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The Properties and Use in Catalysis of Zeolites of the Pentasil Type

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Progress in the study of the structure, physicochemical, and catalytic properties of high-silica zeolites of a new structural type—pentasils— has been reviewed. The bibliography contains 289 references.

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I. INTRODUCTION

In recent years in the field of zeolite catalysis, there has been intensive development of studies of the physicochemical and catalytic properties of zeolites of a new structural type—pentasils. These zeolites are characterised by an unusually high SiO_2 content, and are therefore sometimes called "super-high-silica" (SHS) zeolites. The best known of these materials are the Mobil Oil ZSM zeolites[1-6], for which x, the molar ratio SiO_2/Al_2O_3, usually lies in the range 12–100, but may reach much higher values. The final member of this series is silicalite[7], which does not contain any aluminium ($x = \infty$) and consists of crystalline silicon dioxide. Analogues of the ZSM zeolites have also been synthesised and are being extensively studied in the Soviet Union; in the Soviet scientific literature they are usually called SHS zeolites.

Interest in the new generation of zeolites increased after the publication, by Mobil Oil in 1974-75, of a large number of patents which showed that ZSM zeolites are much more effective catalysts for a number of processes of practical importance in petroleum refining and petroleum chemistry than their predecessors (faujasites, mordenite, etc.). Processes based on the use of ZSM zeolites include, for example, the catalytic dewaxing of petroleum fractions[8,9], the alkylation of aromatic hydrocarbons by alkenes[10], the aromatisation of individual C_2–C_4 alkenes and their mixtures[11-13], the cracking of gas oil fractions, giving a higher yield of aromatic hydrocarbons[16,17], the isomerisation of xylenes[18-21], and the conversion of synthetic gas into petrol[22]. In 1975, a number of patents[23-31] were published on the production of high-octane petrols (octane number ≥95) from various oxygen-containing and other heteroatomic compounds in the presence of ZSM zeolites.

A unique place among these processes is occupied by the production of high-octane petrol from methanol on ZSM zeolites[28,32-37]. This process, which at the time of the energy crisis and the search for new sources of energy revealed a realistic way of obtaining high-quality motor fuels without using petroleum raw materials, stimulated the study of the properties and potential use of the new zeolites as catalysts.

Although only slightly more than ten years have passed since the appearance of the first papers on pentasils, extensive information has accumulated in the literature on

the structure, physicochemical, and catalytic properties of these zeolites. These data have to some extent been reflected in a number of reviews of problems in zeolite catalysis[38-51]. Some of the reviews were published a comparatively long time ago, however, and they do not include recent results. The authors of other reviews either restricted themselves to an examination of data on the use of pentasils as catalysts of one single reaction, or use these data to illustrate the current state and trends in the development of zeolite catalysis. Thus in the compilation of the present review an attempt has been made, as completely as possible, to survey, systematise, and analyse data available in the scientific literature on zeolites of the pentasil family, with the exception of patents, although in a number of cases reference to these has been necessary.

II. SYNTHESIS, STRUCTURE, AND PHYSICOCHEMICAL PROPERTIES OF PENTASILS

The synthesis of zeolites is an independent and very specific field at the boundary between inorganic and physical chemistry. The main characteristics of the method of preparing pentasils will therefore be examined only briefly, and the conditions for their crystallisation and the regular features, kinetics, and mechanism of this process will not be discussed in detail. A large number of published papers have been devoted to these questions[52-61].

The synthesis of pentasils is based on the hydrothermal crystallisation of alkali aluminosilicate gels in the presence of the cations of organic bases. This method has been described in Mobil Oil patents dealing with the production of various representatives of the ZSM zeolite family[2-6]. At the present time this family alone includes more than fifteen different zeolites (ZSM-4, -5, -8, -10, -11, -12, -20, -21, -34, -35, -38, etc.), which are synthesised by varying the temperature of the process, the ratio of the components in the reaction mixture, and other conditions, and also using different organic compounds as additives.

The addition of organic bases (tetramethylammonium compounds) was first used in 1961 by Barrer[62,63] in the synthesis of the first generation of zeolites. The zeolites obtained in this way (zeolites of type A, erionite, chabasite, offretite, faujasite) were characterised by higher values of the ratio SiO_2/Al_2O_3 than the same zeolites synthesised in the absence of organic cations. In a development of this method, Mobil Oil studied the possible use in zeolite synthesis of tetraethyl-, tetrapropyl-, and tetrabutylammonium and tetrabutylphosphonium cations and the cations of pyrrolidine, ethylenediamine, and other organic compounds. This led to the preparation of the high-silica zeolites of the large ZSM family.

The study of these zeolites[5,6] showed that some of them, for example ZSM-21 and -34 zeolites, have a familiar structure (ferrierite and erionite–offretite respectively). At the same time, the zeolites ZSM-5, ZSM-11, and apparently ZSM-12 belong to a previously unknown pentasil structure[2-4] which has no natural analogues. The same structure is shown by silicalite and fluorosilicalite (analogues of ZSM-5), obtained in the presence of the tetrapropylammonium cation[64,65]; silicalite-2 (analogue of ZSM-11), synthesised using tetrabutylammonium cations[66]; and tetraethylammonium silicate (analogue of ZSM-12), which was crystallised in the presence of tetraethylammonium cations[67]. It is now known that zeolites with a pentasil structure can be synthesised using as organic additives, for example, lower aliphatic alcohols, or without using any organic additives[68].

In the ZSM zeolite family, the most detailed studies have been carried out for ZSM-5 and ZSM-11 zeolites[69-73], which show unusual catalytic properties, and also silicalite[48], the structural analogue of ZSM-5 zeolite. The ZSM-5 zeolite crystallises in the orthorhombic system with crystal lattice parameters $a \cong 20.1$, $b \cong 19.9$, and $c \cong 13.4$ Å, and the ZSM-11 zeolite crystallises in the tetragonal system with lattice parameters $a = b = 20.12$ Å and $c = 13.44$ Å. The composition of the unit cell of both zeolites in the Na form is given by the formula $Na_nAl_nSiO_{96-n}O_{192}\cdot\sim 16H_2O$, where $n < 27$ for ZSM-5 and $n < 16$ for ZSM-11. The densities of the crystal lattice of the zeolites ZSM-5 and ZSM-11 are 17.9 T and 17.6 T per 1000 Å^3 respectively (T = Si + Al).

The crystal lattice of ZSM-5 and ZSM-11 zeolites is based on structural elements (Fig. 1*a*) which consist of five-membered rings. Because of the low Al concentration (which can be determined with a high accuracy in the pentasil framework by X-ray diffraction[74]), these five-membered rings are formed chiefly by silicon–oxygen tetrahedra[69-72]. Chains of these elements (Fig. 1*b*) are connected in layers (Fig. 1*c*), and each chain in the layer is the mirror image of its neighbours. The layers of chains of structural elements can be connected in pairs in two ways. If the connection of two neighbouring layers is accompanied by their inversion relative to one another, a crystal lattice of the ZSM-5 zeolite type is formed, whereas with mirror arrangement of neighbouring layers, a crystal lattice of the ZSM-11 type is formed.

It has been suggested[70] that structurally, ZSM-5 and ZSM-11 zeolites are the extreme members of a very extensive series of mixed structures formed as a result of the large number of possible combinations of chains and layers of structural elements. All these structures belong to the pentasil family, which also includes silicalite, whose crystal lattice is made up of only silicon–oxygen tetrahedra[64].

The production of the crystal lattice of pentasils involves the formation of a system of channels which intersect one another at right angles and which in cross-section have the form of ten-membered rings (Fig. 1*c*). For ZSM-5 zeolite this system consists of straight and "sinusoidal" channels (Fig. 2*a*).[69,70,72] The straight channels in cross-section have the form of an almost regular circle (5.4 × 5.6 Å), and the cross-section of the sinusoidal channels has the form of an ellipse (5.1 × 5.5 Å). An analogous system of channels has been detected in silicalite, which differs from ZSM-5 zeolite only in the fact that the straight channels have an elliptical cross-section (5.0 × 5.6 Å), and the cross-section of the sinusoidal channels has the form of a circle with diameter 5.3 Å.[64] In contrast to ZSM-5 zeolite and silicalite, the system of pores in ZSM-11 is formed only by straight channels, which in cross-section have the form of an ellipse (5.4 × 5.6 Å) (Fig. 2*b*).[71,72] In a number of cases, the synthesis may be accompanied by the formation of zeolites of the pentasil family, having a mixed pore system (for example 2*c*).[47]

The unusual structures and composition of the pentasils give them characteristic catalytic and adsorption properties, which make them different from the first generation of zeolites. This raises the question of the reasons for the high catalytic activity of pentasils, which are characterised by a low aluminium content. According to existing ideas[1], the activity of zeolites in a whole series of catalytic reactions involving carbenium ions is due to the presence on their surface of acidic OH groups, joined to the Al atoms of the crystal lattice.

Of particular importance in this connection is the question, not yet fully resolved, of the localisation and distribution of Al atoms in the framework of pentasils. In the opinion of some authors[69-71], the small number of Al atoms is distributed

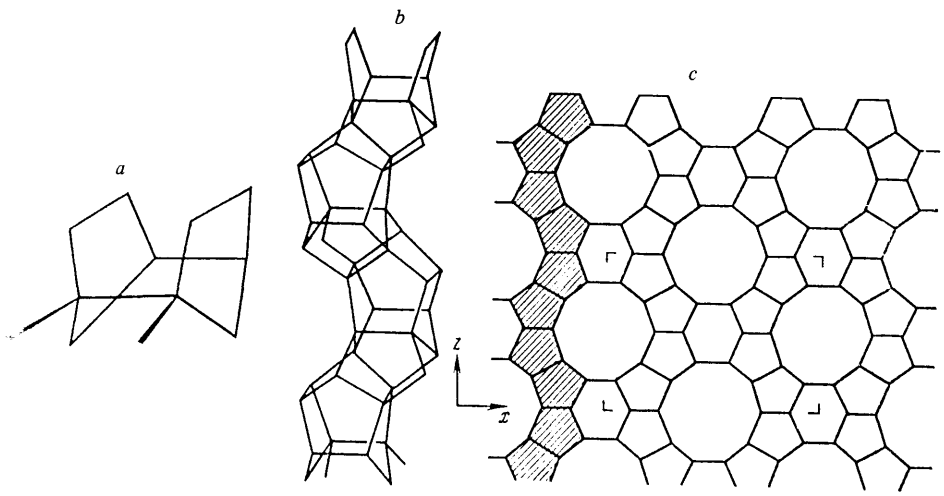


Figure 1. Schematic representation of the structural element (*a*), chains (*b*) of these elements, and the layer (*c*) formed by these chains, for ZSM-5 and ZSM-11 zeolites[69-72].

uniformly through the volume of the crystallites, as confirmed for ZSM-5 zeolites by Auger spectroscopy[75] and secondary ion mass spectrometry[76]. X-Ray photoelectron spectroscopy (XRPES), however, established[77] that the surface of specimens of the Na- and H-forms of ZSM-5 zeolite are enriched in silica. According to the data of other authors, obtained by the same method for ZSM-5 zeolite[78], and also for its analogues of the TsVK and TsVM type[79], the surface layers of the crystallites are enriched in alumina. This is also indicated by the results of a study of large (60–200 μm) crystallites of ZSM-5 zeolite by scanning electron microscopy and scanning X-ray microanalysis[53]. The conclusion that Al is uniformly distributed in pentasil crystallites was also reached in Refs.80–83.

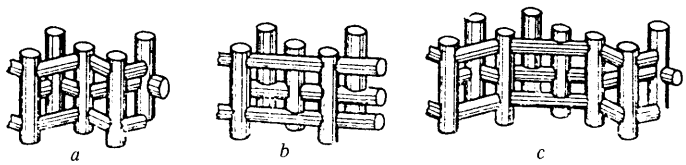


Figure 2. Schematic representation of the structure of the pores in zeolites of different types: *a*) ZSM-5 and silicalite, *b*) ZSM-11, *c*) mixed type[44,64,69-72].

The reasons for this are not completely clear. It is considered[53], for example, that enrichment of the surface layers of pentasil crystallites in aluminium is related to the characteristic features of the final stage of crystallisation. It is pointed out, however, that in small crystallites, the concentration of Al may be the same on the surface and in the volume. It is also known that the nature of the distribution of Al in pentasil crystallites may change with change in the conditions of thermal treatment and treatment with acids (see below).

Because of the low aluminium concentration, zeolites of the pentasil family have a much higher thermal stability than the zeolites of the first generation, whose structure in most cases breaks down at temperatures of 700–800 °C. In contrast to this, X-ray diffraction shows that heating ZSM-5 and TsVK zeolites at temperatures up to 1000° does not lead to breakdown of their crystal structure[2,78,84,85], and the structure of silicalite begins to become amorphous only at 1300°.[64] At the same time, according to XRPES,[78] high-temperature treatment apparently leads to the migration of ~15% of the Al atoms from the framework of the ZSM-5 zeolite. This may indicate slight breakdown of the zeolite structure at the points where aluminium is localised. The possibility of slight changes in the structure of pentasils on high-temperature treatment is also indicated by data on the change in the catalytic activity and selectivity of TsVK zeolite after its activation at 900–1000°.[84,85]

The ion-exchange properties of zeolites of the zeolite family are determined by the characteristic features of their composition. The presence of small quantities of aluminium in these zeolites determines the low value of the negative charge on their lattice and hence the low concentration of cations compensating these charges[57,86]. The latter include both Na^+ cations and the bulky non-exchangeable cations of organic bases (R_4N^+), used in the synthesis of the zeolite. The Na^+ cations, whose concentration in the original Na-form of the pentasils usually does not exceed 1.0–1.5% (calculated as Na_2O), can readily be replaced by NH_4^+ cations or protons by ion exchange with NH_4Cl or HCl. The organic cations are readily decomposed by heating the zeolite in air (350 to 450°), and are removed as ammonia, amines, and the corresponding hydrocarbons. The decationated or proton H-forms of the zeolites produced by this treatment have a higher sorptive capacity[2,86,87] and a higher catalytic activity[86-88] than the original Na form.

When caesium cations are introduced into the H-forms of a series of ZSM-5 zeolites with different compositions ($SiO_2/.Al_2O_3$ = 89–8660), a very good correlation is observed between the concentration of exchangeable caesium and the concentration of Al in the zeolite framework (Fig.3).[89] Thus the ability of pentasils to undergo ion exchange shows the

same dependence on the Al concentration in the crystal lattice as in the case of zeolites of the first generation. Moreover, the protons of the H-forms of ZSM-5, TsVK, and TsVM pentasils can be replaced by the cations of Na, Ca, Ag, the lanthanides, Pt, and Pd,[2,90,91] and this opens up new possibilities for the directed control of the catalytic properties of these zeolites.

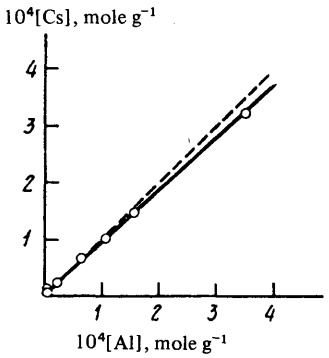


Figure 3. Influence of the Al concentration in the framework of H-ZSM-5 zeolite on its ability to undergo exchange with caesium[89]; the broken line corresponds to a ratio [Cs]/[Al] = 1.

Pentasils are much more hydrophobic than first-generation zeolites[2,64,89,92-95]. For ZSM-5 zeolite heated in air at 550°, the ratio of the quantities of sorbed n-hexane and water is ~1.5, whereas for zeolites of types A, X, and Y, the ratio is ~0.5.[2] According to other data[93], the same ratio (which for zeolites of types A, X, and Y, and mordenite is 0.4–0.9) increases to 1.4–2.4 for ZSM-5 and ZSM-11 zeolites. The water adsorbed by ZSM-5 zeolite occupies only 20–25% of the total volume of its pores[64,89]. For different ZSM-5 zeolite specimens in which the ratio SiO_2/Al_2O_3 varied from 75 to 8660 [89] and from 50 to 900,[95] with decrease in the Al concentration of the zeolite, the quantity of water sorbed by it decreased linearly to a very low value, corresponding to the adsorption of water by silicalite (~15 H_2O molecules per unit cell[64]). A similar result was obtained[96] for a number of ZSM zeolite specimens and their analogues with different Al concentrations.

These data on the hydrophobic properties of pentasils are in good agreement with the suggestion that there is a relationship between the affinity of the zeolites for water and the concentration of aluminium in them, and also that a bond is formed between the molecules of sorbed water and the protons joined to $[AlO_2]^-$ groups in the zeolite structure[94].

The hydrophobic character of the zeolites is combined with an ability to adsorb small molecules of various inorganic compounds. O_2, N_2, CO_2, and H_2S molecules easily penetrate into the channels of ZSM-5 and ZSM-11 zeolites[72], and the sorptive capacity of the latter is slightly lower, because of the characteristic features of its porous structure (see above). A significant contribution to the sorptive capacity of pentasils is apparently made by the cavities which are formed at the points of intersection of the channels and which have different shapes in ZSM-5 and ZSM-11. The H-form of ultrasil (an analogue of ZSM-8 zeolite) has a high sorptive capacity for hydrogen, equal to ~80% of its capacity for nitrogen[97].

A study of the adsorption of substances of different chemical character (inorganic compounds, hydrocarbons, methanol) on a zeolite of the ultrasil type[98,99] showed a definite relationship between the quantity of the substance sorbed by the zeolite and the volume of the sorbate molecules (Fig. 4). The curve giving this relationship shows a maximum in the region of n-heptane, whose existence was attributed to steric hindrance, preventing the diffusion into the pores of the zeolite of molecules with a chain length of more than seven carbon atoms. In contrast to this, for NaX zeolite, the quantity of adsorbed substance is independent of the volume of the adsorbate molecule.

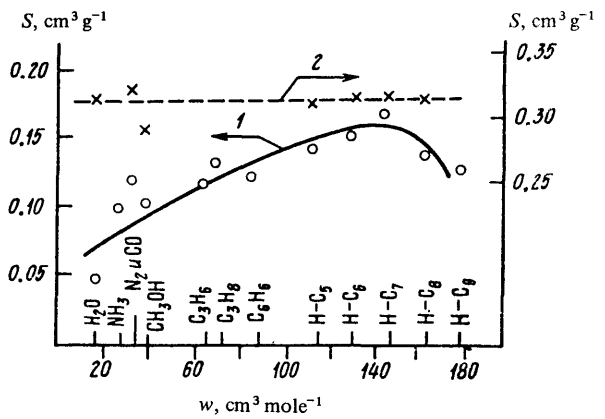


Figure 4. Change in the volume (*S*) of substances adsorbed by ultrasil (*1*) and NaX zeolite (*2*) on the volume of their molecules (*w*) (from published data[99]).

Pentasils readily adsorb normal alkanes[2-4,64,70,72,87,95,98-103]. The adsorption of branched alkanes and alkylaromatic and other hydrocarbons is limited considerably by the size and shape of the pores in the pentasils. For example, ZSM-5 zeolites readily adsorb n-hexane (4.3 Å)†, but sorb the isomeric methylpentanes (5.5 Å) and dimethylbutanes (6.1–6.3 Å) to a much smaller extent, and the extent of the sorption of these hydrocarbons decreases with increase in the degree of branching of the adsorbate molecules. H-ZSM-5 zeolite selectively adsorbs 2-methylpentane from its mixture (1:1) with 2,2-dimethylbutane[104,105]. Benzene, toluene, and *p*-xylene (which all have a diameter of 5.8 Å) are the aromatic hydrocarbons most readily adsorbed. An interesting feature is that the volume of benzene sorbed by H-ZSM-5 zeolite is much smaller than the volume of *p*-xylene. This is apparently because of the closer packing of the *p*-xylene molecules in the pores, and the interaction of the hydrogen atoms of this isomer with the surface of the walls of the zeolite pores[70,72].

The pore volumes occupied by adsorbed hydrocarbons with different structures are different, and always less than the true volume of the entire system of channels in the pentasil[72]. The system of pores in these zeolites is evidently not equally accessible to adsorbate molecules with different structures.

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†The figures in brackets give the values of the kinetic diameter of the molecules from Refs. 1 and 70.

The accessibility of the porous structure of pentasils (ZSM-5, ultrasil) to molecules of different hydrocarbons has been studied in detail[100,101,106]. The sorptive capacity of ZSM-5 zeolite for n-hexane is greater by approximately 30% and 50% than its capacity for 3-methylpentane and benzene respectively[72]. The sorptive capacity of pentasils depends to a significant extent on the nature of the adsorbate[107].

In the examination of sorption processes in zeolites, it is desirable to take account of the rate of penetration of the molecules into the pores of the adsorbent[108]. There are as yet, however, very few published data on the kinetics of sorption and diffusion for pentasils. The diffusion coefficients of benzene and *p*-xylene in ZSM-5 zeolite are approximately 10^3 times that for *o*-xylene, and 10^5 times those for 1,3,5-trimethylbenzene and pentamethylbenzene[70,109]. The initial rates of the adsorption of the xylene isomers in TsVK zeolite decrease in the following order[84]: *p*-xylene > *m*-xylene > *o*-xylene.

Thus pentasils whose maximum pore diameter is ~5.8 Å show clearly defined molecular-sieve properties. Unlike the first-generation zeolites, they can sorb molecules whose kinetic diameter exceeds the width of their channels by ~1 Å.[100] At the same time, in the pentasil pore system there is steric hindrance to the diffusion of molecules whose shape does not correspond to the shape of the zeolite channels[110,111].

Molecular-sieve properties of this kind, requiring correspondence between the size and shape of the adsorbate molecules and the pores of the adsorbent, were previously observed for various first-generation zeolites (zeolite of type A, erionite, mordenite, etc.).[110-112] As with these zeolites, the molecular-sieve properties of the pentasils have a significant influence on their catalytic properties. This influence is revealed as the so-called "configurational selectivity" (shape selectivity)[110] of catalytic reactions with respect to the original reagents, the products, or the transition state. These effects have made it possible to use pentasils as catalysts for dewaxing petroleum fractions[8,9], for the selective production of *p*-xylene[18-21,109], and for other processes[113].

The sorptive properties of pentasils depend both on the diameter and on the shape of the channels forming their porous structure. The straight and sinusoidal pores of ZSM-5 zeolite differ in relation to the adsorption and diffusion of hydrocarbons[70,72,102]. ZSM-5 zeolite has a higher sorptive capacity for hydrocarbons than ZSM-11 zeolite[114]. The geometry of the pores of ZSM-5 zeolite evidently corresponds more effectively to the shape of the molecules of the hydrocarbons being sorbed. A relationship has been established between the length of adsorbate molecules, the length of the channels in the pentasils, and their sorptive capacity, and it has been shown that the cavities which are formed by the intersection of the channels and which have different shapes in ZSM-5 and ZSM-11 zeolites play a part in the processes of sorption and diffusion[72,102]. In ZSM-11 zeolite, in which all the pores are straight, the molecules of normal and branched C_3–C_{10} hydrocarbons can be adsorbed in channels passing through the crystallite in only one crystallographic direction. In contrast to this, in ZSM-5 zeolite, small n-alkane molecules (C_3–C_5) are adsorbed in all the pores. Higher n-alkanes (C_6–C_8), C_4 and C_5 isoalkanes, and *p*-xylene are adsorbed only in the straight channels, and C_9 and C_{10} n-alkanes only in the sinusoidal channels. For the isomers of decane (methylnonanes), depending on the position of the methyl group in the chain, the adsorption of the isomers may take place only in the straight channels (4-methylnonane) or only in the sinusoidal channels (5-methylnonane) of ZSM-5 zeolite[72].

Published data on the adsorption of hydrocarbons on ZSM-5 zeolites[102] indicate that the movement of the molecules inside the crystallites is controlled by the pentasil pore system itself (molecular traffic control). According to this hypothesis, which has been questioned[115,116], in catalytic processes (for example the transformation of methanol into hydrocarbons), reagent molecules with a definite size diffuse into the crystallites along channels of one type, and the molecules of products with a different size are removed from the zeolite through channels of the other type. This should stop back-diffusion, which lowers the reaction rate.

The influence of the pore structure of pentasils on their molecular-sieve and catalytic properties is also revealed in the high stability of zeolites of this type with respect to coke formation, compared with first-generation zeolites. The restricted diameter of the channels in the pentasils, and the absence of large cavities, apparently prevent the formation, in the crystallites, of large molecules of polycondensed aromatic compounds, which cannot diffuse out of the pores and which provide one source of the coke which deactivates the catalyst[78,112,117-120]. In H-ZSM-5 zeolite, in contrast to mordenite and offretite, coke is formed on the outer surface of the crystallites, and not inside the pores, where the most strongly acidic centres, responsible for the catalytic activity of the pentasils, are situated[119]. In the transformation of C_3 and C_4 alkanes (450–550 °C), TsVK pentasils shows practically no loss of activity for 6–8 h, whereas zeolites of types A, X, and Y, and mordenite under the same conditions are rapidly deactivated as a result of intensive coke formation[121].

The shape and diameter of the pentasil channels evidently are not the only factors determining their adsorption and catalytic properties. For example, the study of the sorption of a series of hydrocarbons, methanol, and dimethyl ether on different specimens of H-ZSM-5 zeolite has shown[107,108] that the extent and kinetics of the sorption depend on the $SiO_2/.Al_2O_3$ ratio and on the size of the crystallites. It is suggested that the sorptive properties of the pentasils may be influenced by various other factors which cannot be estimated by a simple analysis of the structure and composition of the zeolite, since they are determined by the previous history of the specimen[107]. They apparently include the nature of the localisation of the Al atoms in the crystal lattice, the phase purity of the zeolite, and the structural type to which it belongs (ZSM-5, ZSM-11, or a mixed structure).[70]

The chemical character of the adsorbate also has a significant influence on the nature of the sorption processes on pentasils. For example, ethylene and propylene, unlike ethane and propane, are adsorbed irreversibly and in larger quantities on the H-forms of ZSM-5 zeolites[103,107,122,123]. Infrared spectroscopy and other methods have shown that on pentasils, ethylene molecules are chemisorbed, activated, and react with other molecules of this alkene from the gas phase, forming a linear oligomer, which fills the pores of the zeolite[103,107,123]. When propylene is adsorbed, molecules of non-branched macromolecular compounds again accumulate in the pores of the pentasil. It is suggested that propylene undergoes conjugated polymerisation, and not oligomerisation, which leads to the formation of oligomers with quaternary carbon atoms, whose formation is prevented by the small diameter of the channels in the pentasil[122].

The formation of macromolecular compounds in the pores was also observed in a study of the adsorption of C_4–C_6 alkenes and cycloalkenes (cyclopentene, cyclopentadiene, and cyclohexene) on HZ-79 zeolite, an analogue of ZSM-5 zeolite[123]. In contrast to this, an infrared spectroscopic study of the adsorption of hex-1-ene, hept-1-ene, and cyclohexene on H-ZSM-5 zeolite detected only the interaction of the alkenes with the active (acidic) centres of the zeolite[124].

Because of the low concentration of Al atoms, the centres active in catalysis and adsorption are evidently situated at comparatively large distances from one another, and this lowers the probability of interaction between the sorbed molecules.

With increase in temperature, the oligomers or polymers filling the pores of the pentasil undergo cracking, and their decomposition products are readily removed as various hydrocarbons from the channels by a stream of inert gas[122,123]. In this way it has been possible, for example, to regenerate TsVK zeolite modified by added vanadium, which had been completely deactivated in experiments with ethylene by its oligomerisation products[125].

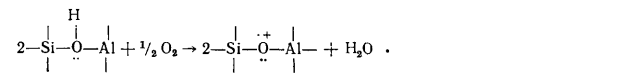
The sorption and catalytic properties of zeolites are due to the presence of active centres on their surface. It is therefore necessary to examine the question of the nature of these centres in pentasils and to determine whether there are any differences in this respect between pentasils and first-generation zeolites. Studies by infrared spectroscopy, mass spectrometry, and various other methods have shown[78,126-129] that the surface of pentasils, like that of first-generation zeolites[130], is covered by OH groups of two types. In the infrared spectra these correspond to two bands in the hydroxyl group stretching region at 3720 cm^{-1} and 3600 cm^{-1}.

The band at 3720 cm^{-1} is assigned to silanol or terminal OH groups (Si–OH), which do not have acidic properties and play no part in catalysis[78,130]. It is suggested[78] that these groups may also be joined to the amorphous SiO_2 present as impurity in pentasils. A recent study of the infrared spectra of a series of carefully prepared specimens of H-ZSM-5 zeolite with a high purity and different concentrations of Al atoms in the lattice (from 0 to 47 Al atoms in the unit cell) showed that the band at 3720 cm^{-1} is in fact due to a small quantity of structureless silicon dioxide, and also a very small quantity of terminal OH groups. Thus the presence or absence of this band in the infrared spectra of pentasils can be used as an indicator of the degree of crystallinity and the phase purity of the zeolite[131].

The band at 3600 cm^{-1} is due to acidic groups formed by the decationation of the Na- or NH_4-forms of the zeolites. It is usually assumed that they act as Brönsted acidic centres and are responsible for the catalytic activity of zeolites in acidic reactions[78,126-130]. These groups are joined to three-coordinate Al atoms in the zeolite framework (Si–OH–Al); the number of groups should therefore correspond to the concentration of Al in the crystal lattice. The infrared spectra of very pure specimens of H-ZSM-5 zeolite contain only the band at 3600 cm^{-1}.[131] Its width indicates that the acidic OH groups are apparently localised in cavities formed by the intersection of the channels of the pentasil.

The activation of zeolites at increased temperatures (T_{act}) is accompanied by the removal of both terminal and acidic (bridging) OH groups. As a result of dehydroxylation, the Brönsted acidic centres are converted into Lewis centres[130]. In first-generation zeolites, Brönsted centres can be regenerated by hydrating the dehydroxylated zeolites. In contrast to this, repeated hydration of an H-ZSM-5 zeolite activated at $T_{act} = 800°$ does not lead to regeneration of the Brönsted centres[78]. At a high T_{act}, apparently, a certain fraction of the Al atoms is removed from the zeolite framework and prevents the hydration of the Lewis centres, localised in the depth of the channels of the pentasil. This migration of aluminium as Al^{3+} cations from the framework of zeolites of type Y, and, to a lesser extent, mordenite was observed by ^{27}Al NMR spectroscopy after thermochemical treatment of the specimens[129,132]. It is assumed that the strong electron-acceptor properties of the Al^{3+} cations and the possibility of the heterolytic ionisation of water molecules in the field of these cations lead to the production in zeolites of type Y and mordenite of strong proton-donor centres of the type $[Al-O-Si]_3^-[O-Si].Al_3^+(OH)^-...H^+$. Since in zeolites of the TsVK type and erionite the migration of Al could not be detected, the authors cited[129,132] assumed that in these zeolites such centres are either absent or present at very low concentrations. It should also be noted that there are no published data confirming the existence of proton-donor centres of this type in zeolites.

Recent EPR data[133] indicate that the activation of pentasil at $T_{act} \geq 500°$ is accompanied by the conversion of Brönsted acidic centres into "solid state defects":



In the opinion of the authors[133], organic molecules adsorbed on a pentasil surface and capable of ionisation can react with these defects to form radical-cations, which undergo subsequent transformations. The reactions of this kind examined include the isomerisation of 3,3-dimethylbut-1-ene to 2,3-dimethylbutene, and the cyclotrimerisation of 1,2-dimethylacetylene.

As already noted, the quantity of Al atoms in the pentasil framework is much smaller than that in first-generation zeolites. Thus the concentration of Brönsted (and correspondingly Lewis) acidic centres in pentasils should be appreciably lower[78]. This is confirmed by data obtained by H–D exchange and from the infrared spectra of pyridine adsorbed on the zeolites (Table 1),[128] and also by ^{27}Al NMR spectroscopic data[129].

Table 1. Comparison of the acidic properties of H-ZSM-5 and HNaY zeolites[128].

Parameters	H-ZSM-5	HNaY
T_{act}, °C	400	500
Concentration of OH groups*	$2.2 \cdot 10^{20}$	$8.7 \cdot 10^{20}$
Concentration of Brönsted centres**	$3 \cdot 10^{19}$	$3 \cdot 10^{20}$
Concentration of Lewis centres	$2 \cdot 10^{19}$	$3 \cdot 10^{20}$

*Calculated for 1 g of zeolite (from H–D exchange data).
**The concentration of acidic centres in 1 g of zeolite was calculated from the infrared spectra of adsorbed pyridine.

The number of Brönsted acidic centres in the unit cell should correspond exactly to the number of Al atoms in the crystal lattice of the zeolite[131,132]. The calculation of the number of these centres in pentasils from the heats of adsorption of NH_3 (q), however, gives low values, and this has been attributed to the existence in the pentasils of very weak acidic centres ($q \leq$ ~60 kJ $mole^{-1}$), which cannot be detected by this method[78].

At the same time, the high acidity of the pentasils is combined with a comparatively low concentration of acidic centres. This suggested that these zeolites contain centres having an anomalously strong acidity. The microcalorimetric determination of the heats of adsorption of NH_3 revealed the existence in pentasils of acidic centres of different strength (acidity spectra);[132,134-137] however, only a very small proportion of the centres adsorbed ammonia with q ~150 to

160 kJ mole^{-1}, which was slightly greater than the corresponding value for zeolites of type Y and mordenite (120 to 140 kJ mole^{-1}).[132-137] Zeolites of the ultrasil and mordenite type showed practically no difference from one another in the heats of adsorption of NH_3 on the strongest centres (q ~150 kJ mole^{-1}).[134]

The infrared spectra of pyridine adsorbed on H-ZSM-5 showed that with increase in T_{act} from 500° to 800°, the intensity of the bands at 1550 cm^{-1} and 1460–1450 cm^{-1} in these spectra decreases, that is there is a decrease in the concentration of both the Brönsted and the Lewis centres[78]. An EPR study of the adsorption of NO, however, indicated that the number of the strongest Lewis centres, capable of adsorbing nitric oxide, begins to increase sharply at T_{act} > 500°.[78] The discrepancy in the data obtained by the two methods is apparently due to the greater accessibility of the strongly acidic centres of the zeolite for NO molecules, compared with pyridine. Moreover, these data also indicate that such centres are localised inside the pores of the zeolite[72,80,119,137]. Data on the acidic properties of ZSM-5 zeolite are also given in Ref.138.

The published data on the hydroxyl covering and the acidic properties of Soviet pentasils of the TsVK type and ultrasil[84, 134,139-147] agree with and supplement available data for ZSM-5 zeolites. For example, the highly sensitive infrared diffuse reflectance spectroscopy[145] confirmed the above data[78] on the existence of two types of OH group on the pentasil surface, and showed that high-temperature activation leads to the removal of OH groups from the zeolite surface, and that at T_{act} ≅ 900–1000°, some Al atoms migrate from the pentasil framework. These results[145] show good agreement with data obtained by H–D exchange[84], which show that there is an almost two-fold decrease in the concentration of the surface OH groups in a TsVK zeolite with increase in T_{act} from 300° to 700° (curve *1* in Fig.5). It should be noted that the removal of this quantity of OH groups had practically no influence on the catalytic properties of the zeolite in the transformations of lower alkenes (isobutene): both the total yield of liquid products and the yield of aromatic hydrocarbons remained unchanged (curves *2* and *3* respectively in Fig.5). Even the activation of the zeolite at 900 to 1000° has little influence on its total activity, although the ability of the zeolite to bring about dehydrocyclisation decreased appreciably. The catalytic activity of TsVK pentasil is apparently due to a small quantity of OH groups present in the active centres, which may break down only at T_{act} > 800°. After high-temperature treatment, the zeolite also showed a significant increase in selectivity in the formation of *p*-isomers of dialkylbenzenes, and this was attributed[84] to slight changes in the zeolite structure at high temperatures. These changes possibly involve the removal of Al atoms from the zeolite framework[145], lead to a decrease in the pore diameter, and create hindrance for the diffusion of molecules larger than *p*-dialkylbenzene molecules.

A number of other studies have established a relationship between the acidity and catalytic activity of pentasils[135,142, 143,148,149]. For example, it has been shown[143] that a decrease in the number of strongly acidic centres in a zeolite of the ultrasil type by dehydroxylation is accompanied by a sharp decrease in the activity of this zeolite in the cracking of n-octane and iso-octane. According to Ref.148, the rate constant for the transformation of methanol into hydrocarbons increases linearly with increase in the acidity (that is the number of acidic centres) of a catalyst based on a ZSM-5 zeolite. A correlation has been established between the acidity and the catalytic activity of H-ZSM-5 pentasil in the cracking of cumene, the isomerisation of *o*-xylene, and the decomposition of methanol and ethanol[149]. The number and strength of the acidic centres in the H-form of this zeolite depend on the conditions of its preparation from the NH_4-form.

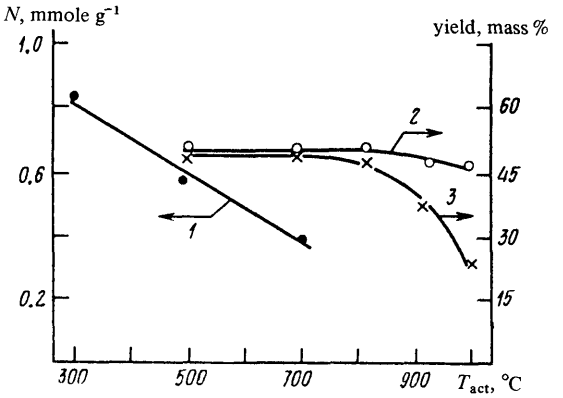


Figure 5. Dependence of the concentration of OH groups (N) in TsVK zeolite (*1*) and the yield of liquid catalysate (*2*) and aromatic hydrocarbons (*3*) from isobutene (500 °C) on T_{act}.[84]

Thus the composition and structure of the pentasils determine a number of specific properties which distinguish them from first-generation zeolites. These properties include, in particular, their hydrophobic nature, high thermal stability, and configurational molecular-sieve selectivity. The surface of the pentasils, like that of zeolites of any other type, carry hydroxyl groups, some of which show acidic properties, and apparently act as the source of the catalytic activity, playing the part of Brönsted acidic centres. The concentration of these centres in pentasils is appreciably lower than that in first-generation zeolites. Nevertheless, they show a high activity as catalysts in a whole series of reactions, and differ from zeolites of other types in their high stability. Data on the use of pentasils as catalysts in various reactions are examined below.

III. TRANSFORMATIONS OF OXYGEN-CONTAINING COMPOUNDS ON PENTASILS

1. Transformations of Methanol

The transformations of various oxygen-containing compounds, including methanol, on first-generation zeolites (chiefly of types X and A) have been the subject of a number of studies and reviews[38,40,42,150,151]. On these zeolites, methanol decomposes to give water, dimethyl ether, and small quantities of lower alkenes and alkanes; the catalysts rapidly lose their activity as a result of coke formation. In contrast to this, on ZSM-5 pentasils, methanol at 350–400° is completely converted into water (~56%) and a mixture of hydrocarbons (~44%).[28,32-37]

According to Ref.152, the mixture of hydrocarbons formed from methanol contained propane (~16%), n-butane and isobutane (~25%), isopentane (~8%), aliphatic C_6–C_{10} hydrocarbons (~4%), and also toluene (~10%), xylenes (~17%), and

C_9 and C_{10} alkylbenzenes (~11%). The fact that the reaction products did not contain molecules with more than 10 carbon atoms was attributed to the influence of the porous structure of the zeolite, responsible for its molecular-sieve selectivity, as discussed above. This selectivity was also revealed in an increased concentration in the products, compared with the equilibrium concentration, of durene and isomers of tri- and tetramethylbenzenes, whose molecular size enabled them to diffuse comparatively easily from the pores of the zeolite into the gas phase.

The compositions of the products of the transformations of methanol on pentasils have also been studied in detail by other authors[87,138,149,153–167]. In addition to the hydrocarbons indicated above, these products contained small quantities of C_5–C_7 cyclanes and cyclenes, naphthalene, and alkylnaphthalenes[154,156,157]. Data on the composition of the products of the transformations of methanol on pentasils under similar conditions are given in Table 2.

Table 2. Characteristics of the transformations of methanol on ZSM-5 zeolite and the composition of the products.

Parameters of the process[1]	[152]	[153–154]	[155]	[156][3]	[87][3]	[157][4]	[158]	[159]
T, °C	370	350	370	370	400	340–360[5]	400	380
v, h^{-1}	1.0	1.0[6]	0.8	1.0	3.0	1.6	1.0	—
α, %	100	100	99	100	100	—	100	100
w, mass %	44	44	45	43	—	—	44	—
Hydrocarbon composition, mass %								
Aliphatic hydrocarbons, total:	58.8	73.3	55.6	71.8	21.6	63.8	84.7	47.0
including:								
C_1	1.0	—	41.3	0.9	2.9	2.1	0.7	3.0
C_2	1.1	3.2		5.1		1.3	3.6	11.0
C_3	17.2	20.4		9.0	10.3	11.7	10.8	13.0
C_4	25.6	26.7		21.8	8.4	14.9	29.7	20.0
C_5	9.6	13.2[7]	14.3	15.5[7]	traces	13.8[7]	39.9	
C_6–C_{10}	4.3	9.8[8]		19.5[8]	traces	20.0[8]		
Aromatic hydrocarbons, total:	41.2	26.7	44.4	28.2	78.4	31.6	15.3	45.0
including:								
benzene	1.7	1.4	41.8	—	traces	0.4	—	2.0
toluene	10.5	6.4		1.4	4.9	4.4	—	15.0
xylenes	17.2	13.4		6.1	73.5	12.2	—	28.0
ethylbenzene	0.8			0.2		0.9	—	
C_9 alkylbenzenes	7.5	5.5		9.7		10.8	—	
C_{10} alkylbenzenes	3.3	—		5.4		6.6	—	—
C_{11}+ alkylbenzenes	0.3	—	2.6	5.4[9]		0.9[9]	—	—

[1] T = temperature, v = volume flow rate, α = degree of transformation, w = yield of hydrocarbons.

[2] Pilot plant, fluidised-bed catalyst, N_2 carrier gas.

[3] Pilot plant, stationary catalyst layer, H_2 carrier gas.

[4] After 73 h catalyst use without regeneration in a pilot plant.

[5] Temperature at reactor inlet; temperature at outlet 404°.

[6] Calculated for the pure zeolite, mixed in the catalyst with SiO_2 (1 : 1).

[7] Including C_5 naphthenes.

[8] Including C_6 and C_7 naphthenes.

[9] Including naphthalene and alkylnaphthalenes.

In spite of the significant differences in the conditions of these reactions (in laboratory[87,152–154,158] or pilot-plant[155–157] assemblies with stationary or fluidised-bed[156] layers of catalyst) and the fact that different ZSM-5 zeolite specimens were used, the data in Table 2 show considerable agreement. Thus in all cases the conversion of the alcohol is ~100%, the yield of hydrocarbons is stoichiometric (~44%), and the products contain 1–3% methane and an appreciable quantity of alkanes, in which iso-alkanes predominate. At the same time, appreciable differences are observed in the distribution of individual products and in the ratio of the quantities of aliphatic and aromatic hydrocarbons formed. Thus the composition of the products of the transformation of methanol depends on the reaction conditions (temperature, volume rate, pressure) and on the composition of the catalyst (the SiO_2/Al_2O_3 ratio).

In a flow reactor with a stationary catalyst layer (H–ZSM-5), the conversion of methanol increased rapidly with temperature, and reached 100% at 340–375°.[152] Below 300°, methanol was converted chiefly into dimethyl ether with the formation of small quantities of C_2–C_5 alkanes and alkenes (7–10%) and aromatic hydrocarbons (~1–3%). At 300–400° the products contained only aliphatic and aromatic hydrocarbons (60% and 40% respectively). Increase in temperature to 450–500° led to the formation of methane and lower alkanes by secondary cracking reactions, and above 500°, methanol decomposed directly to CO and H_2.

Analogous results were obtained when other H-ZSM-5 zeolite specimens were used[153–155,158], including specimens with added phosphorus[158]. With a fluidised-bed catalyst based on ZSM-5 zeolite[156], the reaction rate increased by a factor of 1.5 for each increase in temperature by ~27–30 K. The influence of temperature on the distribution of the products of the transformation of methanol on H-ZSM-5 zeolite was studied in detail[124], and the results showed good agreement with earlier data[152].

The transformations of methanol on ZSM-5 zeolites at different volume rates have been studied[152,154,156,160,163,168]. Increase in the volume rate (v) by a factor of more than 1000 (from 1 h^{-1} to 1080 h^{-1}) lowers the conversion of methanol (370°, p_{CH_3OH} = 1 atm) by a factor of approximately 3 (from 100% to ~30%) and has a significant influence on the direction of the transformations of the alcohol[152]. The change in the composition of the products of the transformations of methanol with change in the volume rate for different partial pressures of alcohol (p_{CH_3OH}) is shown in Figs. 6*a* and 6*b*.[152,160] These data also indicate that p_{CH_3OH} influences the composition of the products formed from methanol on ZSM-5 zeolites. Increase in p_{CH_3OH} leads mainly to an increase in the selectivity of the process with respect to the formation of polyalkylbenzenes, in particular durene[155,156,160]. Thus the aromatic fraction of the products formed from CH_3OH on H-ZSM-5 zeolite at p_{CH_3OH} = 1 atm (370°, v = 1 h^{-1}) contains only ~2 mass % durene[152], whereas at p_{CH_3OH} = 50 atm under the same conditions, the durene concentration increases to ~60 mass %.[160] It is suggested[160] that polyalkylbenzenes are formed by alkylation taking place with simultaneous dehydration of the oxygen-containing compounds and aromatisation of the hydrocarbons (hatched region in Fig. 6*a*). With increase in p_{CH_3OH}, this range broadens considerably (Fig. 6*b*), leading to an increase in the range of conditions favouring the formation of polyalkylbenzenes. With decrease in p_{CH_3OH} to 0.04 atm, the range corresponding to simultaneous dehydration and aromatisation practically disappears, and polyalkylbenzenes are formed in very small quantities.

The degree of transformation of methanol and the composition of the reaction products depend to a significant extent on the SiO_2/Al_2O_3 ratio and the concentration of Na in the pentasil. In the transformation of methanol (400°, v = 3 h^{-1}) on the original form of silicalite (0.22 mass % Na,

SiO_2/Al_2O_3 = 1125), the initial conversion of alcohol was ~50%, and the reaction products contained chiefly dimethyl ether and a small quantity of propane[87]. With decrease in the concentration of Na in the silicalite, the conversion of methanol gradually increased to 100%, and the resulting mixture of aliphatic and aromatic hydrocarbons showed an increased concentration of arenes (up to ~45 mole %). The original and decationated forms of ZSM-5 zeolite were much more active in the transformations of methanol, although the concentration of Na in them (2.03 mass % and 0.38 mass % respectively) were much higher than in the original form of silicalite. In both cases the conversion of the alcohol was 100%. As with silicalite, decrease in the concentration of Na in the zeolite was accompanied by an increase in the concentration of aromatic hydrocarbons in the reaction products (from 20 mole % to 78 mole %).

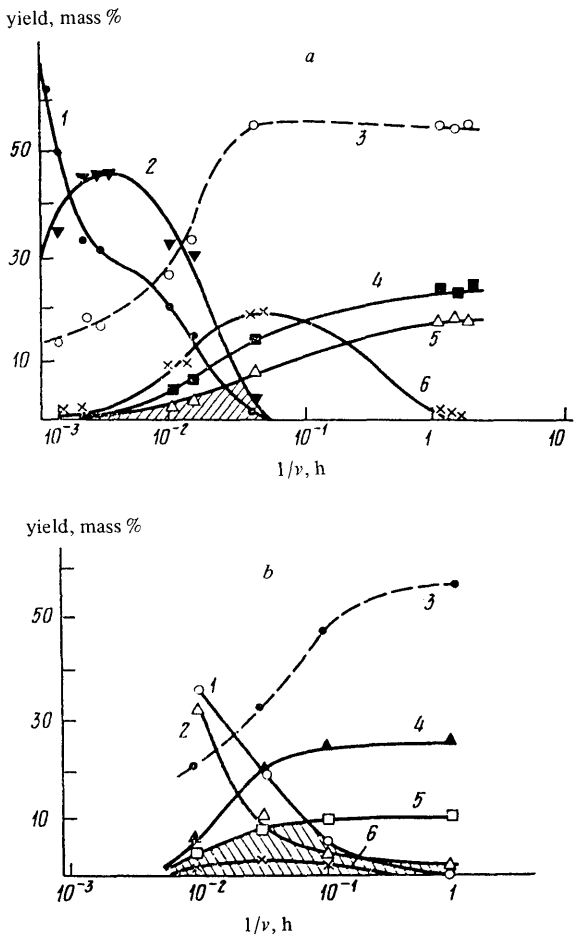


Figure 6. Dependence of the composition of the products of the transformation of methanol on H-ZSM-5 zeolite (370 °C) on the reciprocal of the volume flow rate at $p_{CH_3OH} = 1$ atm (*a*) and 50 atm (*b*): [*1*) CH_3OH; *2*) $(CH_3)_2O$; *3*) H_2O; *4*) alkanes; *5*) aromatic hydrocarbons; *6*) C_2–C_5 alkenes].[160]

Thus to obtain silicalite specimens active in the transformation of methanol, it is necessary to have much more extensive decationation than with ZSM-5 pentasil, which is active even in the Na-form. Thus the lower the Al concentration in the zeolite, the greater the extent to which its catalytic activity is suppressed by sodium.

The influence of the SiO_2/Al_2O_3 ratio on the catalytic properties of H-ZSM-5 zeolite in the transformations of methanol can be judged from the published data[161] in Table 3. For the zeolite specimens *1* and *2* with SiO_2/Al_2O_3 ratios of 38 and 54.5 respectively, the conversion of the alcohol and the composition of the reaction products were practically the same, in spite of the difference in the Na concentration in the zeolites and the difference in the reaction temperatures. Increase in this ratio to 158 (specimen *3*), however, decreased the conversion of the alcohol by a factor of almost 2, and in this case the alcohol was converted chiefly into dimethyl ether. Thus the activity of ZSM-5 zeolites in the transformation of methanol into hydrocarbons depends on the concentration of Al atoms in the zeolite framework. Below a definite concentration of these atoms (~0.5%), the number of active centres in the zeolite evidently becomes insufficient for the formation of hydrocarbons from methanol.

Table 3. Transformations of methanol on H-ZSM-5 zeolites with different SiO_2/Al_2O_3 ratios.

Parameters of the process	H-ZSM-5 zeolite specimens		
	1	2	3
x	38	54.5	158
[Al], %	2.16	1.51	0.53
$[Na_2O]$, mass %	0.05	0.10	0.15
T, °C	372	380	372
v, h^{-1}	10	11	11
α, %	89	89.7	48.6
Composition of products, mass %			
Methanol	11.0	10.3	51.4
Dimethyl ether	7.8	10.6	44.9
Hydrocarbons, total:	81.2	79.1	3.7
including: aromatic	9.1	5.4	0.5
aliphatic	90.9	94.4	99.5

In an examination of the relationship between the composition of pentasils and their activity in the transformations of methanol, mention must be made of patent data[23,24,28,30,169,170], according to which modification of ZSM-5 zeolites by the addition of various elements (Mg, B, Zn, Cd, Sb, Ni, Pd, P, etc.) leads to an increase in the yield of liquid products from methanol and to an increase in the concentration of aromatic hydrocarbons in them. Treatment of a ZSM-5 zeolite with various phosphorus compounds (for example trimethyl phosphite) lowers slightly its activity in transformations of methanol, but increases the selectivity of the reaction with respect to the formation of ethylene and other lower alkenes, particularly at low temperatures[158]. After this treatment, the zeolite showed an increase in the quantity of acidic centres, but these centres were weaker than the centres of the non-modified pentasil[158].

An increase in the selectivity of the transformations of methanol with respect to C_2 and C_3 alkenes was also detected[171] on MnNa-ZSM-5 and MgNa-ZSM-5 zeolites prepared by cation exchange. These zeolites are more stable than MnNaY and MnNaX zeolites.

The production of ethylene and propylene from methanol with a good selectivity (more than 75%) was observed on non-modified ZSM-34 pentasil[6]. This catalyst rapidly lost its activity, however, as a result of coke formation. Improvement of the method of synthesis of ZSM-34 zeolite by using seed crystallites led to a significant change in its catalytic properties. The total yield of hydrocarbons from methanol at 400° increased by a factor of ~2, the selectivity with respect to C_2 and C_3 alkene formation increased to ~80%, and the time of service of the catalyst increased by a factor of 2.2.[172,173] These positive effects are due to the high uniformity of the size and shape of the zeolite crystallites formed in the presence of the seed crystals. Detailed information on the influence of the nature and quantity of added seed crystals on the structural, catalytic, adsorptive, and other properties of ZSM-34 zeolite has been published[174,175]. On the basis of this zeolite, synthesised using a seed crystal, a technical process has been proposed for converting methanol into C_2–C_4 alkenes with a selectivity of more than 86%.[176]

Comparison of the products of the transformation of methanol on H-ZSM-5 and H-ZSM-11 pentasils[113] showed that on H-ZSM-5, aromatic C_8 hydrocarbons are formed preferentially, whereas on H-ZSM-11, more C_9 hydrocarbons are obtained. These results[113] were attributed to differences in the volume of the cavities formed at the intersections of the pores in zeolites of these two types. It was also established that the products of the transformations of CH_3OH on large crystallites of H-ZSM-11 zeolite have approximately the same composition (more aliphatic C_1 and C_2 hydrocarbons, less C_6 hydrocarbons and aromatic C_9 hydrocarbons), as on H-ZSM-5 crystallites with the same size.

The low degree of coke formation characteristic of pentasils, and the corresponding high stability of operation as catalysts, also depend on the composition of the zeolite. Na silicalite and Na-ZSM-5 zeolite are deactivated completely after use for 5 h under the conditions of methanol transformation at 400°.[87] Under the same conditions, the activity of decationated silicalite remains unchanged for ~6 h, and H-ZSM-5 zeolite is not deactivated after ~12 h.

It should be emphasised again that the high stability of pentasils is due primarily to their unusual porous structure[112,117,118]. A study of the transformations of methanol on H-ZSM-5 zeolites, H-offretite, and H-mordenite[119] showed that the maximum quantity of coke deposited on these catalysts after use for 12 h at 380° increased in the order H-ZSM-5 < H-mordenite < H-offretite, and amounted to 2.2, 8.7, and 16.8 mass % respectively. H-mordenite and H-offretite are almost completely deactivated after 30 min and 55 min respectively, whereas the activity of H-ZSM-5 zeolite decreased only slightly after this catalyst had been used for 1.5 h. For all three zeolites, increase in the quantity of coke formed was accompanied by various changes in the distribution of the hydrocarbons formed. For example, for H-ZSM-5 zeolite the ratio C_4H_{10}/C_4H_8 gradually decreased, approaching a constant value. Simultaneously, the products showed an increase in the already high concentration of *p*-xylene. Overall, the ratio of the concentrations of *p*-xylene and *o*-xylene for H-ZSM-5 zeolite reached values >40, whereas for the other two zeolites it was 0.5–2.0 and remained unchanged throughout the experiment. EPR showed that the coke deposited on H-ZSM-5 has a low hydrogen content, and is similar to graphite in character. In contrast to this, the coke on H-mordenite, and H-offretite corresponds more to polynuclear atomatic systems. It was suggested[119] that as a result of the size and shape of the channels in H-ZSM-5 zeolite, coke formation takes place chiefly on the outer surface of the zeolite and does not influence the strongly acidic centres which are localised within the pores and which are responsible for the catalytic activity. The surface coke may partly block the entry to the pores, however, increasing the molecular-sieve properties of the pentasil, as revealed by the change in the selectivity of the process during the operation of the catalyst.

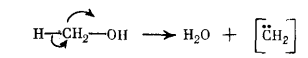
H-ZSM-5 zeolite has a high stable activity under the conditions of the formation of aromatic hydrocarbons from methanol under pulse conditions (450 °C), whereas the new SHS zeolite Nu-1 ($SiO_2/Al_2O_3 \cong 53$), whose structure does not correspond to the pentasil family, is rapidly deactivated by coke formation[177].

Considerable attention has been paid to the study of the stability of catalysts based on H-ZSM-5 zeolite in the development of a technical process for producing petrol from methanol in pilot plant[155–157]. By carrying out the stage of alcohol dehydration and the stage of the production of a mixture of hydrocarbons from the dehydration products in two different reactors with a stationary layer of zeolite catalyst[155], it was shown that the deactivation of the latter takes place predominantly in the second stage as a result of coke formation. The period of use of this catalyst in the second stage without regeneration reached 167 h, and after this period a significant change in the selectivity of the process was observed: the yield of C_3 and C_4 alkenes and hydrocarbons containing five and more carbon atoms decreased. The results were confirmed under prolonged testing conditions, in which ten working cycles with a total duration of ~207 d were carried out without replacing the catalyst. Under fluidised-bed conditions, a catalyst based on ZSM-5 zeolite functioned for more than 50 d. During this time it was regenerated six times using air[156]. In each working cycle the high initial activity of the catalyst gradually decreased with time, and after each regeneration the activity of the catalyst at the start of the next cycle was lower than that at the start of the previous cycle.

2. Mechanism of Formation of Hydrocarbons from Methanol

The intensive study of the transformations of methanol to hydrocarbons on the new generation of zeolites has led to the development of earlier[178–180] suggestions about the mechanism of this process.

From the ideas of Venuto and Landis[179] on the mechanism of the decomposition of methanol on zeolites of type X, it was suggested[152] that on ZSM-5 zeolites, methanol or its decomposition product dimethyl ether can decompose to give carbene-like methylene biradicals



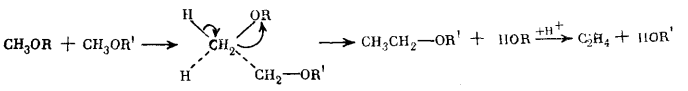
These biradicals may then either dimerise

$$2\,[\ddot{C}H_2] \rightarrow C_2H_4$$

or react with molecules of methanol or dimethyl ether

$$[\ddot{C}H_2] + CH_3OR \rightarrow CH_3CH_2{-}OR \xrightarrow{+H^+} C_2H_4 + HOR \qquad R = H,\ CH_3$$

Since the molecules of alcohol or ether act as both donors and acceptors of methylene biradicals, this mechanism can be represented as a conjugated bimolecular reaction

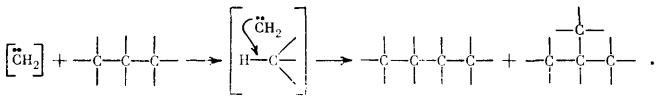


R and R' = H, Alk.

After the formation of the first molecules of alkene (ethylene), the carbene biradicals can add on across the double bond, giving hydrocarbons with higher molecular weight.

Later, on the basis of this mechanism, a kinetic model was developed[181] for the transformation of methanol to hydrocarbons on ZSM-5 zeolites, making it possible to determine with satisfactory accuracy the extent of the conversion of alcohol and the selectivity of the process over a wide range of pressures.

Because of the doubts expressed by various authors about the correctness of the carbene mechanism, data were published[182], which in the author's opinion proved that carbene biradicals are formed from methanol on ZSM zeolites. According to these data, in the transformations of $^{13}CH_3OH$ on H-ZSM-5 zeolite (370°, 1 atm, $v = 0.4\ h^{-1}$), dilution of the alcohol by propane (whose conversion under these conditions is ~0.3%) decreases by a factor of more than three the ratio of isobutane to n-butane in the reaction products compared with experiments in which methanol was diluted with helium. The data on the distribution of the ^{13}C isotope between the butane isomers formed made it possible to attribute this effect to the direct methylation of the "inert" propane by carbene biradicals. The reaction can take place by the introduction of this biradical at one of the sp^3 C–H bonds of propane



This reaction should give 75% n-butane and 25% isobutane, which corresponds to the results obtained.

One objection to the carbene mechanism is that it does not explain the formation from methanol of methyl ethyl ether and large quantities of isoalkanes, and the increase in the yield of alkenes with decrease in the conversion of alcohol[153,154]. The authors cited suggested that on ZSM-5 zeolites, whose surface has strong Brönsted acidic centres, methanol may undergo dehydration, being converted successively to dimethyl ether and ethylene[178,180]

$$2CH_3OH \xrightarrow[-H_2O]{} CH_3OCH_3 \xrightarrow[-H_2O]{} CH_2{=}CH_2 .$$

According to this scheme, methanol should be converted chiefly to ethylene, which does not agree with data on the composition of the products on the transformation of this alcohol, which contain only small quantities of ethylene (see Table 2). It was therefore suggested that ethylene is highly reactive and readily forms carbenium ions by reacting with Brönsted acidic centres

$$CH_2{=}CH_2 + HOZ \rightarrow CH_3\overset{+}{C}H_2 \cdots \bar{O}Z .$$

The reaction can then proceed in two directions

$$CH_3\overset{+}{C}H_2 \cdots \bar{O}Z \left\{ \begin{array}{l} \xrightarrow[a]{CH_3OH} CH_3CH_2{-}O{-}CH_3 + HOZ \\ \xrightarrow[b]{CH_2=CH_2} CH_3CH_2CH{=}CH_2 + HOZ . \end{array} \right.$$

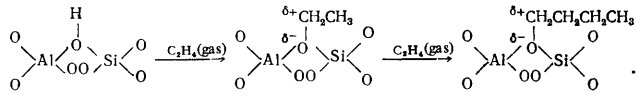
Path *a* gives methyl ethyl ether, which can be dehydrated to give propylene

$$CH_3CH_2{-}O{-}CH_3 \rightarrow CH_3CH_2{=}CH_2 + H_2O .$$

Propylene ether is converted into propane by redistribution of hydrogen, or, like ethylene, reacts with Brönsted acidic centres (path *a*) giving a more stable secondary carbenium ion, leading to the formation of iso-alkanes.

The linear hydrocarbons which are formed according to path *b* by polymerisation, and which contain not less than six carbon atoms, can then undergo cyclisation to give aromatic hydrocarbons. According to the proposed mechanism, the development of the process in the system requires the continuous presence of unconverted methanol. It is therefore suggested that in addition to the forward reaction of alcohol dehydration, the back reaction of alcohol formation also takes place, and both of these reactions compete with the processes of polymerisation, cyclisation, and aromatisation.

To confirm the carbenium-ion mechanism, the adsorption of ethylene on dehydrated H-ZSM-5 zeolite was studied[103]. Thermogravimetric and ^{13}C NMR and infrared spectroscopy indicated that on the strong Brönsted acidic centres of the zeolite, low-temperature chemosorption and activation of ethylene can take place according to the scheme



The addition of ethylene to OH groups corresponds to the formation of carbenium ions, which take part in chain growth giving macromolecular aliphatic hydrocarbons capable of undergoing isomerisation and aromatisation at higher temperatures (300–400°).

In a study of the transformations of methanol on H-ZSM-5 zeolite in the presence of carbon monoxide[183], ^{13}C NMR spectroscopy showed that the products contained saturated and unsaturated aliphatic (and aromatic) aldehydes and ketones. Their formation is attributed only to the reaction of CO with carbenium ions present on the surface

$$CH_3\overset{+}{C}H_2 + CO \rightarrow CH_3CH_2{-}\overset{+}{C}O \xrightarrow{\text{alkane}} CH_3CH_2CHO ,$$
$$CH_3CH_2CHO + C_2H_4 \rightarrow CH_2{=}CH{-}CHO + C_2H_6 .$$

These data also indicate the impossibility of the formation of carbenium biradicals, which in the reaction with CO should give ketene, capable of reacting with the water, methanol, and ethylene present in the system. No products of these reactions (acetic acid, its methyl ester, and cyclobutane) were detected.

These results[103,153,154,183] made it possible to develop a detailed scheme for the transformations of methanol to various hydrocarbons on pentasils with the participation of carbenium ions[166]. According to this scheme, the reaction of carbenium ions with various components of the reaction system can give a broad spectrum of aliphatic and aromatic C_6–C_{10} hydrocarbons, including appreciable quantities of xylenes, ethylbenzene, and 1,2,3-trimethylbenzene. It was subsequently shown[184] that aromatic hydrocarbons are formed predominantly on centres localised in the cavities formed at the intersection of the channels in the pentasils. Since the geometry of the pores in these zeolites permits the simultaneous dehydrocyclo-oligomerisation of only two aliphatic C_5 molecules, the aromatic hydrocarbons formed cannot contain more than ten carbon atoms.

A slightly different mechanism has also been proposed[185], according to which not ethylcarbenium but methylcarbenium (CH_3^+) ions, differing from carbenium biradicals, are formed from methanol on pentasils.

The presence of small quantities of ethylene in the products of the transformation of methanol on pentasils, and also the low degree of conversion and poor reproducibility of the results in experiments with this alkene, led to the suggestion[87] that ethylene is not highly reactive on these zeolites. Thus the role of active intermediate species in the formation of hydrocarbons from methanol is played not by ethylcarbenium ions but by "unsaturated C_3 and C_4 residues", as

shown in the scheme

$$CH_3OH \xrightarrow{H^+_{surf}} (\text{unsaturated } C_3 \text{ and } C_4 \text{ residues})_{surf} \begin{cases} \longrightarrow C_3 \text{ and } C_4 \text{ alkenes} \\ \longrightarrow \text{aromatic hydrocarbons} \end{cases}.$$

Here, H^+_{surf} is an acidic centre on the zeolite surface. To obtain more details of this scheme, the transformations of methanol and various hydrocarbons on H-ZSM-5 zeolite were studied using deuteriated compounds[186]. The results, with allowance for the reaction of methanol on Brönsted acidic centres, indicated that in the first stage of the reaction, activated species $(CH_3)\overset{+}{R}OH$ (R = H, CH_3) are formed on the zeolite surface. Simultaneously, methanol is dehydrated to give alkenes, in which the number of carbon atoms ≥3. This is followed by growth of the carbon chain according to the scheme

$$(CH_3)\overset{+}{R}OH_{surf} + R'R''C{=}CH_2 \rightarrow R'R''\overset{+}{C}{-}CH_2CH_3{}_{surf} \xrightarrow{+ROH} R'R''C{=}CHCH_3 + H^+_{surf}$$
$$R', R'' = H, Alk$$

Isomerisation and dehydrocyclisation, and also the rupture and formation of C=C bonds, can take place, depending on the temperature.

To supplement this mechanism, a scheme was proposed for the transformation of methanol to alkenes with the intermediate formation of methyl isopropyl ether with the subsequent elimination of methanol and the formation of propylene[187]. This scheme has been considered unlikely, however, since the size of the molecule of the intermediate compound is much greater than the diameter of the pores of the zeolite[188].

The formation of hydrocarbons from methanol on H-ZSM-5 zeolite, modified by phosphorus, has also been represented by a general scheme giving only the possible routes and the sequence of transformations of the alcohol[158]. In addition, it was suggested[158] that with a zeolite containing phosphorus, a significant part begins to be played by reactions, catalysed by the acidic centres, involving the alkylation of methanol by methanol (to give dimethyl ether), of ether by ether (to give methyl ethyl ether, which by the removal of an alcohol molecule gives ethylene), and of alkenes by methanol (chain growth). Oligomerisation of alkenes, cracking of oligomers, cyclisation, and hydrogen transfer may also take place.

The mechanism proposed in[189] assumes the formation of intermediate alkyloxonium ions $[R_3O]^+$, where R = H, CH_3, C_2H_5, etc., which can undergo intramolecular rearrangements. According to this mechanism, methanol is dehydrated to dimethyl ether, which on Brönsted acidic centres may be converted into the dimethyloxonium ion $[(CH_3)_2HO]^+$. The reaction of this ion with a dimethyl ether molecule gives an intermediate compound, and the removal of a methanol molecule from the latter gives the stable trimethyloxonium ion $[(CH_3)_3O]^+$. The C–H bonds in this ion may be polarised on the basic centres of the zeolite, formed by the deprotonation of the Brönsted acidic centres. The trimethyloxonium ion can then undergo rearrangement to the methylethyloxonium ion, which can give up a methanol molecule to form ethylene and regenerate the Brönsted acidic centre.

Simultaneously, the dimethyloxonium ion formed at the start of the process can react in six directions with the molecules of water, methanol, and dimethyl ether present in the system. This should lead to the predominant formation of ethylene, whose subsequent transformations give a whole spectrum of hydrocarbons, detected in the reaction products. In spite of its complexity, the mechanism involving alkyloxonium ions explains many experimental facts. Some authors suggest that the formation of hydrocarbons from methanol is autocatalytic[138,148,168]. In an isothermal system on catalysts containing 1.4–10% H-ZSM-5 zeolite and an inert diluent (γ-Al_2O_3 or metallic copper powder), it was shown[148] that at low CH_3OH concentrations the rate of consumption of alcohol is very low, but increases rapidly with increase in the concentration of the alkenes formed. The increase in the reaction rate is apparently due to the autocatalytic reaction of the original alcohol with the alkene (propylene) formed. Kinetic calculations showed that the rate constant of this autocatalytic stage of the process is 50 times the rate constant for the formation of the alkene from the alcohol[148].

The conclusion that the transformations of methanol on ZSM-5 zeolites is autocatalytic was also reached from data which showed a sharp increase in the rate of transformation of the alcohol when an alkene was introduced into the system[138] and data which showed an abrupt increase in the yield of hydrocarbons for a comparative small increase in the temperature of the reaction (from 280° to 300°).[168] It was suggested that the first stage of the process involves the reaction of methanol with a Brönsted acidic centre to give the *methylcarbenium ion*. The reaction of this ion with an alcohol molecule gives a proton and an ether, which decomposes to give ethylene

$$\overset{+}{C}H_3 + CH_3OH \rightarrow \left[\begin{matrix} H \\ CH_3 \end{matrix} \!\!>\!\!\overset{+}{O}\!\!<\!\! CH_2OR \right] \rightarrow CH_3CH_2OR + H^+ .$$

Thus there is still lack of agreement about the mechanism of formation of hydrocarbons from methanol on zeolites of the new generation. At present, apparently, there is agreement only on the first stage of the process, involving the dehydration of the alcohol to dimethyl ether. There is lack of agreement about the mechanism of all the other stages, because of the lack of convincing proof. Up to the present, no unambiguous answers have been obtained to the questions of how the first C–C bond is formed from methanol (or dimethyl ether), and what is the nature of the resulting compound, which is the precursor of all the other hydrocarbons detected in the reaction products. The nature of the intermediate compounds involved in the development of the transformation of methanol into hydrocarbons is also not clear. According to existing ideas, these compounds may be carbene biradicals, carbenium ions, or alkyloxonium ions. The suggestion that intermediate carbenium biradicals are formed has been criticised[153,154,187,191], and these criticisms have been answered, and the suggestion clarified[188,192]. Thus it has been shown[188] that the decomposition of dimethyl ether or methanol can be represented by a scheme involving both carbenium biradicals and carbenium ions. It was concluded that the carbenium mechanism is to some extent provisional, and does not assume the existence of free carbenium biradicals.

It is at present difficult to give preference to any of the proposed mechanisms. The most reliable mechanisms, however, agreeing with current ideas on catalysis, are those involving carbenium ions.

3. Transformations of Other Oxygen-Containing Compounds

Alcohols. In addition to methanol, the transformations of various other alcohols, primarily ethanol, on pentasils have been studied. Comparison of the results of the most detailed study[154] of the products formed from ethanol on H-ZSM-5 zeolite (SiO_2/Al_2O_3 = 43.6; 0.05 mass % Na_2O) with the analogous data for methanol shows that C_2H_5OH undergoes transformations more readily than CH_3OH. Even at 250°, its conversion reached more than 99% (85% methanol), and the reaction products contained more than 98% hydrocarbons (2 to 11% in the case of methanol). At high rates of supply, ethanol is almost completely converted into ethylene[154]. Beginning at 300°, the formation of aromatic hydrocarbons

is observed, and the quantity decreases with increase in the rate of supply of the alcohol, but increases with increase in the reaction temperature. More ethylbenzene and ethyltoluene are formed from ethanol than from methanol. The start of the formation of aromatic hydrocarbons in the gaseous reaction products is accompanied by a sharp decrease in the ethylene concentration, but the concentration of C_4 alkanes and alkenes increases[154].

The formation of aromatic hydrocarbons from ethanol on H-ZSM-5 zeolite has also been observed[193]. The yield of aromatised products increases with increase in temperature (>260°), with decrease in the rate of supply of alcohol, and with the addition of water to the reaction mixture. Water prevents deactivation of the zeolite catalyst[193]. Unlike pentasil, dealuminated Y and M zeolites in the H-form showed only dehydrating properties, and H-mordenite rapidly lost its activity even in the presence of water.

H-ZSM-5 zeolites are deactivated more rapidly in the transformations of ethanol than in experiments with methanol[194]. In addition, ethanol gave more trimethylbenzenes and aromatic hydrocarbons with higher molecular weights, the quantity of which in the reaction products increased with deactivation of the zeolite. A study of the adsorption of n-hexane and toluene on H-ZSM-5 before and after the experiments showed that during use with ethanol, the sorptive capacity of the zeolite decreases, but it can be restored by regeneration in a stream of oxygen.

Ethanol has been transformed into ethylene with a high selectivity on the Na- and H-forms of ZSM-5 zeolite at 200 to 250°.[195] The products contained almost no diethyl ether, but contained acetaldehyde, the quantity of which increased with temperature.

Table 4. Composition (mass %) of the products of the transformations of various alcohols and dimethyl ether on H-ZSM-5 zeolites (for all compounds, $\alpha \cong 100\%$).

Products	Original compound					
	CH_3OH[1]	C_2H_5OH[2]	t-C_4H_9OH[1]	$C_7H_{15}OH$[1]	$(CH_3)_2O$[2]	$(CH_3)_2O$[3]
Methane	1.0	—	0.1	—	—	4.8
Ethane + ethylene	1.1	5.2	1.2	0.4	15.8[4]	15.2
Propane	16.2	10.8	18.8	16.4	11.1	23.4
Propylene	1.0	2.7	1.1	0.2	6.9	
Isobutane	18.7	17.9	18.4	19.3	8.6	16.0
n-Butane	5.6	5.9	8.6	11.0	4.3	
Butenes	1.3	6.6	0.7	0.1	10.0	
Isopentane	7.8	—	6.2	8.7	—	
n-Pentane + pentenes	1.8	18.3	1.6	1.6	14.6	
Hexane + hexenes	4.3	12.2	7.6	3.0	17.2	
Benzene	1.7	0.5	3.3	3.4	0.3	4.6
Toluene	10.5	3.5	11.6	14.3	1.2	12.0
C_8 alkylbenzenes	18.0	6.5	13.7	12.8	6.9	12.7[5]
C_9–C_{11} alkylbenzenes	11.0	10.1	7.1	8.8	3.4	—

[1]From published data[152] at 370°.
[2]From published data[189] at 310° after zeolite use for 28 min.
[3]From published data[159] under pulse conditions; 550°, TsVK zeolite.
[4]Only ethylene.
[5]Only xylenes.

At 350° under a pressure of 50 atm, ethanol on H-ZSM-5 zeolite gave quantities of durene smaller by a factor of 65 than those obtained from methanol, but the quantities of various alkylbenzenes (ethyl-, methylethyl-, dimethylethyl-, and diethylbenzenes) were ~7 times greater[160].

Thus the transformations of ethanol on pentasils show characteristic features, although the products of the transformations of ethanol and methanol have approximately the same composition (Table 4), in spite of the significant difference in the conditions of the reactions and in the pentasil specimens used[149,152,189]. The similarity in the products formed from the two alcohols has been noted by other workers[160,195]. It was therefore suggested[154,195] that the mechanisms of the transformations of ethanol and methanol on pentasils are the same, and involve the formation of carbenium ions on Brönsted acidic centres with the participation of ethylene, as the primary unsaturated hydrocarbon. According to another view[194], the ease of formation of C_9–C_{12} aromatic hydrocarbons from ethanol indicates that its molecules are split into C_2 fragments, whereas CH_3OH gives mainly C_1 fragments.

The transformations of alcohols with higher molecular weights than ethanol on pentasils have been described in only two papers[152,196]. The data for t-butyl, heptyl, and methyl alcohols (Table 4) show that the composition of the products is approximately the same in all cases[152]. Irrespective of the original alcohol, these products contain less than 1% methane, and the main products are propane, isobutane, toluene, and xylenes. The data for heptan-1-ol, however, were obtained at a lower volume rate ($0.7\ h^{-1}$), and this may indicate that this alcohol is less reactive than t-butyl alcohol and methanol.

A study of the transformations of 2-methylbutan-2-ol on TsVK pentasil and on zeolites of type Y (NaY, CaY, HY) [196] showed that at 120–200°, the alcohol decomposes to give 2-methylbut-1-ene, 2-methylbut-2-ene, and 3-methylbut-1-ene. The Na-form of the TsVK zeolites was more active than NaY, but less active than CaNaY and HNaY.

Simple ethers. Among these compounds, the transformations of dimethyl ether—the intermediate product in the formation of hydrocarbons from methanol on pentasils—have been studied in greatest detail. In most cases the experiments with dimethyl ether were carried out to investigate the mechanism of formation of the hydrocarbons from the alcohol[107,152,158,189]. In addition, the transformations of dimethyl ether have been used as a model reaction in the study of the influence of various factors on the catalytic properties of ZSM-5 zeolites[159,197] and in their comparison with the properties of amorphous aluminosilicate, prepared using organic bases[166].

Table 4 shows that the transformations of dimethyl ether on pentasils give (in addition to water and methanol) the same hydrocarbons as in the products of the transformations of methanol and other alcohols. In contrast to alcohols, the decomposition of dimethyl ether on ZSM zeolites gives considerable quantities of ethylene. It was therefore suggested[189] that it is ethylene that is the primary hydrocarbon in this process, and that its rapid methylation gives propylene. Data on the composition of the products of the transformation of dimethyl ether formed the basis of the mechanism, examined above, for the formation of hydrocarbons from methanol involving alkyloxonium ions[189].

The influence of the reaction conditions on the composition of the products formed from dimethyl ether has been studied[152,189]. At a temperature below 300°, the products contain chiefly C_2–C_5 alkenes, whereas at 350°, the formation of appreciable quantities of aromatic hydrocarbons (~20 mass %) and also C_2–C_5 alkanes (~20 mass %) is observed. The nature of the dependence of the conversion of dimethyl ether and the composition of its transformation products on the reciprocal of the volume rate agrees satisfactorily with the

analogous data for methanol (see Fig.6). Similar results were obtained on H-ZSM-5 zeolite modified with phosphorus[158].

Pentasils show a slightly lower stability under the conditions of the transformations of dimethyl ether than when used with methanol. For example, after the operation for 1.5 h of a catalyst based on H-ZSM-5 zeolite (SiO_2/Al_2O_3 = 55) mixed with SiO_2 (1:1), the conversion of dimethyl ether into hydrocarbons decreased by 30%.[189] Simultaneously, the reaction products showed a marked increase in the concentration of ethylene and propylene, and a decrease in the concentration of C_3 and C_4 alkanes. The low stability of the catalyst in these experiments[189] was apparently partly due to the extensive dilution of the pentasil by silicon dioxide. On H-ZSM-5 zeolite in the pure form, the conversion of dimethyl ether at 350° decreased by only ~10% in the first 9 h, and after use for 100 h it decreased by ~40%.[197]

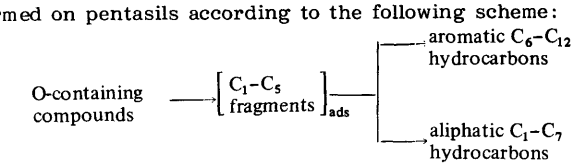
Comparison with first-generation zeolites showed that the conversion of the ether on HY after 9 h decreases by 92%, and erionite and mordenite in the H-forms are almost completely deactivated after use for 6–7 h under the same conditions.

The deactivation of all the zeolites is due to the formation of coke, the quantity of which in the H-ZSM-5 zeolite amounted to only ~2.5 mass % after 9 h, whereas in other zeolites it amounted to ~7–9 mass %.[197] After 100 h, the concentration of coke in the H-ZSM-5 zeolite increased to ~7%. It is suggested that during use, coke formation in the pentasil takes place chiefly on its outer surface, since the small diameter of the zeolite pores prevents bimolecular reactions in them between large molecules, leading to coke precursors (see section II). The coke deposited on the outer surface has little influence on the pentasil activity, which is apparently suppressed by oligomers (or polymers) of ethylene and propylene, which accumulate in the pores on prolonged catalyst use.

The method of preparation of the pentasil has a slight influence on the nature of the transformations of dimethyl ether. Thus ether is converted to a greater extent into ethylene on H-ZSM-5 specimens synthesised in the presence of tetrapropylammonium cations than on specimens obtained using 1,2-diaminohexane[198].

The rate of formation and composition of the products of the transformations of dimethyl ether on H-ZSM-5 pentasil are practically independent of the size of the zeolite crystals and the concentration of Al in them, but change significantly with change in the diameter of the zeolite catalyst pellets[107]. From this and the results of a study of the kinetics of the diffusion and transformations of dimethyl ether on these zeolites, it was concluded[199] that in catalyst pellets with a diameter >2 mm, the rate of the reaction and its selectivity are limited by the diffusion of the molecules in the secondary porous structure. For a smaller pellet diameter, diffusion between the crystallites plays almost no part[107,199]. It was also shown[199] that diffusion in the pores of the pentasil also have very little influence on the rate and selectivity of the transformations of dimethyl ether.

In addition to dimethyl ether, the transformations of diethyl, di-isopropyl, and dibutyl ethers on pentasils have been studied[159]. Since there are no significant differences in the compositions of the products formed from these ethers and also from dimethyl ether, methanol, and acetone, it was concluded that all oxygen-containing compounds are transformed on pentasils according to the following scheme:



Other oxygen-containing compounds. In contrast to alcohols and simple ethers, there have been almost no published studies of the transformations of oxygen-containing compounds of other types (ketones, aldehydes, acids, etc.) on zeolites of the pentasil family. For example, the transformations of acetone have been described only in Refs.152 and 159. Of the total quantity of hydrocarbons formed at 250°, ~60% corresponds to mesitylene, apparently formed on the outer surface of the zeolite by the condensation of three acetone molecules[152]. In addition, the products contain ~19% isobutene and ~19% C_6 and higher aliphatic hydrocarbons. The oxygen-containing products consist chiefly of mesityl oxide (~27%)—the product of the condensation of two acetone molecules—and also C_4 alcohols. At 320°, the total conversion of acetone increases to only ~25%, but the composition of the products changes significantly: among the hydrocarbons, the chief product is isobutene (~83%), and the concentration of mesitylene is only ~2.5%. Approximately 10% of the acetone reacting is converted into CO and CO_2. Increase in temperature to ~400° leads to the almost complete conversion of acetone into C_1–C_{10} hydrocarbons, among which the chief components are xylenes (~22%), C_9 alkylbenzenes (~20%), toluene (13%), a mixture of propylene and propane (~10%), and C_{6+} alkanes and alkenes (~8%).

Table 5. Composition (mass %) of the products of the transformations of aldehydes, esters, and acetic acid on H-ZSM-5 zeolite (371°, 100% conversion).[152]

Products	Original compound				
	CH_3CHO	CH_3CH_2CHO	n-C_3H_7—OOCCH$_3$	n-C_4H_9—OOCCH$_3$	CH_3COOH
Methane	1.5	0.8	0.1	0.1	0.4
Ethane	0.7	0.4	0.1	0.4	0.1
Ethylene	0.3	0.4	2.7	0.2	0.4
Propane	16.4	7.3	2.1	19.4	0.9
Propylene	0.9	0.6	32.1	0.9	3.3
Isobutane	15.1	4.6	1.0	19.3	1.0
n-Butane	5.8	3.0	0.6	9.2	0.6
Butenes	0.9	0.3	6.9	0.6	71.5[2]
Isopentane	5.8	1.8	0.3	7.9	0.1
n-Pentane	1.0	0.6	0.5	1.9	—
Pentenes	0.2	0.2	2.0	0.1	0.4
C_{6+} aliphatic hydrocarbons	3.2	1.3	3.3	4.8	—
Benzene	1.1	4.1	0.8	2.1	0.1
Toluene	7.9	23,7	6.1	10.9	2.0
Xylenes	20.5	26,4	16.7	11.6	5.1
Ethylbenzene	0.7	2.6	1.4	1.1	0.5
C_9 alkylaromatic hydrocarbons	12.4	18.6	15 2	6.2	11.4
C_{10+} alkylaromatic hydrocarbons	5.6	4.3	8.1	3.3	13.6

[1]Conversion 29.9%.
[2]Including 66.5 mass % isobutene.

Published data[152] on the composition of the products of the transformations of various other oxygen-containing compounds on H-ZSM-5 zeolite are summarised in Table 5. All the compounds studied (except acetic acid) are readily transformed into mixtures of hydrocarbons, whose composition depends on the nature of the starting material. Thus propionaldehyde gives products whose composition is extremely close to the products of the transformations of alcohols (see Table 4). Acetaldehyde and n-butyl acetate, in addition to hydrocarbons, give appreciable quantities of CO and CO_2. The transformation of these compounds into

aromatic hydrocarbons is more selective than the transformation of alcohols. The products of the transformation of n-propyl acetate, in addition to a large quantity of aromatic hydrocarbons (~50%), contain more than 30% propylene.

The most stable compound under these conditions is acetic acid, whose conversion amounts to less than 30%, and only ~58% of the quantity of acid reacting is converted into hydrocarbons. The latter consist chiefly of butenes (66.5% isobutene + 5% butenes) and C_9 and C_{10} alkylaromatic hydrocarbons (~25%).

Thus zeolites of the pentasil family are effective catalysts for the transformations of methanol, dimethyl ether, and other oxygen-containing compounds to give mixtures of C_1–C_{10} hydrocarbons with approximately identical compositions; most of the work in this field has been devoted to the transfromations of methanol. The importance of these studies is not limited to the accumulation of data which can be used to develop the important practical process of motor fuel production. They have developed to a considerable extent the study of the structure and physicochemical properties of zeolites of the new generation and have made a significant contribution to the development of ideas about the catalytic activity of zeolites. They have also initiated studies of the possible application of pentasils in other catalytic processes, in particular the transformations of various hydrocarbons.

IV. TRANSFORMATIONS OF HYDROCARBONS ON PENTASILS

The ability of first-generation zeolites (faujasites, mordenite) to catalyse the transformations of various hydrocarbons was established by a large number of studies, reviewed earlier[40,130]. Thanks to this property, these zeolites have found extensive application as catalysts of a number of processes in petroleum refining and petroleum chemistry. The reactions of hydrocarbons carried out on first-generation zeolites include, for example, cracking, isomerisation, oligomerisation, disproportionation, etc. These and various other reactions of hydrocarbons also take place on zeolites of the pentasil family.

1. Transformations of Alkenes

The possibility of using pentasils to catalyse the transformation of individual C_2–C_5 alkenes and their mixtures into aliphatic and aromatic hydrocarbons with higher molecular weights was shown in the first Mobil Oil patents in 1973–74. In the scientific literature, the first reports of the study of these reactions appeared only in 1979.[87,128,200] In the last two or three years, the number of papers on this topic has increased considerably, and most have been devoted to the study of the transformations of ethylene and other lower alkenes on pentasils.

Transformations of ethylene. The large number of studies of the transformations of ethylene on pentasils[87,103,107,122,125,128,159,161,166,184,186,189,200–205] differ considerably in the reaction conditions and in the types and compositions of the catalysts used. There is therefore often lack of agreement between the data obtained by different authors. For example, in Ref.87 it is reported that on H-ZSM-5 zeolite ($SiO_2/.Al_2O_3 = 59$; 0.38 mass % Na) at 400° and a rate of supply of hydrocarbons of 1.2×10^{-2} mole h^{-1}, ethylene usually shows a low reactivity, but sometimes its conversion reached high values. A low degree of conversion of ethylene on zeolites of the same type was also observed by other workers[122,158,161]. At the same time it is reported that under selected (usually milder) conditions, the conversion of ethylene exceeds 90%.[125,159,189,200–202,204] The available data show that the extent of the conversion of ethylene depends on the rate of supply of the alkene, the temperature of the reaction, and the presence of modifying additives in the zeolite. The influence of these factors on the degree of transformation of ethylene and the composition of the reaction products has not been studied in detail, however.

Experiments with ethylene on different TsVK zeolites with approximately equal SiO_2/Al_2O_3 ratios (~80–82) [200] showed that decrease in the quantity of Na_2O in the zeolite from 1.2 mass % to 0.6 mass % not only increases the conversion of the alkene (from 72% to 98%) but also changes significantly the composition of the reaction products: the gases show a decrease in the concentrations of C_3 and C_4 hydrocarbons by factors of 2 and 5 respectively, and the liquid catalysate, whose yield remains almost unchanged, is enriched in aromatic hydrocarbons, with the simultaneous disappearance of C_4–C_6 alkanes and alkenes. Approximately the same influence on the composition of the gaseous and liquid reaction products is shown by an increase in temperature from 350° to 530°. A significant increase in the concentration of benzene and toluene in the catalysate was observed, however.

The activity, stability, and selectivity of pentasils in the transformations of ethylene depend to a significant extent on the SiO_2/Al_2O_3 ratio[205]. For ultrasil zeolites, at values of this ratio in the range 26–80, the conversion of ethylene at 350° is ~97%, and remains practically unchanged during the experiment. At $SiO_2/Al_2O_3 = 190$, however, the degree of transformation of C_2H_4, which at the start of the experiment is ~53%, decreases to ~18% in 80 min. Moreover, with increase in this ratio from 29 to 190, the concentration of alkanes in the reaction products decreases considerably. It was therefore suggested[205] that the reactions involving the redistribution of hydrogen take place on the strong acidic centres produced in the pentasils with decrease in the concentration of Al and the total quantity of acidic centres. As already noted in section II, however, no anomalously strong acidic centres have been detected in pentasils. With decrease in the Al concentration, the total number of active centres in the zeolite apparently decreases, and below a certain limit it becomes insufficient for the competing reactions to take place simultaneously on them. The secondary processes, including, for example, the reactions involving the redistribution of hydrogen, should evidently be suppressed to a greater extent.

A comparative study of the transformations of ethylene on H-ZSM-5 and HNaY zeolites by infrared spectroscopy and mass spectrometry also showed[128] that unsaturated hydrocarbons predominate in the products of the reaction on pentasil. Depending on the temperature, the products on this zeolite are either aliphatic C_3–C_7 hydrocarbons (at 100 to 200°) or C_5–C_7 cyclanes and cyclenes (at 200–300°), or C_6 to C_{10} aromatic hydrocarbons (at 320–430°), and the pentasil had a much higher aromatising power than HNaY zeolite. In Refs.204 and 205, no mention was made of the formation of aromatic hydrocarbons in the transformations of ethylene on pentasil.

In the discussion of the products of the transformations of ethylene on pentasils, it should be noted that according to infrared spectroscopy, thermogravimetric analysis, and ^{13}C NMR spectroscopy, ethylene even at 20° is adsorbed on the Brönsted acidic centres of these zeolites and is activated and oligomerised to give long unbranched molecules[103,189,202,203]. It is suggested[103,184] that the oligomerisation of ethylene takes place by a carbenium-ion mechanism, and also that

above 300° the ethylene oligomers may undergo cracking and dehydrocyclisation.

In attempts[103,122,128,189] to model the conditions of the transformation of methanol (and dimethyl ether) into hydrocarbons, the decomposition of ethylene on pentasils in the presence of water was studied. The study of the combined sorption of ethylene and water on H-ZSM-5 zeolite[103] showed that at 20°, the strong Brönsted centres of this zeolite adsorb water preferentially, suppressing the activation and oligomerisation of the alkene. Above 250°, some of the centres become accessible for the adsorption of ethylene, which undergoes transformations to give chiefly alkenes with higher molecular weight, and also aromatic hydrocarbons. The poisoning by water of the acidic centres of H-ZSM-5 zeolite, responsible for the oligomerisation and aromatisation of ethylene, was also observed at a higher temperature (370°).[122] At the same time, water increased the stability of the zeolite and the degree of conversion of ethylene, facilitating cracking reactions. In spite of the suppression by water of the aromatisation of ethylene, the formation of the products of this reaction was observed at lower temperatures in the presence of water than in experiments with the dry alkene. It was suggested[122] that water facilitates the desorption of aromatic hydrocarbons from the zeolite channels by lowering their boiling point, as in steam distillation. The ability of water to increase the rate of desorption of the reaction products was confirmed in a study of the thermal decomposition of ethylene oligomers formed on H-ZSM-5 zeolite[198]. At the same time it was shown that water apparently acts as an additional source of protons, since in its presence there is an increase in the proportion of alkanes in the reaction products.

A fairly complete picture of the influence of water on the transformations of ethylene on ZSM-5 zeolites and on the composition of the products of this reaction is given in a paper[189] which mainly confirms data obtained by other workers[122,198]. According to Ref.189, however, water not only does not decrease the selectivity of the formation of aromatic hydrocarbons from ethylene, but increases it significantly, although this effect becomes slightly weaker on prolonged zeolite use.

Transformations of C_3 and C_4 alkenes. These alkenes are more reactive than ethylene in transformations on pentasils. On three specimens of H-ZSM-5 zeolites at 285–310°, propylene was transformed much more rapidly than ethylene[107].

In a study of the transformations of propylene on ZSM-5 zeolites and silicalite (SiO_2/Al_2O_3 = 59 and 1125 respectively) at 400°, the conversion of the alkene reached 85–94%. The reaction products contained aliphatic and aromatic hydrocarbons with a predominance of C_4 (~40%) and C_6 (~25%) alkanes and alkenes, and also xylenes (~30%).[87] With decrease in temperature to 370°, the conversion of propylene decreased to ~55%, and the reaction products contained ~30% butenes and only ~3% aromatic hydrocarbons[122,167]. Approximately the same results were obtained for but-1-ene.[167] In the transformations of propylene on H-ZSM-5 at 285° and 310°,[107] the predominant formation of C_4 and C_6 aliphatic hydrocarbons and the almost complete absence of aromatisation products were observed.

The transformations of C_3 and C_4 alkenes on TsVK zeolites have been studied in detail[84,88,121,125,206,207]. On the Na-form of this zeolite, propylene at 230–240° and isobutene at 140 to 150° gave liquid products containing C_6–C_9 alkanes and alkenes with normal and *cis*-structures. The yield of these products increased sharply with temperature, reached a maximum (>80%) at 310–320°, and then gradually decreased (broken lines in Figs.7*a* and 7*b*). An increase in the yield of gaseous products, consisting of C_2–C_5 alkanes and alkenes and small quantities of methane (not more than 5–7% at 580°) was observed. Above 320°, the liquid catalysates from both alkenes contained aromatic hydrocarbons (mainly benzene, toluene, and xylenes), whose concentration gradually increased with temperature to 91–93% at 550–580°.

Similar results were obtained on a more active decationated TsVK zeolite (<0.1% Na_2O).[88,207] Comparison with the data for Na-TsVK shows that on H-TsVK (continuous lines in Figs.7*a* and 7*b*), the formation of liquid products begins at lower temperatures; at 320° the catalysates contain not only aliphatic but also aromatic (~15–20%) hydrocarbons, and beginning at 450°, both the yield of liquid catalysate and the concentration of aromatisation products in it remain practically constant (up to 580°). The differences between the Na- and H-forms of TsVK are revealed most clearly under the conditions of the transformations of isobutene (Fig.7*b*), which are characterised by distinct temperature ranges corresponding to different reactions: up to 200°, only dimerisation and trimerisation of isobutene take place; at 200–300°, isomerisation of the resulting oligomers is also observed; and above 300°, aromatisation of aliphatic hydrocarbons begins, and this process predominates at 450–550°. These processes are accompanied by reactions involving

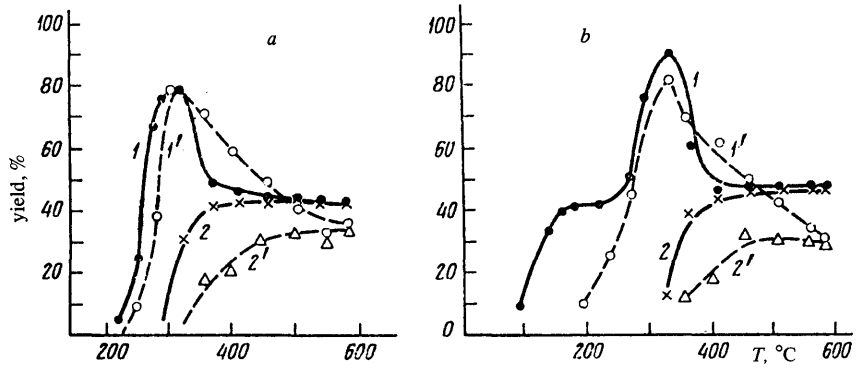


Figure 7. Temperature dependence of the yield of liquid catalysates (*1*, *1'*) and aromatic hydrocarbons (*2*, *2'*) from propylene (*a*) and isobutene (*b*) on the Na-form (broken line) and the H-form (continuous line) of TsVK zeolite[88].

the redistribution of hydrogen, cracking, and interconversion of aromatic hydrocarbons. For propylene, a distinct range corresponding to only oligomerisation was not observed, since significant quantities of the liquid catalysate appeared only at temperatures above 200°, that is under conditions in which intensive isomerisation took place. The small quantities of liquid products formed below 200°, however, contained isomeric hexenes, that is dimers of propylene.

The influence of temperature on the yield and composition of the gaseous products of the transformations of isobutene on H-TsVK zeolite[88] is shown in Fig.8.

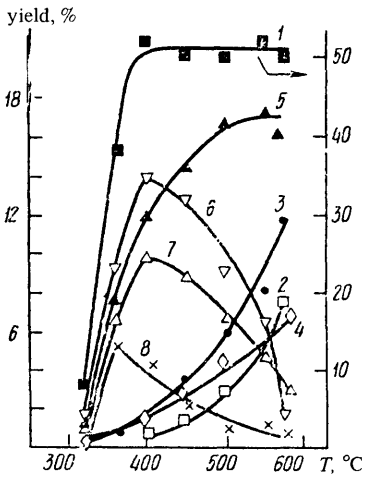


Figure 8. Temperature dependence of the yield of gaseous hydrocarbons from isobutene on H-TsVK zeolite: *1*) total yield of gaseous products, *2*) methane, *3*) ethane + ethylene, *4*) propylene, *5*) propane, *6*) isobutane, *7*) n-butane, *8*) C_5 hydrocarbons.[88]

Comparison with first-generation zeolites (types A, X, Y, and mordenite) [121] showed that the original and decationated forms of TsVK zeolites are much more active in the aromatisation of lower alkenes (450–550°). Neither change in the reaction conditions nor modification of the zeolites by decationation, cation exchange, or the introduction of additives, in the case of first-generation zeolites, led to the production of the high yields of aromatic hydrocarbons reached on pentasil. In addition to high activity in aromatisation, TsVK zeolites were stable and retained their activity for 6–9 h, since coke formation was slight. In contrast to this, first-generation zeolites and catalysts based on them were almost completely deactivated in the first 1–1.5 h of use, as a result of the deposition of coke, the quantity of which reached 10–20%, calculated for the propylene passed. On the TsVK pentasil, the quantity of coke deposited was ~10 times smaller, because of the characteristic features of its porous structure.

A study of the transformations of C_3 and C_4 alkenes on TsVK pentasil containing different quantities of Na and activated at different temperatures (T_{act}) revealed the relationship between the catalytic properties of the pentasil, its composition, and the activation conditions[84]. Increase in the concentration of Na_2O in the zeolite from 0.1 mass % to 1.1 mass % decreased slightly the conversion of the alkene and the yield of liquid catalysate, and also suppressed the aromatisation considerably. The lowest activity was shown by the zeolite specimen containing 1.3 mass % Na_2O, and also 0.25 mass % iron oxide impurity. The complete removal of this impurity and almost all the sodium by decationation gave the most active catalyst specimen, which brought about the greatest conversion of the original alkene and the highest yields of liquid catalysate and aromatic hydrocarbons[84].

Activation at 900–1000° had the greatest influence on the catalytic properties of TsVK zeolite[84]. This thermal treatment led to a decrease in the yield of liquid catalysate and the overall yield of aromatic hydrocarbons from isobutene at 320° and 500°, but at the same time the selectivity of *p*-xylene formation increased considerably. Moreover, with increase in T_{act} from 500 to 1000°, the gaseous reaction products showed a decrease in the concentration of alkanes and an increase in the concentration of alkenes (Fig.9), indicating a decrease in the activity of the zeolite in hydrogen redistribution reactions. These reactions apparently take place on Brönsted acidic centres, the quantity of which decreases on high-temperature treatment as a result of dehydroxylation of the surface (see section II). These data provide another example of the existence of a relationship between the intensity of hydrogen redistribution reactions and the quantity of Brönsted acidic centres in the pentasils, also observed in the transformations of ethylene on ultrasil zeolites[205].

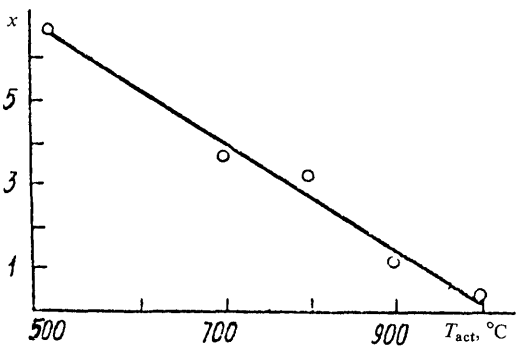


Figure 9. Influence of T_{act} on the ratio of the concentrations (x) of C_2–C_4 alkanes and alkenes in the products of the transformations of isobutene (500 °C) on TsVK zeolite[84].

The addition of vanadium (2.8 mass %) to the Na-form of TsVK zeolite (SiO_2/Al_2O_3 = 70.5, 0.7 mass % Na_2O) decreased considerably the conversion of C_3 and C_4 alkenes (and ethylene), the yield of liquid catalysate, and the total yield of aromatic hydrocarbons[125]. For the more active H-form of this zeolite, the influence of the additive depends on its concentration and on the reaction temperature[208]. The addition of 0.3 mass % vanadium to H-TsVK not only did not decrease, but even increased by a factor of ~1.5, the total yield of aromatic hydrocarbons from isobutene at 320°. Approximately the same effect was observed at 500°, but in this case it was reached at a vanadium concentration of 0.9 mass %. At both temperatures, the conversion of the original alkene remained at 100% throughout the entire range of vanadium concentrations studied (0.3–10.3 mass %).

It was also found[125,208] that the modification of TsVK zeolites by vanadium increases sharply the selectivity of the formation of *p*-xylene (and *p*-ethyltoluene) from lower alkenes, estimated from the ratio of the concentrations of *p*- and *m*-xylenes ([PX]/[MX]) in the reaction products. For the non-modified zeolite[209], the ratio [PX]/[MX] did not exceed 0.44, corresponding to the concentration of these isomers in the equilibrium mixture. In the presence of vanadium, however, this ratio increases by a factor of not less than ~19. For the decationated zeolite, the addition of V led to a slightly smaller increase in the selectivity of the formation of the *p*-isomers of dialkylbenzenes, and this effect increased with increase in the concentration of the additive and with decrease in the reaction temperature (Fig. 10).[208] The results were attributed[125,208] to the influence of the added vanadium on the molecular-sieve and diffusion properties of the TsVK zeolites (see section II). The reasons for the selective formation of the *p*-isomers of dialkylbenzenes will be discussed later, since this phenomenon was observed not only in the transformations of lower alkenes but also in other reactions.

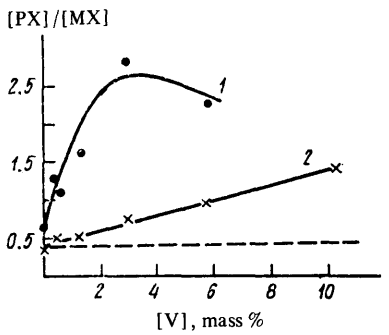


Figure 10. Dependence of the selectivity of formation of *p*-xylene ([PX]/[MX]) from isobutene on the vanadium concentration in H-TsVK zeolite at 320 °C (*1*) and 500 °C (*2*); the broken line gives the ratio at equilibrium[207].

Apart from these studies, only a comparative kinetic study of the isomerisation of but-1-ene and *cis*-but-2-ene on H-ZSM-5 and H-Fu-1 zeolites (SiO_2/Al_2O_3 = 60 and 22 respectively), and also on an amorphous aluminosilicate, at 0° in a static system, has been carried out[210]. The results indicated that the isomerisation of butenes on these catalysts takes place by a carbenium-ion mechanism on the Brönsted acidic centres, which are much more stable in H-ZSM-5 than in H-Fu-1 or in the amorphous aluminosilicate.

The transformations of alkenes with higher molecular weights on pentasils have been described in only a few papers. The transformations of oct-1-ene on the Na-form of TsVK zeolite at 175–550° have been studied in most detail[212]. Only the reaction involving the movement of the double bond in octene took place intensively below 250° on this zeolite. At 250 to 300°, structural isomerisation of the octene began, and the yield of linear isomers decreased to 10%. Under these conditions, appreciable cracking of oct-1-ene and its isomers was observed, leading to a decrease (to ~75%) in the yield of liquid catalysate, in which aliphatic C_6 and C_7 hydrocarbons appeared. At 400°, oct-1-ene gave appreciable quantities of aromatic hydrocarbons, the concentration of which in the catalysate increased sharply with increase in temperature and when the zeolite was modified by added V, Pt, and Rh.[212] Thus as with lower alkenes, the introduction of added vanadium increased to a considerable extent the selectivity of the formation of the *p*-isomers of xylene and ethyltoluene from oct-1-ene, but this selectivity decreased with increase in temperature. These effects were not observed on the catalysts prepared by modifying the pentasil by added Pt and Rh.

The studies have included not only oct-1-ene but also the transformations of 3,3-dimethylbut-1-ene, which on H-ZSM-5 zeolite at 370° readily underwent isomerisation to 2,3-dimethylbut-1-ene and 2,3-dimethylbut-2-ene, and also cracking to give appreciable quantities of propane and butane. The reaction products contained a small quantity of C_6–C_9 aromatic hydrocarbons[161].

Thanks to the molecular-sieve properties of ZSM-5 zeolite, the rate of the isomerisation of C_6–C_8 alkenes on this catalyst (150–175°) decreases with increase in the degree of branching of the molecule (hex-1-ene > 6-methylhept-1-ene ≫ 3-ethylpent-1-ene ≫ 4,4-dimethylhex-1-ene).[113] The selective hydrogenation (at 275°) of hex-1-ene in its mixtures with 4,4-dimethylhex-1-ene on a Pt-ZSM-5 ion-exchange zeolite catalyst is also possible[113].

The transformations of cycloalkenes on pentasils has not been specially studied. Infrared spectroscopy has shown[212], however, that even at 40–45°, cyclopentene, cyclopentadiene, and cyclohexene are strongly adsorbed on HZ-79 zeolite (an analogue of ZSM-5 zeolite) with the formation of the same oligomers as with the linear alkenes. Partial transformation of the cycloalkenes into aromatic hydrocarbons was observed. With increase in temperature to 200–360°, the infrared spectra of the adsorbed cyclenes show an increase in the strength of the bands corresponding to the formation of aromatic structures. The mechanism of formation of linear oligomers and aromatic hydrocarbons from cycloalkenes has not yet been determined.

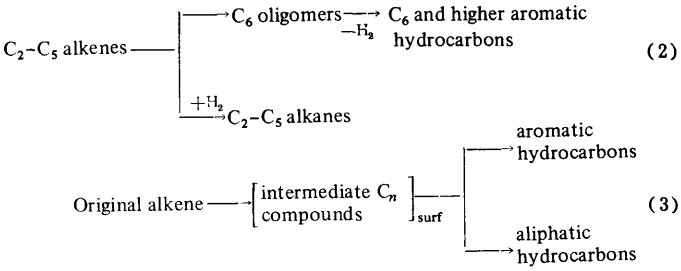
2. Mechanism of the Transformations of Alkenes on Pentasils

As already noted in section II, the nature of the catalytic activity of zeolites of the pentasil family and first-generation zeolites is the same and is determined by the presence of surface OH groups, which act as Brönsted acidic centres. Thus the mechanism of the transformations of alkenes on pentasils apparently corresponds to present-day ideas, according to which these reactions on zeolites involve the formation of carbenium ions as a result of the protonation of the reacting molecules on the acidic OH groups[130]. There are very few published papers, however, specially devoted to the study and examination of the mechanism of the transformations of alkenes on pentasils. In most cases, this question is discussed in direct relation to the mechanism of formation of hydrocarbons from methanol and dimethyl ether (see section III), which assumes the participation of molecules of oxygen-containing surface compounds either in the growth of the hydrocarbon chains or in the regeneration of the Brönsted acidic centres.

The transformations of lower alkenes in mixtures of various hydrocarbons in the absence of oxygen-containing compounds is usually represented by the general schemes (1),[186] (2),[184] and (3):[87,159,20]

$$C_nH_{2n} + HOZ \rightleftarrows [C_nH_{2n+1}OZ \leftrightarrow C_n^{+}H_{2n+1}\,\overline{O}Z] \rightarrow C_mH_{2m} + HOZ \quad (1)$$

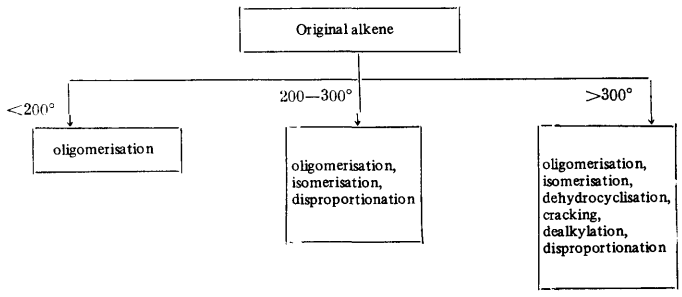
Z = zeolite, $m \gg n$



In Eqn.(3), the intermediate compounds are either "unsaturated residues" of the original molecules[87] or C_1–C_4 fragments of these molecules, adsorbed on the zeolite surface[159,200].

From the composition of the products formed from lower alkenes on TsVK pentasils of different temperatures, a sequence of transformations of the original hydrocarbons and the products formed from them was proposed[88,207] (scheme 1).

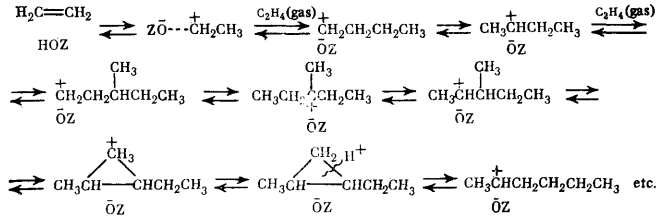
Scheme 1



Although this scheme says nothing about the mechanism of the transformations of the alkenes, all the reactions in it can take place on the acidic centres of zeolite catalysts by a carbenium-ion mechanism[130]. Moreover, this scheme shows good agreement with the conclusion that there are three temperature ranges of transformations of C_2–C_4 alkenes on ZSM-5 zeolites, reached on the basis of thermogravimetric analysis and high-resolution ^{13}C NMR spectroscopy[189,201,202]. According to these data, the alkenes below ~30° readily undergo oligomerisation to give long unbranched molecules, and the rate of this reaction for ethylene is lower than that for other alkenes. These oligomers are formed and strongly adsorbed inside the pores of the zeolites, filling them completely. With increase in temperature, the rate of oligomerisation, calculated for one active centre, increases for all the alkenes. At ~130°, slight cracking of the oligomers is observed, and above 230° the rate of cracking begins to exceed the rate of oligomerisation. Thus above 230 °C, blocking of the pores of the zeolite by oligomers does not take place, and the reacting molecules diffuse freely through the channels of the pentasil, which at these temperatures is an active catalyst for the transformations of lower alkenes. An infrared spectroscopic study of the sorption of alkenes on HZ-79 zeolite indicated that the alkene oligomers formed apparently act as the source of aromatic hydrocarbons[197], whereas on HNaY zeolite they are mainly transformed into coke[212].

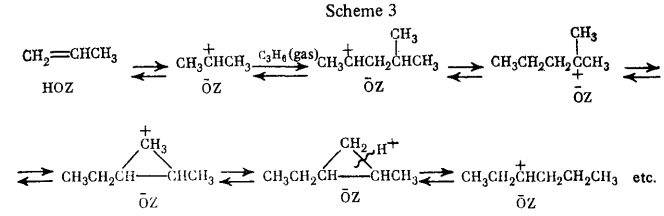
The mechanism of the oligomerisation of ethylene with the formation of hydrocarbon chains containing an average of 25 carbon atoms is represented by scheme 2 [201,202] involving carbenium ions formed on the Brönsted acidic centres of the pentasil:

Scheme 2



The last stages of this scheme explain the formation of linear molecules from propylene and other alkenes, whose oligomerisation should give only branched molecules (scheme 3).

Scheme 3



The oligomers formed from propylene and isobutene contain an average of 6–8 carbon atoms. The differences in the rates of the oligomerisation of ethylene and the C_3 and C_4 alkenes were attributed to a difference in the stability of the primary, secondary, and tertiary carbenium ions formed from these alkenes[201,202].

Similar schemes have been used to represent the transformations of alkenes with higher molecular weights (3,3-dimethylbut-1-ene), including not only oligomerisation but also other reactions such as the aromatisation of lower alkenes[161].

These ideas on the mechanism of the reactions of alkenes on pentasils, together with data on the specific molecular-sieve properties of these zeolites, have made it possible to explain the predominance of certain hydrocarbons and the absence of others in the products of the transformations of alkenes[184].

Thus the mechanism of formation of carbenium ions on Brönsted acidic centres has been successfully applied to the transformations of alkenes on zeolites of the pentasil family. At the same time there are a number of unsolved problems, related to the nature of the catalytic action of these zeolites, which can be solved only by further studies.

3. Transformations of Saturated Hydrocarbons

The ability of zeolites of the pentasil family readily to adsorb and bring about the selective cracking of alkanes with the normal structure has made these zeolites promising catalysts for processing high-alkane petroleums and petroleum products[8,16,17,213]. It will be shown below that pentasils can apparently catalyse not only cracking but also other transformations of saturated hydrocarbons of practical importance. The reactions of alkanes on pentasils have been insufficiently studied, however.

Transformations of alkanes. Recently published data[214] on the possibility of transforming methane and ethane into C_6–C_{10} aromatic hydrocarbons on TsVM zeolites are of considerable interest. In a pulse reactor on this zeolite ($SiO_2/.Al_2O_3$ = 33.3), containing added group VIII metals (0.2 to 1.0%), methane at 600° in the absence of oxidising agents gives benzene in >6% yield, calculated on the hydrocarbon passed. The yield of aromatic hydrocarbons from ethane on the non-modified zeolite was ~10%, and on the zeolite containing added metal the yield reached 20%, but the reaction was less selective.

The formation of benzene, toluene, xylenes, and trimethylbenzenes from methane has also been observed under the conditions of its oxidative dehydrogenation on pentasils modified by added transition metal compounds[215]. In this case the selectivity of the reaction corresponds to 10–20% of the transformed methane.

Pentasils can bring about the aromatisation of alkanes with higher molecular weights—hexane, 3-methylpentane, 2,2-dimethylbutane, and iso-octane[87,159,216]. The liquid catalysates formed from n-hexane, 3-methylpentane, and iso-octane on TsVK zeolite (flow reactor, 450°), in addition to the non-transformed alkane and cracking products, contained 50, 42, and 10% aromatic hydrocarbons respectively. Similar results were obtained on the same zeolite under pulse conditions, and also in a flow system on H-ZSM-5 zeolite at 400°.[87] According to these data[87], the conversion of the hexane isomers decreased with increase in the kinetic diameter of their molecules. Together with the results of sorption measurements, these data indicated that the rate of the transformations of the alkanes is limited by the rate of their diffusion into the zeolite pores. Thus n-hexane penetrates rapidly into the pores and is readily transformed on the active centres localised in them. 2,2-Dimethylbutane, however, must apparently first undergo isomerisation on the outer surface to give isomers which can more readily diffuse into the zeolite channels, where they undergo further transformations. These suggestions were confirmed in experiments using 4-methylquinoline and ammonia, introduced into the reactor together with the hydrocarbons. The addition of 4-methylquinoline, which can be adsorbed only on the outer surface of the zeolite, had practically no influence on the conversion of n-hexane, but suppressed almost completely the transformations of 2,2-dimethylbutane. The addition of ammonia, which readily penetrates into the pores, deactivated the catalyst for the transformations of both hydrocarbons. When the supply of ammonia was stopped, the catalytic activity of the pentasil was gradually restored as desorption took place.

The acidic properties of the pentasils indicate that they may be active in the isomerisation of alkanes. In fact, n-butane, n-pentane, and n-hexane undergo isomerisation on TsVK zeolites (SiO_2/Al_2O_3 = 33.3, 47, and 83) at 250–400° under a pressure of 30 atm.[91] Extensive hydrocracking and disproportionation of these alkanes took place simultaneously. The relative extent to which these last reactions took place decreased sharply when the zeolites were modified with palladium. The greatest activity and selectivity in the isomerisation of n-pentane was shown by the 0.5% Pd/TsVK catalyst prepared by ion exchange, on which the yield of isopentane at 330° reached ~60 mass %, and the yield of the products of hydrocracking and disproportionation amounted to only 2.8 mass % and 1.3 mass % respectively[91].

It should be noted that n-decane, which has a higher molecular weight, underwent hydrocracking preferentially on the 0.5% Pt/H-ZSM-5 ion-exchange catalyst, and underwent isomerisation to only a slight extent[90]. The composition of the products of the isomerisation of n-decane, in which 2-methylnonane predominated, differed considerably from the equilibrium composition. The results were attributed[90] to the influence of the molecular-sieve properties of the zeolite, which prevents the formation of highly branched isomers.

The isomerisation of isobutane on H-ZSM-5 zeolite ($SiO_2/.Al_2O_3$ = 100; 0.01 mass % Na; 350°) took place much more intensively than that of n-butane, and the rate of reaction on pentasil was ~70 times slower than that on H-mordenite.[217] Moreover, the pentasil showed almost no activity on the disproportionation of isobutane to propane and pentanes, accompanying the isomerisation. Since the isomerisation and disproportionation of isobutane are bimolecular reactions, the low activity of the pentasil in these reactions was attributed to the difficulty of formation of bulky intermediate compounds in the narrow pores, that is to the molecular-sieve selectivity with respect to the transition state (see below).

The cracking of alkanes on pentasils has been studied in much more detail than isomerisation. H-ZSM-5 zeolite is more active in the cracking of n-hexane than H-mordenite.[217] The activity of both zeolites in this reaction is much greater than that of other zeolites (NaY, LaY, HY, MgX, and Na-ZSM-5), industrial cracking catalyst (ICC), and amorphous aluminosilicate (AAS).[101] The relative activity ($\alpha = k_X/k_{ICC}$, where k_X and k_{ICC} are the rate constants of the cracking on the catalyst being studied and on ICC respectively) for H-ZSM-5 and HM were more than 10^5, whereas for the other catalysts the values of α did not exceed 10^3.[101] The ZSM-5 zeolites showed a high resistance to treatment with steam at a high temperature, and a high stability due to the low degree of coke formation in these catalysts. The products of the cracking of n-hexane on these zeolites at low degrees of conversion of the hydrocarbon (5–20%) contained chiefly propane, n-butane, and isobutane. With increase in the conversion of the original alkane to ~90% at higher temperatures, the formation of aromatic hydrocarbons and an increase in the concentration of ethylene in the reaction products were observed[101].

The cracking of n-octane on TsVK pentasil and zeolites of type Y, mordenite, and erionite can be represented by the following general scheme[134]:

Alkane → "unsaturated fragments" → alkanes and aromatic hydrocarbons → polycyclic hydrocarbons (coke)

The reactions involving the redistribution of hydrogen and secondary transformations of alkenes apparently take place at a lower rate on pentasil than on other zeolites[134]. Moreover, for pentasil the rate of desorption of monocyclic aromatic hydrocarbons is much greater than the rate of their transformation into polycyclic systems, which act as coke precursors. These characteristic features were attributed[134] to the unusual geometry of the pentasil pores and the low density of hypothetical proton-donor centres (see section II), whose existence in zeolites has not yet been proved.

The activity of pentasils of different type (ZSM-5, TsVK, TsVM, ultrasil) in the cracking of alkanes decreases with decrease in the Al concentration in the zeolite framework[89,101,218], with increase in T_{act},[85] and with decrease in the quantity of acidic OH groups on treatment of the zeolite with ammonia[143].

The relative rate of the cracking of alkanes decreases with decrease in the length of the carbon chain of the molecules ($n\text{-}C_7 > n\text{-}C_6 > n\text{-}C_5$) and with increase in the degree of branching of the alkane (n-alkane > 2-methylalkane > 3-methylalkane > dimethylalkane > ethylalkane).[100] The rate of transformation of the different molecules is apparently limited by the rate of their diffusion into the zeolite pores, which is determined by the size and shape of the

molecules; the length of the molecules is slightly less important than the kinetic diameter[100]. A decrease in the reaction rate with increase in the degree of branching of the molecules was also observed in the cracking of n-octane and iso-octane on ZSM-5 pentasils and ultrasil[101,141,143,164]. With increase in temperature, the differences in the rate of cracking of alkanes with different structures on these zeolites decreased considerably[100,143]. It was suggested[100] that in contrast to the first-generation zeolites, pentasils have a "dynamic" molecular-sieve selectivity with respect to the reacting molecules, as a result of which the molecules whose kinetic diameters differ by more than 1 Å can diffuse into the pores of these zeolites at approximately equal rates. Unfortunately, no explanation for the reasons for this phenomenon was given[100].

A number of papers have been devoted to the cracking of individual alkanes or high-alkane petroleum fractions on complex catalysts containing pentasils as one of the components. For example, the cracking of n-hexane has been studied on zeolites of the ultrasil type mixed with 30–90% of a binding agent (Al_2O_3, Al_2O_3–SiO_2, etc.).[219] The high cracking activity of these catalysts was combined with good isomerisation properties. The cracking products contained chiefly C_4 and C_5 hydrocarbons, including the iso-compounds. The addition of 1% Pd to these catalysts increased their isomerisation activity considerably, but decreased significantly the yield of cracking products. Increase in the quantity of binding agent and in the ratio SiO_2/Al_2O_3 in the zeolite had a similar effect.

A number of papers deal with the preparation and study of two-zeolite ("hybrid") cracking catalysts containing TsVM zeolites or ultrasil, and also first-generation zeolites (types X, Y, and Ln-Y).[220–225] The study of the catalytic properties of these systems in the cracking of individual alkanes (n-heptane) and petroleum fractions (gas oil, kerosene–gas oil fraction) showed that the yield of unsaturated hydrocarbons increases considerably in the presence of pentasil.

The possibilities provided by the use of zeolites of the pentasil family as industrial cracking catalysts, and the present state of the production of these zeolites in the Soviet Union have been examined in detail[226].

The transformations of cycloalkanes on zeolites of the pentasil family are described in very few papers. The possibility of obtaining high yields of aromatic hydrocarbons (benzene, toluene, xylenes, and other alkylbenzenes) from cyclopentane, cyclohexane, and methylcyclohexane on TsVK zeolite at 450° under flow and pulse conditions has been reported[159,216]. The same products in approximately the same proportions were formed in all cases, irrespective of the original hydrocarbon. Comparison with corresponding data for ethylene and n-hexane indicated that the reactions of the lower alkenes, alkanes, and cycloalkanes take place according to the same scheme involving the initial splitting of the original hydrocarbon into C_1–C_4 fragments, which are adsorbed on the zeolite surface.

In addition to these data, it has been reported[227] that decalin is transformed to a very slight extent on an experimental industrial cracking catalyst containing 20% H-ZSM-5 zeolite in a kaolin matrix.

4. Reactions of Aromatic Hydrocarbons

The interconversion and alkylation of aromatic hydrocarbons, which are of considerable practical importance, have been studied in detail on first-generation zeolites[130,209]. An important contribution to these studies has been made by Soviet scientists[40]. Pentasils have also been recommended as extremely effective catalysts for these reactions[18–21,228–239].

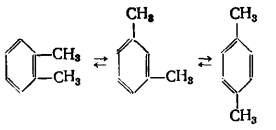
The primary reaction of aromatic hydrocarbons on pentasils is the *selective isomerisation* of *m*- and *o*-xylenes to give the *p*-isomer. In some countries, this process, based on ZSM-5 pentasil, has been carried out on the industrial scale in recent years[38,110].

A number of scientific papers deal with the study of this reaction on pentasils[149,240–245]. For example, the isomerisation of *m*- and *o*-xylenes on the Na- and H-forms of TsVK zeolite, on H-mordenite (HM), and on dealuminated mordenite (DM) was studied in detail[240] to determine the reasons for the high selectivity of the formation of *p*-xylene from different alkenes on pentasils[84,88,125]. The activity of the catalysts studied in this reaction increased in the order Na-TsVK < H-TsVK < HM < DM. With the exception of HM, whose activity decreased by a factor of 2 after 70 min, all the catalysts showed stable operation for 1.5–2 h. The TsVK zeolites catalysed practically only the isomerisation of xylenes, whereas on HM and DM, appreciable disproportionation of xylenes took place to give toluene and trimethylbenzenes (Fig.11). A significant difference was also observed in the ratio of the products of the isomerisation of *m*- and *o*-xylenes on TsVK zeolites and mordenite. For Na- and H-TsVK, the values of the ratio of the concentrations of the isomers formed from *o*-xylene ([PX]/[MX]) were the same, were appreciably greater than the corresponding values for HM and DM, and approached the equilibrium value more rapidly with increase in the degree of conversion (Fig.12*a*). In the isomerisation of *m*-xylene on H-TsVK, the values of the corresponding ratio [PX]/[OX] were greater than the equilibrium value throughout the entire range of degrees of conversion, and with decrease in the conversion from 50% to 15%, this ratio increased from 1.5 to 3.6. In contrast to this, for DM the values of the ratio [PX]/[OX] practically corresponded to the equilibrium value for all degrees of conversion of the original isomer (Fig.12*b*).

Similar results were obtained in experiments with *m*-xylene on H-TsVK and HY zeolites[241]. The data given in Ref.240 were completely confirmed in a comparative study of the transformations of all three xylene isomers on H-ZSM-5, HY, and HM zeolites[242]. The H-ZSM-5 zeolite showed a high activity in the isomerisation of the xylenes, which took place selectively to give the *p*-isomer. This zeolite also showed a very low activity in the disproportionation of dialkylbenzenes, and was completely inactive in the transformations of 1,2,4-trimethylbenzene. All these date made it possible to reach conclusions about the size of the zeolite channels and the cavities formed by the intersection of these channels. It was suggested[242] that the isomerisation of xylene could be used to estimate the porous structure of pentasils instead of the method widely used at present, involving the determination of the "permeability index" (constraint index)[243] $\omega = k_{nh}/k_{2mp}$, where k_{nh} and k_{2mp} are the rate constants for the cracking of n-hexane and 2-methylpentane respectively.

The activity of pentasil in the isomerisation of *m*-xylene and the selectivity of this reaction under pulse conditions are influenced considerably by the composition of the zeolite, its degree of decationation, and the activation conditions, and also by the extent of the poisoning of the acidic centres by ammonia, pyridine, or quinoline[244]. The selective poisoning of the pentasil NiH-ZSM-5 by ammonia suppresses the activity of the acidic centres responsible for dealkylation and disproportionation side reactions, leading to an increase in the selectivity of the isomerisation of *m*-xylene to the *o*- and *p*-isomers.[245]

In contrast to these studies[240-242], other studies[246] reported the selective formation of *p*-xylene from the *m*- and *o*-isomers on H-ZSM-5 zeolite only after its modification by added phosphorus and magnesium. In other respects, the data[246] agreed with the data obtained by other workers. The rates of isomerisation of the xylenes decrease in the order *p*-xylene > *m*-xylene > *o*-xylene in the ratio 5 : 2.5 : 1. Since bimolecular reactions in the channels of the zeolites of the pentasil family are difficult, it was suggested[246] that the isomerisation of xylenes can apparently take place by the intramolecular successive displacement of the methyl group:



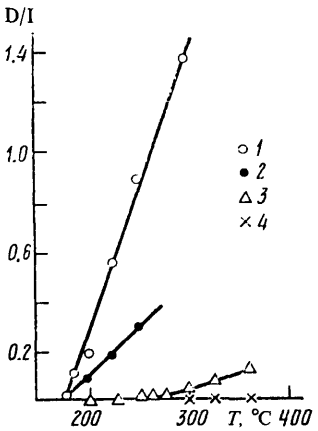
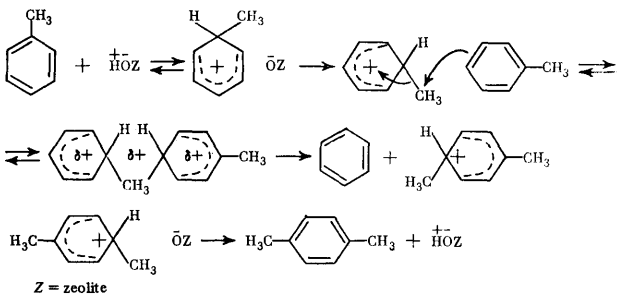


Figure 11. Temperature dependence of the ratio of the concentrations of disproportionation and isomerisation products (D/I) of *o*-xylene for the zeolites DM (*1*), HM (*2*), H-TsVK (*3*), and Na-TsVK (*4*).[242]

In addition to the isomerisation of xylenes, the *disproportionation of toluene* to benzene and xylenes takes place selectively on pentasils. It should be noted that this reaction takes place on pentasils less intensively than isomerisation, and the selective formation of *p*-xylene is observed only when the zeolite is modified by various additives, or when the conversion of toluene is decreased by changing the reaction conditions.

With increase in temperature from 400° to 600° (at a mass rate of supply of toluene of ~3.5 h^{-1}), the conversion of toluene to benzene and xylenes on H-ZSM-5 zeolite increased from 8% to 52%, but the ratio of the xylene isomers in the reaction products remained almost unchanged and practically corresponded to the equilibrium value[109,246,247]. A significant increase in the yield of *p*-xylene was observed only at 550°, when as a result of an increase in the rate of supply of toluene to 30 h^{-1} its conversion decreased from 40% to ~13%. The xylene fraction contained 35, 46, and 19% of the *p*-, *m*-, and *o*-isomers respectively[109,246]. Approximately the same effect was observed on large (~3 μm) crystallites of H-ZSM-5 zeolite at a high rate of supply of toluene. The greatest selectivity of *p*-xylene formation was achieved on zeolite specimens modified by the addition of various elements, in particular magnesium and boron[246,247]. As in the modification of TsVK zeolite by vanadium (see above), however, the introduction of these additives decreased considerably the conversion of the original hydrocarbon. The rate of the disproportionation of toluene on modified H-ZSM-5 zeolite specimens was 10^2 times lower than the rate of isomerisation of xylenes[246]. It was suggested that the mechanism of disproportionation involves the reaction of the toluene molecule with the proton of a Brönsted acidic centre and subsequent transfer of a methyl group (scheme 4).[247]

Scheme 4



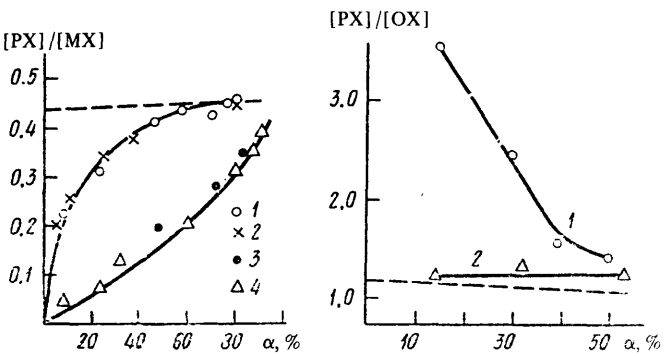


Figure 12. Dependence of the ratio of the concentrations of the products of the isomerisation of *o*-xylene (*a*) and *p*-xylene (*b*) on their conversion (α) on the zeolites H-TsVK (*1*), Na-TsVK (*2*), HM (*3*), and DM (*4*); the broken lines give the ratio at equilibrium[242].

In experiments with toluene (420° and 500°) in the absence of a carrier gas, HY zeolites, HM, omega, and offretite showed a much higher initial activity than H-ZSM-5 zeolite, catalysing both disproportionation and other reactions[248,249]. The pentasil, however, was distinguished by its high stability and ability to bring about the selective conversion of toluene into benzene and a mixture of xylene isomers with the equilibrium composition. An increased concentration of *p*-xylene in this mixture, relative to the equilibrium concentration, was obtained only in experiments with H-ZSM-5 zeolite in which the toluene was diluted with a carrier gas (Ar or H_2), accompanied by a decrease in the conversion of the original hydrocarbon[250]. The greatest yield of *p*-xylene was observed in the presence of H_2, although the side reaction of toluene demethylation simultaneously increased.

Under the conditions of the disproportionation of toluene without a carrier gas (350°), HY zeolites and HM are rapidly deactivated as a result of coke formation, and with increase in their deactivation there is a significant increase in the concentration of *p*-xylene in the reaction products[248]. This was also observed for HY and H-ZSM-5 zeolites when the reaction was carried out in a stream of nitrogen[251]. An increase in the selectivity of *p*-xylene formation was not observed in a stream of H_2.

A study of the disproportionation of toluene on H-ZSM-5 and H-ZSM-11 zeolites showed a slight difference in the behaviour of these pentasils: H-ZSM-11 was slightly less active but more stable than H-ZSM-5, on which *p*-xylene is formed with a greater selectivity than on H-ZSM-11.[251]

The disproportionation of ethylbenzene takes place selectively on HNa-ZSM-5 zeolite, and its total conversion at 200° is 4.4%.[252]

The alkylation of aromatic hydrocarbons, which has been studied in detail on first-generation zeolites[209], is another reaction which takes place on pentasils. Considerable attention has been paid to the study of the reaction of pentasils between toluene and methanol, which may give considerable quantities of *p*-xylene. On different cation-exchange forms of Y zeolite, this reaction gives products containing up to 40–50% *p*-xylene.[253,254] The conversion of methanol on pentasils in this reaction was usually 100%, and the reaction products, in addition to unreacted toluene, contained a mixture of xylene isomers and small quantities of benzene and C_9 and C_{10} alkylbenzenes[109,246,255]. The proportion of aromatic hydrocarbons formed from methanol was very low. Under the mildest conditions (t < 300°, short contact time), the products also contained traces of methanol, dimethyl ether, formaldehyde, CO, and CO_2.[255] The conversion of toluene, the yield of xylenes, and the concentration of the *p*-isomer in them depended on the reaction conditions and the catalyst composition.

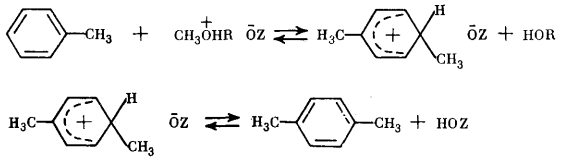
On non-modified H-ZSM-5 and H-ZSM-11 zeolites, this reaction gave a mixture of xylene isomers with a composition close to the equilibrium composition[246,255,256]. The selectivity of *p*-xylene formation on H-ZSM-11 was slightly higher than that on H-ZSM-5. This conclusion requires verification, however, because of the marked differences in the reaction conditions on these zeolites[255].

As in the case of the disproportionation of toluene, a significant increase in the concentration of *p*-xylene in the products of the alkylation on pentasils was observed when large crystals (~3 μm) were used[109,246], and also after an interval from the start of the catalyst operation at high temperatures (550° and 700°).[246,255,256] The selective formation of *p*-xylene in the alkylation of toluene by methanol was also observed not under flow conditions but under pulse conditions[257,258].

A sharp increase in the selectivity of this reaction with respect to *p*-xylene, as in the case of other reactions, was observed when H-ZSM-5 zeolite was modified by various additives[109,246,255,256]. For example, when not less than 16% MgO was introduced by impregnation into H-ZSM-5, the alkylation products showed an increase to ~90% in the concentrations of xylenes, of which more than 90% corresponded to the *p*-isomer. The cation-exchange Mg-H-ZSM-5 zeolite, in which the quantity of Mg was ~13 times lower than that in MgO-H-ZSM-5, at 400° showed approximately the same activity as the non-modified zeolite, but the selectivity of the reaction with respect to *p*-xylene was slightly greater.

The alkylation of toluene by methanol on H-ZSM-5 zeolite with added P, B, Mg, and other elements has been studied in detail at different temperatures, pressures, reagent ratios, and reagent supply rates[246,255]. The greatest effects were obtained on H-ZSM-5 modified using phosphorus (~3–8%), introduced by impregnating the zeolite with solutions of phosphoric acid, diphenylphosphinic acid, methyl phosphite, chlorodiphenylphosphine, or dichlorophenylphosphine. On these catalysts, by varying their composition and the reaction conditions, it was possible to obtain alkylation products containing up to 80–90% xylenes, of which 50–80% corresponded to the *p*-isomer.

In an examination of the possible mechanism of the alkylation of toluene by methanol on pentasils with allowance for the presence of Brönsted acidic centres on these zeolites, it was suggested[186,255] that this reaction takes place according to the following scheme:



R = H, CH_3; Z = zeolite.

According to the rules of electrophilic substitution in aromatic compounds, the chief products of this reaction should be *o*- and *p*-xylenes. The formation of a mixture of all three isomers is due to the isomerisation of the alkylation products formed initially. On non-modified pentasils, the rate of isomerisation of xylenes (w_i) is 10–15 times greater than the rate of alkylation (w_a), whereas on the modified specimens, w_a is 7–15 times smaller than w_i.[246] At the same time, the isomerisation of xylenes takes place preferentially on the strongest Brönsted acidic centres of the pentasils[256]. Thus the selective formation of *p*-xylene in the alkylation of toluene by methanol on pentasils should apparently take place in those cases where these centres are suppressed either by a modifying additive or as a result of treatment with water vapour at high temperature.

In the alkylation of benzene by ethanol on ZSM-5 zeolites (in the pure form or forms modified by phosphorus or boron), the ethyl group is introduced into benzene directly from the alcohol without the intermediate formation of ethylene[186,258].

Like first-generation zeolites, zeolites of the pentasil family are effective catalysts for the alkylation of aromatic hydrocarbons by alkenes. A process was recently developed for obtaining ethylbenzene by the alkylation of benzene by ethylene on ZSM-5 pentasils[238,239]. Pilot-plant and large-scale industrial experimental tests of this process demonstrated a number of advantages of the new catalyst, particularly its high stability and ease of regeneration.

The alkylation of aromatic hydrocarbons by alkenes can take place during any process on pentasils if alkenes and aromatic compounds are present in the system as starting materials or final products. For example, this reaction has been observed[100] under the conditions of the cracking of mixtures of alkanes, accompanied by the formation of a small quantity of benzene and toluene. The ratio of the rates of the alkylation of toluene and benzene by the fragments of molecules undergoing cracking is ~0.7, whereas for the usual heterogeneous or homogeneous systems this ratio is 1.4.

In the alkylation of benzene by ethylene on TsVK zeolites[259], in addition to ethyl and diethylbenzene, the reaction products contained cumene and s-butylbenzene, the yields of which decreased with increase in temperature (Table 6). The formation of these products is evidently due to the

ability of the temperatures to catalyse the oligomerisation of ethylene with the subsequent splitting of the oligomers and disproportionation of the fragments formed. The products of these transformations can then alkylate benzene.

Table 6. The alkylation of benzene by ethylene on ultrasil zeolites (v = 1.2 h^{-1}, *molar ratio* $C_6H_6 : C_2H_4$ = 3 : 1).[259]

T, °C	C_2H_4 conversion, %				S, A/B	T, °C	C_2H_4 conversion, %				S, A/B
	to EB (A)	to IPB	to SBB	total (B)			to EB (A)	to IPB	to SBB	total (B)	
	H-TsVK (x = 60)						H-TsVK (x = 172)				
250	20.2	12.2	6.4	55.0	36.7	250	18.6	9.5	7.3	34.0	54.6
300	53.6	3.5	0.7	80.2	67.0	300	41.7	7.4	1.2	68.4	61 1
350	81.0	1.3	traces	99.0	81.8	350	73.0	1.6	traces	95.0	76.9

Note: EB = ethylbenzene, IPB = isopropylbenzene, SBB = s-butylbenzene, x is the molar ratio SiO_2/Al_2O_3, and S is the selectivity.

The formation of "anomalous" alkylation products was also observed in a study of the reaction of benzene with propylene on ultrasil zeolites[260–262]. These products contained s- and n-butylbenzenes, s- and n-pentylbenzenes, and s- and n-hexylbenzenes. Unlike zeolites of type Y, ultrasil did not give polyalkylbenzenes, and the formation of monoalkylbenzenes with a branched side chain was hindered. The temperature dependence of the composition of the products is complex[260,261], since change in temperature leads to a change in not only the rate of alkylation but also the rate of the transformations of propylene and its oligomers, taking place by a carbenium-ion mechanism. With increase in the degree of decationation of the pentasil there is an increase in its activity and an increase in the selectivity of the reaction with respect to the formation of n-propylbenzene and "anomalous" alkylation products. There is a simultaneous decrease in the stability of the zeolite, probably as a result of the blocking of the active centres by condensation products.

Published information on other reactions of aromatic hydrocarbons on pentasils is limited to data[113] on the selective hydrogenation of styrene in its mixtures with 2-methylstyrene on Pt-ZSM-5 ion-exchange catalyst (400°) and the selective oxidation of *p*-xylene in its mixtures with the *o*-isomer on 1% Cu-ZSM-5 catalyst (390–450°). These reactions provide a good illustration of the molecular-sieve mechanism of the action of zeolites of the pentasil family, examined below.

5. Molecular-sieve Properties of Pentasils and the Selectivity of Reactions Taking Place on Them

Many examples of the molecular-sieve action of pentasils and the consequent high selectivity of the reactions are now known. These include the selective cracking of alkanes, the transformation of alcohols and lower alkenes to hydrocarbons containing not more than 10 carbon atoms in the chain, the absence in the products of these reactions of polyalkylbenzenes with branched side chains, condensed aromatic systems, etc. The most striking example is the selective formation of *p*-xylene in the isomerisation of xylenes, the disproportionation of toluene, and its alkylation by methanol.

It is possible to distinguish three types of molecular-sieve selectivity of zeolites[110,111], each of which is due to one of the following factors: 1) the size of the molecules of the original reagent, that is their ability to penetrate into the zeolite pores to the active centres localised in them; 2) the size of the molecules of the products, that is their ability to diffuse from the zeolite pores into the gas phase; and 3) the size of the intermediate complex, that is the possibility of the formation of this complex in the restricted space of the pores and cavities of the zeolite.

When the diameter of the zeolite channels is commensurate with the diameter of the molecules of the starting materials and the products, the reaction apparently takes place under internal-diffusion conditions, which may have a significant influence on the selectivity of the process[263]. The rate of diffusion of the molecules depends both on their size and on their shape or their ability to adopt a configuration which corresponds more closely to the size and shape of the zeolite channels. Under these conditions, which have been called "configurational diffusion" conditions[110], the selective formation of a definite reaction product may take place, that is there is "configurational selectivity".

The transformations of xylenes on pentasils take place under these conditions. Data on the composition and distribution of the reaction products, and also on the rate of the transformation of different xylene isomers[240,242,246] have shown that in this case all the above types of molecular-sieve selectivity are observed. Steric hindrance leads to a very marked decrease in the rate of the disproportionation of xylenes, but does not prevent their isomerisation, in which *p*-xylene is formed with a high selectivity. The molecules of this isomer, which has a smaller kinetic diameter (6.4–7.0 Å) than the molecules of *m*- and *o*-xylenes (6.9–7.6 Å), diffuse into the pentasil channels at the highest rate and readily migrate from the pores into the gas phase[70, 84,87,110]. The molecules of *m*- and *o*-xylenes, which are present in the zeolite channels for a longer time, may undergo additional isomerisation into *p*-xylene, increasing the concentration of the latter in the reaction products. For zeolites with wider pores (for example mordenite[240]), the selective formation of *p*-xylene does not take place, since the molecules of all three isomers diffuse in the channels of this zeolite at approximately equal rates[240,242].

The influence of diffusion factors on the reaction rate is estimated using the dimensionless parameter $Q = [k(R^2/D)]^{1/2}$, where k is the reaction rate constant, R the radius of the zeolite crystallites, and D the effective diffusion coefficient of the molecules[110,263]. This parameter is related to the efficiency factor (η—the degree of utilisation of the internal surface of the catalyst) and to the configurational selectivity of the reaction ($S = D_p/D_a$, where D_p and D_a are the diffusion coefficients of the molecules p and a, which respectively diffuse easily and with difficulty into the zeolite pores).[111,263] A mathematical theory was recently developed for the selective formation of *p*-xylene in the isomerisation of xylenes, the disproportionation of toluene, and its alkylation by methanol under conditions of configurational diffusion on catalysts showing molecular-sieve properties[264].

The concept of the limiting role of the diffusion of the molecules in the pores of the zeolite makes it possible to explain the increase in the selectivity of *p*-xylene formation in various reactions on pentasils when partial coke formation takes place in the zeolite, when it is modified by various additives, or when the size of the crystallites increases. For example, the introduction of additives or partial coke formation in the zeolite during its operation leads to a decrease in the effective diameter of the channels and creates additional steric hindrance for the diffusion of molecules.

The modification of TsVK pentasil by vanadium decreases the sorptive capacity of the zeolite and the initial rate of adsorption for all three xylene isomers[211]. The sorption characteristics of the pentasil change to the smallest extent for *p*-xylene, however. In the alkylation of benzene by propylene on ultrasil pentasil[264], the change in the selectivity of the reaction with time is due to the accumulation in the zeolite channels of "condensation products" (that is coke or its precursors), which apparently restrict the access of the reacting molecules to the active centres.

It is also possible that when coke is formed in the pentasil or when various additives are introduced into it, the acidic properties of its surface may change, with a consequent change in the selectivity of the reactions. For example, when H-ZSM-5 zeolite is treated with phosphorus compounds, there is a marked increase in the number of surface acidic centres[158], and selective formation of *p*-xylene takes place on these zeolites[247,255]. According to data obtained by H–D exchange[208], however, modification of TsVK pentasil by vanadium does not lead to a change in the concentration of the surface OH groups, that is it has no influence on the acidic properties of the pentasil surface.

These data indicate the existence of a definite relationship between the selectivity of the reactions on pentasils, the nature of their porous structure, and the rate of diffusion of the molecules of the reagents and products in the zeolite pores. The question of the relationship between the acidity of zeolites and the selectivity of the reactions which they catalyse, and the influence of modifying additives on the acidic properties of the pentasils, is still not clear. A significant part in this relationship may be played by the nature of the additive, its localisation in the system of zeolite pores, and the state in which this additive may exist under the reaction conditions. Further studies are required in order to solve these problems, which are important for the directed control of the catalytic properties of zeolite catalysts.

V. THE USE OF PENTASILS IN OTHER CATALYTIC REACTIONS

A number of studies have shown that pentasils can be used as catalysts not only in the above transformations of oxygen-containing compounds and hydrocarbons, but also in various other reactions. Among these, an important place is occupied by processes directed towards the production of motor fuels from non-traditional raw materials, capable of replacing the petroleum products used for these purposes. A promising raw material in this respect is biomass (the waste products from the processing of agricultural products, the timber and timber-processing industries, etc.), on the basis of which a technological process has now been developed for the production of various synthetic fuels by thermochemical and fermentation processes[265–267]. The possibility in principle of using pentasils for the catalytic transformation of various components of plant raw materials into high-quality motor fuel was demonstrated[268] in a study of the transformations of polyisoprene latex, corn oil, castor oil, and other plant oils on ZSM-5 zeolite. At 450–500°, a high conversion of the starting materials was achieved, and the composition of the products was close to that of the hydrocarbon mixtures obtained from methanol, although they usually contained more benzene, toluene, and xylene.

The availability of zeolites of the pentasil family has provided a realistic solution to the problem of the production of motor oils from the products of the treatment of coal, including the conversion of synthesis gas[266,267,269–271]. Two versions of this process are usually considered:

$$\text{coal} \xrightarrow{+H_2O} CO + H_2 \begin{cases} \longrightarrow CH_3OH \rightarrow \text{petrol}; & (4) \\ \longrightarrow \text{petrol}. & (5) \end{cases}$$

Process (4) includes the intermediate formation of methanol, which can then be converted on a ZSM-5 zeolite into petrol, by the process developed by Mobil Oil (see section III). Method (5) is more attractive, since it makes it possible in principle to obtain petrol or individual hydrocarbons directly from synthesis gas without the intermediate stage. This process is complicated by the absence of catalysts giving a higher selectivity of the conversion of synthesis gas into hydrocarbons than the familiar catalysts of the Fischer–Tropsch process. Considerable progress has already been made in this direction, by using catalysts based on first-generation zeolites[272,273] and zeolites of the pentasil family[22,41,45,266,267].

The study of the conversion of synthesis gas on Fe-, Zn-Cr-, Zr-, or Co-zeolite catalysts of the ZSM-5 or ultrasil type, prepared by mixing or impregnation, showed that in the presence of a zeolite of the pentasil family there is a significant increase in the conversion of the original mixture and an increase in the yield of hydrocarbons, and aromatic hydrocarbons are formed[274–277]. In contrast to the usual versions of the Fischer–Tropsch process, the reaction products contained much smaller quantities of alkenes; the normal chains of the aliphatic hydrocarbons formed contained not more than 11 or 12 carbon atoms, and the aromatisation products consisted chiefly of benzene, toluene, and xylenes[274–277].

On a catalyst based on H-mordenite, but not pentasil, a decrease in the concentration of alkenes in the reaction products and the formation of aromatic hydrocarbons was also observed[276]. The conversion of synthesis gas, which was partly converted into CH_3OH and $(CH_3)_2O$, was ~4 times lower, however, than in the presence of pentasil. The nature of the metallic component has a significant influence on the catalyst properties. For example, the Zr- and Zn-Cr-ZSM-5 catalysts showed a much lower ability to give methane and a much higher aromatising power than the Fe-ZSM-5 catalyst[275].

The activity at 240° of the Co-ultrasil catalyst obtained by mixing depends on the SiO_2/Al_2O_3 ratio in the pentasil[276]. Increase in this ratio from 42 to 190 led to a decrease in the conversion of the synthesis gas, the total yield of hydrocarbons, and their concentration in the reaction products. At 190°, only a decrease in the proportion of hydrocarbons in the liquid catalysates was observed. The activity of the Co-ultrasil catalysts increased sharply when 3% MgO was added, but this led to a significant change in the composition of the reaction products, which contained C_1–C_{22} hydrocarbons. Increase in the concentration of the additive to 12% lowered the yield of the light C_5 and C_6 hydrocarbon fractions, increased the yield of C_7 and higher hydrocarbons, and suppressed the aromatisation. These additives had approximately the same effect on less active catalysts with the same composition (Co-ultrasil), prepared by impregnating the zeolite with cobalt carbonyl[276].

It is suggested[275] that on catalysts containing a zeolite of the pentasil family, the conversion of synthesis gas takes place according to the following scheme:

$$2H_2 + CO \xrightarrow{\text{metal}} [CH_3OH \rightleftarrows {}^1/_2 (CH_3)_2O + {}^1/_2 H_2O] \xrightarrow{\text{pentasil}} (CH_2) + H_2O .$$

The composition of the reaction products is determined both by the ability of the pentasil to transform the intermediate compounds (alcohol and ether) into hydrocarbons and also by its molecular-sieve properties, which prevent the formation

of long or bulky molecules. The influence of diffusion factors on the selectivity of the conversion of synthesis gas was studied with decrease in the size of the particles of the components of the Zn-Cr-ZSM-5 catalyst, that is with decrease in the path length of the molecules diffusing in the pentasil pores[275]. It is considered[274] that the active centres of the pentasil in the catalyst can interrupt the growth of the hydrocarbon chains by converting the α-alkene molecules into molecules which are inert with respect to the active centres of the metallic component (for example into aromatic hydrocarbons, branched and internal alkenes, etc.).

CO can be adsorbed on ultrasil-containing Co-catalysts of the Fischer–Tropsch synthesis in several forms, characterised by different temperatures of desorption (T_{des}).[276] With decrease in the Al concentration in the ultrasil there is a decrease in the total sorption of CO and an increase in the concentration of carbon monoxide adsorbed in a form with $T_{des} = 400°$, which apparently has the lowest activity in the synthesis of hydrocarbons. The lowest concentration of this form of adsorbed CO was detected for the most active catalyst containing Co-ultrasil + 6% MgO.

A catalyst based on ZSM-5 zeolite has been developed for transforming liquid oxidation products and various side products of the Fischer–Tropsch synthesis into more valuable aliphatic and aromatic hydrocarbons[278]. It has been shown possible to increase considerably the profitability of the Fischer–Tropsch process.

Mixed Co-ultrasil catalysts show a high activity in the carbon monoxide-initiated hydropolymerisation of ethylene, which gives mixtures of C_3–C_{22} hydrocarbons and ethane[279]. The activity of these catalysts decreased with decrease in the Al concentration in the zeolite. Unlike catalysts based on mordenite and zeolites of type Y, they retained their activity over a wide temperature range (190–310°) and gave products with a large proportion of C_5 and higher fractions. The products also contained aromatic hydrocarbons, and this was attributed to the influence of the pentasil. It was suggested[279] that the hydropolymerisation of ethylene is activated by carbon monoxide adsorbed on the zeolite surface.

One of the ways of using the products of the gasification of coal involves the use of carbon monoxide for the carbonylation of hydrocarbons to obtain carboxylic acids and their esters. It was previously shown that it is possible to carry out this reaction on heterogeneous non-zeolite catalysts containing Pd.[280–282] This reaction has also been studied on mordenite and TsVK pentasil containing group VIII metals[283,284]. The Pd-containing pentasils can be used as active catalysts for the production of propionic and butyric acids by the carbonylation of ethylene and propylene respectively.

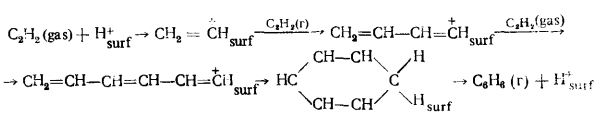
In the carbonylation of ethylene and propylene on catalysts based on pentasils, the formation of considerable quantities of esters such as ethyl propionate, isopropyl isobutyrate, and isopropyl n-butyrate has been observed[283, 284]. An interesting feature is that the H-form of a ZSM-5 pentasil showed no activity in the liquid-phase esterification of acetic acid by ethanol and isopropy alcohol[285].

The gas-phase chlorination of benzene (175°) on pentasils (NaH-ZSM-5, H-ZSM-5, Ce-ZSM-5, NaH-ZSM-11, and silicalite), and also on mordenite and amorphous SiO_2, gives chiefly chlorine addition products—a mixture of stereoisomers of hexachlorocyclohexane[286]. In contrast to this, the reactions on L and Ln-Y zeolites, and also on Al_2O_3, involved chiefly substitution to give chlorobenzenes containing up to 5 or 6 Cl atoms. It was suggested[286] that catalysts with a low Al concentration initiate the homolytic dissociation of chlorine, which is followed by its radical addition. Because of the large diameter of the molecules formed (~8 Å), this reaction apparently takes place only on the outer surface of the zeolite particles or in the openings into its pores.

In the hydrolysis of ethyl acetate (60°), it was shown possible to use pentasils, which have a hydrophobic surface, as catalysts for reactions in an aqueous medium[287]. In this reaction, H-ZSM-5 zeolite showed an activity equal to ~40% of the activity of a cation-exchange resin. Dealuminated mordenites were less active, and the original mordenite, zeolite Y, and amorphous aluminosilicates had a very low activity in this reaction. With increase in the atomic ratio Si/Al, the activity of all the zeolites studied increased, reached a maximum, and then decreased. Decrease in the quantity of Al in the zeolite is evidently accompanied by an increase in the hydrophobic character of its surface and an increase in its affinity for organic compounds. At a very low Al concentration, the zeolite loses its activity as a result of a decrease in the quantity of surface active centres on which the reaction takes place.

A zeolite of the pentasil family ($SiO_2/Al_2O_3 \cong 29$; 0.2 mass % Na_2O), not containing transition metals, can decompose ammonia at 550°.[288] Before the reaction, the zeolite was heated at a high temperature. The degree of dissociation of ammonia was ~42 mass %.

Data on the transformations of alkynes on pentasils are of interest[133,221,289]. For example, on Na- and H-ZSM-5 zeolites at temperatures above 300°, acetylene is very readily transformed (to the extent of more than 99%) into a mixture of C_6–C_{13} aromatic hydrocarbons[221]. Pure acetylene rapidly deactivates the catalyst, so that the reaction is carried out with dilution by an inert gas (He). The composition of the products depends on the volume rate of supply of acetylene. It is suggested[221] that the reaction involves the Brönsted acidic centres, with the intermediate formation of the vinyl cation and its homologues:



1,2-Dimethylacetylene readily undergoes cyclotrimerisation to hexamethylbenzene on ZSM-5 zeolite[133].

Examination of the above material shows that high-silica zeolites of the pentasil family in many respects are similar to the zeolites of the first generation. Because of their characteristic composition and structure, however, they are more stable to high temperatures, water vapour, and mineral acids, have a lower tendency to undergo cation exchange, and exhibit specific adsorption and catalytic properties.

Pentasils as catalysts are distinguished from zeolites of other types by their high stability, which is due to their low tendency to form coke, and their clearly defined molecular-sieve properties, which are responsible for the high selectivity of various reactions taking place on these zeolites. A characteristic feature of pentasils is their ability to transform methanol (and other oxygen-containing compounds) into hydrocarbon mixtures forming a high-octane petrol, to aromatise lower alkenes, and to catalyse various other reactions of practical interest. It may be expected that in the near future, zeolites of the pentasil family will provide a basis for the production of effective catalysts which will make it possible to solve the problem of producing motor fuels without using petroleum raw material, and also to obtain valuable chemical products from accessible and inexpensive starting materials.

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