffins, namely propane and butanes, into aromatic products.

The MOGD process, developed by the Mobil Oil Company is designed to manufacture petrol from diesel fuel.[23,219–221] It is based on reactions involving the oligomerisation of C_2-C_4 alkenes on decationated pentasils of the ZSM-5 and ZSM-11 types.[23,29,30,220,222–224] Information has been published recently concerning the possibility of using borosilicates, ferrosilicates, gallosilicates, silicoaluminophosphates, and other materials with a zeolite structure as catalysts of alkene conversion processes.[19,20,162,225] Under identical process conditions (temperature, pressure, and contact time), the composition of the products formed depends little on the molecular weight of the starting material. Both pure alkenes (ranging from ethylene to hydrocarbons with a boiling point of 204 °C) and various mixtures (fractions) with a fairly high content of unsaturated hydrocarbons can be processed. The liquid catalytic mixture consists of C_5-C_{20} hydrocarbons. The petrol fraction with a high octane number (>85) includes C_5-C_{10} compounds, heavier hydrocarbons being converted after hydrogenation into diesel fuel with a high cetane number (~56).[219] One of the most important features of the MOGD process is the high exothermicity of the alkene oligomerisation reaction—1550 kJ kg^{-1}.[220] In order to remove the heat and maintain isothermal conditions in the reactor, extra-reactor cooling and recirculation of petrol are used. Recirculation results in an increase in the yield of middle distillates. By varying the recirculation conditions, it is possible to regulate the proportions of the petrol and diesel fractions from 100:0 to 10:90.[219,221] Tests of the catalysts on real C_3-C_4 raw

material containing 62% of unsaturated hydrocarbons showed that the reaction products consist of alkenes to the extent of 94%.[219]

Active and stable catalysts based on pentasils of the type H-TsVM and H-TsVK have been developed for the preparation of high-octane petrol from the flame gases in the manufacture of polyethylene (97% ethylene, 2.5% propane).[221,226] During pilot tests, the degree of conversion of ethylene remained at the level of 72–77% for 120 h and the yield of the petrol fraction was 49–57%.

The technological scheme for the MOGD process includes four reactors with a fluidised catalyst bed.[219] The flexibility of the technology, which ensures the possibility of obtaining either petrol or diesel fuel from gaseous alkenes, should be included among the significant advantages of the MOGD process. The process may find extensive applications in petroleum processing, petrochemistry, and the manufacture of synthetic fuels. In the last instance, MOGD can be used in combination with Fischer–Tropsch processes[24,27] or processes for the conversion of methanol into alkenes[26,27] in order to obtain high quality diesel fuel.

The "M2-forming" process is carried out on decationated zeolites of the H-ZSM-5 type at $T > 500$ °C and a pressure of 1–20 atm.[23,227] The ability of the hydrogen-forms of pentasils to convert aliphatic compounds into aromatic hydrocarbons is used in this process. The raw material is a broad fraction comprising C_2–C_8 alkenes and paraffins and containing up to 15% of naphthenes.[227] In contrast to the MOGD process, all the hydrocarbons, except ethane, enter into the aromatisation reactions under the conditions of the M2-forming process. The main bulk of the aromatic products consists of the BTX fraction. The yield of the aromatic pentane and hexane conversion products at 540–580 °C reaches 31–32%. The process includes cracking and hydrogen redistribution reactions, whose contribution increases with increase in temperature.

A common feature of the M2-forming and MOGD processes is a low sensitivity of the composition of the reaction products to the proportions of the components in the starting material.[23] On the other hand, the process temperature is determined by the composition of the starting material. If the initial mixtures are enriched olefins, diolefins, and naphthenes, then aromatic hydrocarbons are formed at comparatively low temperatures. Thus the aromatisation of the petrol fraction of the products of the thermal cracking of low-sulphur masout (12% of aromatic hydrocarbons, 41% of unsaturated hydrocarbons, 47% of paraffin-naphthene hydrocarbons), boiling in the range 35–180 °C, began already at 300 °C.[228] Under these conditions, the content of aromatic hydrocarbons in petrol increased compared with the initial content by a factor of approximately 2. We may note that the content of aromatic hydrocarbons in the M2-forming product can be extremely large, which makes it possible to isolate directly the BTX fraction without an additional extraction stage.[227] For example, petrol having the following composition was obtained at 425 °C:[228] aromatic hydrocarbons—78%, unsaturated hydrocarbons—2%, paraffins and naphthenes—20%. These data indicate a fairly high efficiency of the pentasil-based catalysts in the aromatisation reactions of low-quality petrols obtained as a result of thermodegradative processes.

Apart from low-octane petrols, paraffin-enriched petroleums as well as the effluent gases from petrochemical industries, in particular catalytic cracking gases, can be subjected to the M2-forming process. According to predictions,[227] the M2-forming process together with the MOGD process can become one of the main ways of obtaining high-octane components of motor fuel from olefin-containing gases.

As reported above, modified pentasils are highly effective catalysts of the aromatisation of low-molecular-weight hydrocarbons. Judging from patent data,[142–149] binary catalytic systems are frequently employed for this purpose. Thus, copper, rhenium, platinum, palladium, and gallium are added to stabilise the zinc introduced into pentasils.[144,229–235] A technology for the conversion of light paraffins into aromatic hydrocarbons and hydrogen has been developed by the British Petroleum and the UOP companies in 1984. This process was called "Cyclar".[31–33]

In the "Cyclar" process, active and selective catalysts based on modified pentasils are subjected to constant regeneration, which is ensured by their continuous circulation. As a result, the starting material always comes into contact with the regenerated catalyst and a high level of activity and selectivity is therefore maintained for a long time.

The developments used previously by the UOP Company for the platforming process[31] were used in the technological scheme of the "Cyclar" process. They included a design in which the reactors are placed one on top of the other, a radial flow of the starting material, the use of intermediate heaters, and continuous regeneration of the catalyst. The catalyst for the "Cyclar" process, created on the basis of modified pentasils, satisfies all the principal requirements for industrial catalysts. It is resistant to coke formation and to the action of sulphur, water, and other oxygen-containing compounds and its mechanical strength is high. Either individual propane and butane or propane–propene and butane–butene fractions as well as mixtures of C_2–C_6 hydrocarbons are used as the starting material. On the apparatus for the processing of butane, the yield of aromatic hydrocarbons reaches 67.5% (calculated relative to the starting material which has reacted), while the yield of hydrogen is 5.5%. the overall yield of propane aromatisation products is 63.6%, while the yield of hydrogen is 6%. The proportions of the aromatic propane and butane conversion products are approximately the same. The octane number of the fraction of aromatic hydrocarbons is approximately 112.

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The results examined above indicate considerable advances in the creation on the basis of pentasil-type zeolites of effective catalysts for the aromatisation of lower paraffins as well as progress in the study of the mechanism of their catalytic action and in the development of technological processes for gaining valuable chemical products from hydrocarbon gases. The latest advances in the synthesis of zeolites and zeolite-like materials should constitute a basis for the creation of new more active and more selective catalytic systems.

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