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# Latest Advances and Trends in the Development of Catalysis on Zeolites

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The most important advances in the utilisation of zeolites in catalysis in recent years (1977-1981) and the trends in the development of research in this field are examined.
The bibliography includes 252 references.

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## I. INTRODUCTION

Vigorous systematic studies on the utilisation of synthetic zeolites in catalysis have been prosecuted already for more than 20 years. During this period, the efforts of many teams of research workers have laid the scientific foundations for the creation and preparation of zeolitic and zeolite-containing catalysts; factors determining their activity, selectivity, and stability in various reactions have been found, effective ways of regulating the properties of a wide variety of catalysts have been devised, extensive possibilities in the application of zeolitic sytems in catalytic processes have been discovered, considerable advances have been made in the elucidation of the nature of the active centres and the mechanisms of the action of individual systems in reactions of different types, new effective catalysts, including polyfunctional catalysts, have been devised for many petroleum processing and petrochemical reactions, fundamentally new processes based on the utilisation of the characteristic features of the structure of zeolites (selecto-forming, deparaffinisation of oils, etc.) have been proposed, and the industrial manufacture and utilisation of zeolitic catalysts in many chemical processes have been achieved. A consequence of practical importance of the studies which have been carried out is also the formulation of recommendations for the suppresssion of the "parasitic" catalytic activity of zeolitic adsorbents, manifested when they were employed in the drying and purification of olefins and other reactive compounds (formaldehyde, etc.).

The results of studies in this field have been surveyed in a number of monographs, collections, and reviews[1-19]. Vigorous studies are being continued. New possibilities for the application of zeolites in catalysis are being discovered all the time. Specific search for and synthesis on zeolitic materials, necessary for the solution of the most important scientific and technical problems in modern chemistry, are being prosecuted. The research front is extremely broad; more than 250 papers are published annually and numerous patents devoted to various aspects of the synthesis, investigation, and application of zeolitic catalysts are taken out. The volume of information increases very rapidly, which makes it extremely desirable to examine periodically the accumulated data and to analyse the trends in the development of research and advances in the given field of heterogeneous catalysis, which has acquired great theoretical and practical importance. This review is devoted to such analysis of the results of studies published in 1977–1981. The results of earlier investigations are quoted only in so far as it is necessary.

## II. EXPANSION OF THE APPLICATIONS OF ZEOLITIC AND ZEOLITE-CONTAINING CATALYSTS

The determination of the efficiency of zeolites as catalysts and components of various catalytic systems in a wide variety of chemical reactions (see, for example, Refs.1, 2, 5, and 8) as well as the discovery of reactions specific solely to crystalline aluminosilicates, such as, for example, the synthesis of ethyl and vinyl derivatives of aromatic compounds by the condensation of $ArCH_3$ with methanol or formaldehyde on the K-, Rb-, and Cs-forms of synthetic faujasites (X and Y zeolites)[20,23] and other reactions[2,5,8], stimulated the search for new applications of these materials in catalysis. The primary results of the research carried out in recent years has been a significant extension of the range of reactions accelerated by zeolitic systems.

### 1. Organic Reactions

It has been established[24-29] that the *oxidation of lower olefins to carbonyl compounds* can be achieved with a high selectivity on ion-exchange and impregnated zeolitic catalysts containing the $Pd^{2+}$ and $Cu^{2+}$ cations in the presence of water vapour:

$$RCH{=}CH_2 + 0{,}5O_2 \xrightarrow[115-120^\circ C]{H_2O} RCOCH_3 .$$

Features of the catalysis such as the necessity for the simultaneous presence in the catalyst of palladium and copper ions (the maximum efficiency is attained for the ratio[24] $Cu^{2+}:Pd^{2+} \cong 6:1$), the deactivation of PdCuNaY on treatment with hydrogen (at 400 °C) and on reduction of $M^{2+}$ to the metal, the

important role of water in ensuring the selectivity and stability of the catalyst, and the decrease of the rate of oxidation of olefins in the sequence ethylene > propene > but-1-ene > *cis*-but-2-ene ≅ *trans*-but-2-ene, which is the same as the analogous sequence in the homogeneous catalytic oxidation of $C_nH_{2n}$ in the presence of $CuCl_2$–$PdCl_2$, etc.[24–29], led to the conclusion that the main stages of the oxidation reaction of olefins, in particular of ethylene to acetaldehyde, on zeolitic systems are similar to those found for solutions of palladium and copper salts[30]. On the basis of the data obtained, zeolitic catalysts for the oxidation of lower olefins to carbonyl compounds can be assigned to the class of heterogenised metal complex catalysts. This conclusion is of fundamental importance and gives rise to a new research field.

*The synthesis of ethylene glycol from formaldehyde* is catalysed by the zeolites NaX, CaA, and Na-mordenite[31]. The condensation is carried out in the presence of NaOH and proceeds in accordance with the mechanism

$$HCOH^{\ominus} + HCOH \rightarrow HOCH_2CHO\ ;$$
$$HOCH_2CHO + HCOH + NaOH \rightarrow HOCH_2CH_2OH + NaOOCH\ .$$

This is accompanied by the simultaneous Cannizzaro reaction:

$$HCHO + HCHO + NaOH \rightarrow CH_3OH + NaOOCH\ .$$

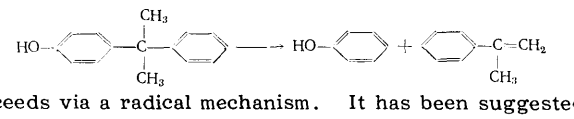
The presence of NaOH in the reaction mixture prevents the formation of free formic acid, which decomposes the catalyst. In the case of Na-mordenite, the degree of conversion of HCOH was ~100% and the selectivity in the formation of glycolaldehyde was ~75% (~24% of HCOH was converted into $CH_3OH$ and HCOOH and <1% was converted into sugars). The synthesis described is of interest as an example of typical base catalysis by zeolitic systems.

Another example of such catalysts is provided by *the crotonic condensation of n-butyraldehyde*, which the authors of the review investigated[32]:

$$C_3H_7CHO + C_2H_5CH_2CHO \rightarrow C_3H_7CH{=}C(C_2H_5)CHO + H_2O\ .$$

At atmospheric pressure and 100–200 °C on zeolites X and Y, butyraldehyde is converted with a high (97–100%) selectivity into 2-ethylhexenal and, in contrast to many other reactions (alkylation, disproportionation, oligomerisation, isomerisation, etc.)[33], in this case the $M^+$-forms of the faujasites are much less active than the specimens containing the $M^{2+}$ and $H^+$ cations and exhibiting the properties of solid acids (Table 1). Carbon dioxide, which intensifies reactions of the carbonium type accelerated by zeolites[19], has a poisoning effect on the catalysts. These results and the earlier data[34] show that the activity of faujasites in the reaction under discussion is associated with their basic properties.

The efficiency of the NaX zeolite as a catalyst of *the decomposition of p-cumenylphenol with formation of phenol and α-methylstyrene* has been demonstrated[35]. The maximum degree of conversion of the initial substance was observed at 400 °C. It is believed[35] that the reaction



proceeds via a radical mechanism. It has been suggested that the dealkylation of *p*-cumenylphenol be used as a test in the study of catalysts with different types of active centres[35].

Interesting features of the catalytic action of zeolites were discovered in *the halogenation of aromatic compounds*. It has been established[36] that type X zeolites are able to accelerate the chlorination of toluene and halogenobenzenes with formation of *para*- and *ortho*-substituted derivatives whose ratio is significantly higher than for the usual chlorination catalysts, in particular $FeCl_2$. It has been shown[37] that zeolites Y are selective catalysts of the bromination of halogenobenzenes:

$$C_6H_5X + n\ Br_2 \xrightarrow[25-65°C]{CaY} C_6H_{5-n}Br_nX + n HBr$$
(X=F, Cl, Br; $n$ = 1, 2)

**Table 1.** Dependence of the degree of conversion of n-butyraldehyde into 2-ethylhexenal (%) in the presence of type X and Y zeolites on their composition and the reaction conditions[32].

| Zeolite | Without carrier gas | In stream of $H_2$ | In stream of $CO_2$ | Zeolite | Without carrier gas | In stream of $H_2$ | In stream of $CO_2$ |
|---|---|---|---|---|---|---|---|
| NaX ($x$=2.5) | 45.5 | 42.2 | 29.8 | 0.13 HNaX | 24.9 | 16.8 | 14.3 |
| 0.75 KNaX | 53.0 | 48.2 | 41.6 | 0.13 BaNaX | 27.8 | 24.2 | 19.1 |
| 0.65 RbNaX | 49.0 | 46.4 | 44.6 | 0.13 NiNaX | 34.8 | 29.5 | 23.7 |
| 0.65 CsNaX | 51.6 | 48.1 | 46.9 | NaY ($x$=4.4) | 23.2 | 17.4 | 12.5 |
| 0.13 CaNaX | 27.5 | 17.9 | 13.9 | 0.70 KNaY | 35.8 | 33.0 | 28.5 |
| 0.81 CaNaX | 17.2 | 13.7 | 9.1 | 0.70 RbNaY | 35.3 | 30.4 | 30.0 |

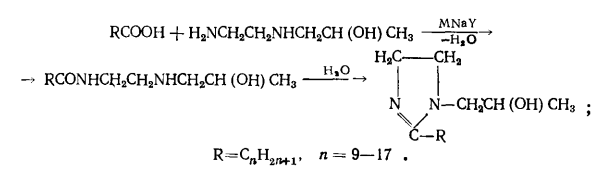
Note; $\nu = 1\ h^{-1}$; $C_4H_8O : H_2(CO_2) = 1:0.8$. For the reaction on the MNaX and MNaY zeolites, the temperature is 125° and 200 °C respectively. Here and henceforth the numerals in front of the cations in the formulae of the zeolites indicate the degree of exchange of $Na^+$ for $M^{n+}$ expressed as a fraction; $x$ is the molar ratio $SiO_2 : Al_2O_3$ and $\nu$ is the volume flow rate (the ratio of the volumes of the liquid reactant supplied in 1 h to the volume of the catalyst); the molar reactant ratio is always quoted.

Under certain conditions in the preliminary treatment and when catalysts were employed, it was possible to obtain monobromination products enriched in the *para*-isomer. According to Huizinga et al.[38], *the gas-phase chlorination of benzene* (175 °C) on zeolites Y as well as amphoteric aluminosilicate (Al–Si) results in the almost exclusive formation of chlorobenzenes—the products of the substitution of H for Cl, whereas on the ZSM-5 and ZSM-11 catalysts, silicalite, H-mordenite, and $SiO_2$, mainly hexachlorocyclohexane—the product of the addition of Cl—is formed (Table 2):

$$C_6H_6 + Cl_2 \xrightarrow{ZSM\text{-}5} C_6H_6Cl_6$$
$$C_6H_6 + Cl_2 \xrightarrow{LnY} C_6H_{6-n}Cl_n\ .$$

The specificity of the catalytic action of high-silica zeolites and $SiO_2$ was explained by the fact that they promote the preferential homolytic dissociation of chlorine, which leads to the radical addition of Cl, whereas substances containing considerable amounts of aluminium (and acid OH groups) favour an ionic process with formation of electrophilic chlorination products[38].

The efficiency of the MgY, AlY, GaY, and InY zeolites as catalysts of *the condensation of N-2-hydroxypropylethylenediamine with carboxylic acids* has been demonstrated:



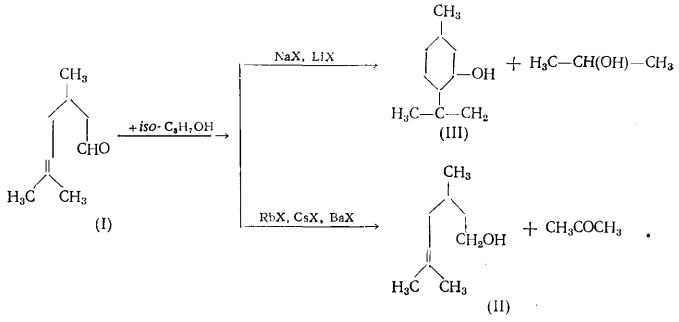
$R = C_nH_{2n+1}$, $n$ = 9–17 .

The reaction results in the formation of 2-alkyl-1-hydroxypropylimidazolines and these are used to synthesise surfactants, which have found extensive applications[39]. The $M^{3+}NaY$ zeolites showed the highest activity; when they were employed, the yields of 1-hydroxypropyl-2-nonyl-2-imidazoline were 50–55% (at 160–220 °C). It was established that acid centres with $H_0 = -(3-8.2)$ are active in this reaction.

**Table 2.** Chlorination of benzene on zeolitic catalysts[38] (175° ± 5 °C, $Cl_2 : C_6H_6 = 5 : 1-10 : 1$).

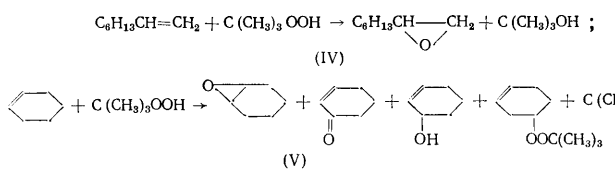
| Catalyst | Conversion of $C_6H_6$, % | Addition products, % | Substitution products, % |
|---|---|---|---|
| NaH-ZSM-5 | 98 | 90 | 10 |
| H-ZSM-5 | 86 | 87 | 13 |
| Ce-ZSM-5 | 90 | 81 | 19 |
| NaH-ZSM-11 | 86 | 72 | 28 |
| Silicalite | 97 | 96 | 4 |
| H-Mordenite | 91 | 84 | 16 |
| LnY (SK-500) | 100 | 3 | 97 |
| Al-Si | 94 | 7 | 93 |
| $SiO_2$ | 82 | 72 | 28 |

The results obtained in the study of the reaction of *citronellal (I) with isopropyl alcohol* led to important conclusions:



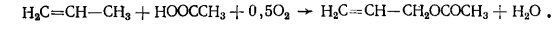

It was shown[40] that, depending on the catalyst, the interaction proceeds via two pathways: with formation of citronellol (II), the product of the reduction of the carbonyl group in compound (I), or of isopulegol (III), the product of the cyclisation of the initial aldehyde. The latter pathway obtains in the presence of the LiX and NaX zeolites, which are relatively coarsely porous and which enable the molecules of compound (I) to assume a configuration favourable for ring closure; the reaction proceeds with a selectivity $S$ close to 100%. The introduction of the large cations $Rb^+$, $Cs^+$, and $Ba^{2+}$ ($r > 1.3$ Å) into the faujasite leads to a narrowing of the channels in the aluminosilicate structure and this is believed[40] to force the molecules of compound (I) to assume preferentially a configuration which is relatively little bent; together with other factors, this promotes the selective ($S$ = 85–90%) reduction of compound (I) to the unsaturated alcohol (II). Thus, by altering the dimensions and geometries of the "windows" and cavities in the zeolites as a consequence the steric factors governing the interaction of the reactants, it is possible to control the selectivity of the reactions on the corresponding catalyst.

*The epoxidation of olefins by t-butyl hydroperoxide* proceeds in accordance with the mechanism




Zeolites X and Y containing transition metal cations ($Cu^{2+}$, $Co^{2+}$, etc.) are active in these reactions[41]. At the same time, the initial hydroperoxide decomposes and other side reactions take place. The selectivity depends on many factors and can reach 50% [in the study of Bergk et al.[41] the selectivity $S$ varied in the range 8.9–20.4% with respect to compound (IV) and 6.9–51.2% with respect to compound (V)]. The epoxidation takes place with participation of transition metal ions, evidently via a radical mechanism, which is analogous to the mechanism for the complexes of transition metals and their oxides[41].

Minachev et al.[42] determined the efficiency of zeolitic catalysts in *the oxidative acetoxylation of propene* to allyl acetate—the intermediate in many industrially important organic syntheses:

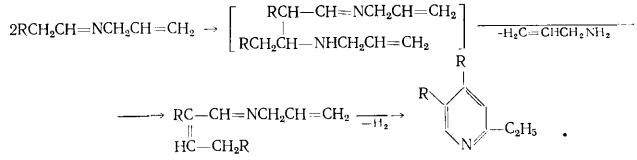



Bimetallic PdCu systems are best for this purpose. Their properties depend on the nature of the exchangeable cation in the zeolite and the type of structure of the aluminosilicate. The dependence of the activity and selectivity of metal-zeolitic catalysts (1% Pd, 0.6% Cu) in the propene acetoxylation reaction on their composition[42] at 1 atm, 180 °C, with a space velocity of the gas mixture of 2333 $h^{-1}$, and for the ratios $C_3H_6 : CH_3COOH : O_2 = 6 : 1 : 0.5$ is illustrated below:

| Zeolite | LiY | NaY | KY | CsY | K, Na-Erionite | Na-Mordenite |
|---|---|---|---|---|---|---|
| Yield, g/litre cat. h | 25.6 | 30.0 | 35.6 | 38.4 | 70.5 | 28.6 |
| $S$, % | 36.1 | 39.5 | 43.2 | 9.6 | 92.3 | 71.2 |

The catalysts prepared on the basis of K, Na-erionite have the highest activity. The productivity and selectivity parameters obtained with their aid are much better than those corresponding to other catalysts of this process.

In the presence of NiNaY, CoNaY, CrNaY, and FeNaY, *azaolefins undergo heteroaromatisation* with formation of alkylpyridines (yield up to 45–50% of theoretical)[43]:




The reaction proceeds with a high structural selectivity. The behaviour of the catalysts depends not only on their composition and the conditions under which they are employed (temperature and carrier gas—He or $NH_3$) but also on the initial azaolefin. In the reaction of propylideneallylamine the highest yields of 6-ethyl-3,4-dimethylpyridine were obtained at 350 °C on the 0.05 NiNaY (43% in an He stream) and 0.05 CrNaY (44.2% in $NH_3$) zeolites. Only 3-ethylpyridine was obtained from ethylideneallylamine on CrNaY. In the aromatisation of cyclohexylideneallylamine the MNaY zeolite showed a lower activity (tetrahydroquinoline was obtained in 8% yield in the presence of 0.05 CrNaY at 350 °C).[43]

*Syntheses based on carbon monoxide* have undergone further development as a result of the application of zeolitic catalysts. The possibility of converting CO + $H_2$ into aromatic hydrocarbons[44] and low-molecular-weight olefins[45,46] and CO + $H_2O$ into methane[47,48] has been demonstrated:

$$4CO + 2H_2O \rightarrow CH_4 + 3CO_2 \ .$$

*The conversion of methanol (or dimethyl ether) into olefins* is of great theoretical and practical value:

$$n\,CH_3OH \rightarrow (CH_2)_n + n\,H_2O \ ;$$
$$n = 2, 3, 4 \ .$$

Various catalytic systems (see, for example, Refs.49–57), including those based on type A and AW-500 zeolites[53], a type X zeolite in the Mn-form[51], dealuminated H-erionite[52], and the ZSM catalyst[49,50,57], are effective in this process. The reaction mechanism apparently depends on the nature of the catalyst. On H-ZSM-5, methanol can be converted with participation of the $H^+$-acid centres via the mechanism[57]

$$CH_3OH + CH_3OH \xrightarrow{H^+} CH_3OCH_3 + H_2O \ ;$$
$$CH_3OCH_3 + CH_3OCH_3 \xrightarrow{H^+} CH_2{=}CH_2 + 2CH_3OH \ ;$$
$$CH_3OCH_3 + H_2C{=}CH_2 \xrightarrow{H^+} CH_3CH{=}CH_2 + CH_3OH \ ;$$
$$CH_3OH + H_2C{=}CH_2 \xrightarrow{H^+} CH_3CH{=}CH_2 + H_2O \text{ etc.}$$

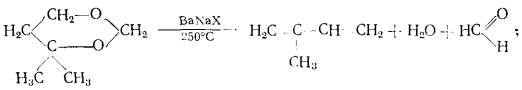
In the case of metal-zeolitic catalysts a reaction pathway involving the dehydrogenation of $CH_3OH$ to formaldehyde, the condensation of the latter, and dehydration of the product is probable[53].

The following reactions in which zeolitic catalysts were shown to be effective are also of theoretical and practical interest:

(1) the synthesis of cyclopropyl methyl ketone from acetylpropyl acetate[58]:

$$CH_3COCH_2CH_2CH_2OCOCH_3 \rightarrow CH_3{-}CO{-}\langle\triangle\rangle + CH_3COOH \ ;$$

(2) the decomposition of 4,4-dimethyl-*m*-dioxan with formation of isoprene[59]:



(3) the addition of α-halogenoethers to asymmetric olefins[60]:

$$C_6H_5CH_2{-}CH{=}CH_2 + ROCH_2Cl \xrightarrow[25°C]{LaNaY} \begin{cases} \rightarrow C_6H_5CH_2CHClCH_2CH_2OR \\ \rightarrow C_6H_5CHClCH(CH_2OR)CH_3 \end{cases} \ ;$$

(4) the synthesis of higher alkanes from methane[61]:

$$n\,CH_4 \rightarrow C_nH_{2n+2} + (n-1)\,H_2 \ ;$$
$$n = 9{-}12 \ .$$

In addition zeolitic catalysts are effective in various oxidative dehydrogenation reactions[62] and in extensive oxidation reactions of organic chloro-compounds ($CH_2Cl_2$, $CH_2ClCH{=}CH_2$, $CH_2Cl{-}CH_2Cl$, $CCl_4$), which are important for the elimination of harmful substances from gaseous waste[63]. This, by no means complete list of reactions investigated in the presence of zeolitic systems in recent years, demonstrates very extensive possibilities in the application of zeolites to organic synthesis.

## 2. Inorganic Reactions

The considerable attention devoted to the study of the properties of zeolitic and zeolite-containing catalysts in inorganic reactions can be accounted for by the relative simplicity of many of the reactions and the convenience of their employment for the elucidation of the nature of the active centres and mechanisms of the action of various systems, the practical value of many of the reactions, in particular, in connection with the problem of the purification of the environment, and also the advances achieved in the industrial application of catalysts based on mordenite in the reduction of nitrogen oxides with ammonia[64,65].

Apart from the reactions involving the isotope exchange of H for D, the oxidation of $H_2$, CO, NO, $NH_3$, $SO_2$, $H_2S$, and NOCl, the synthesis of $NH_3$, the decomposition of hydrogen peroxide, ozone, hydrazine, and carbonyl sulphide, the interaction of CO with $SO_2$ to form COS and $CO_2$,[2] the ortho–para conversion of hydrogen[66], and the reduction of NO with ammonia[67–70], a number of new processes were discovered in recent years.

*The reaction of CO with water vapour*:

$$CO + H_2O \rightleftarrows H_2 + CO_2 \ .$$

This reaction is catalysed by the ruthenium complexes $[Ru(NH_3)_x(OH)_y(CO)_z]^{n+}$ with $n < 3$ in zeolites of the type of faujasite, the complexes being formed in the course of the activation of $[Ru(NH_3)_4]^{3+}NaX$ and $[Ru(NH_3)_4]^{3+}NaY$ in the presence of CO at 240–280 °C.[48] Their activity is higher than that of the industrial low-temperature catalyst based on copper.

*The reduction of NO with carbon monoxide*

$$NO + CO \rightarrow \begin{cases} \rightarrow N_2O + CO_2 \\ \rightarrow N_2 + CO_2 \end{cases}$$

is catalysed by zeolites containing transition metals—Ni, Co, Cu, Cr,[71] Rh,[71,72] and Ru.[73] Depending on the composition of the catalyst, the type of its preliminary treatment, and the conditions under which it is employed, the reaction can proceed with formation of either $N_2O$ and $CO_2$ or of $N_2$ and $CO_2$. According to Minachev et al.,[71] there are at least three temperature ranges in which the characteristics of the reduction of NO are different. At low temperatures (200–300 °C) the product is $N_2O$ and the catalysts are gradually deactivated. Above 350 °C, NO is fully reduced to $N_2$. It has been observed that the complex $[Rh^I(CO)_2(NO)]^+$, believed to be the reactive intermediate in the reduction of NO to $N_2O$, is formed from RhY.[72] It has been noted that the composition of the products of the reaction of NO with CO and the influence of temperature are significantly different for rhodium ions in the zeolite and in the case of deposited metallic rhodium[72].

*The reduction of NO by molecular hydrogen*

$$NO + H_2 \rightarrow N_2 + NH_3 + H_2O$$

is accelerated by the NiY zeolites and the phthalocyanine complexes of nickel in a faujasite matrix (PcNiY), while the CuY, CoY, PcCuY, and PcCoY zeolites are almost inactive[74]. The process selectivity is determined by the reaction temperature and the nature of the ligand environment of the transition metal cations. Only $NH_3$ is formed on PcNiY, while $N_2$ is the only product in the presence of the $Ni^0$/HNaY catalyst obtained by the reduction of NiNaY with hydrogen at 550 °C. In the presence of the NiY zeolite treated with $H_2$ for 3 h at 350 °C, the degree of conversion of NO at 100 °C was 100%, 62% NO being converted into $NH_3$ and 38% into $N_2$.

*The synthesis of nitrosyl chloride* from nitric oxide and chlorine, i.e.

$$2NO + Cl_2 \xrightarrow{250°C} 2NOCl \ ,$$

has been studied in the presence of catalysts obtained by heating $NH_4NaY$ at 260°, 350°, 450°, and 550 °C.[75] The specimen heated at 550 °C showed the highest activity. A correlation was observed between the rate of reaction and the number of Lewis acid centres in the aluminosilicates.

*The decomposition of nitrous oxide*

$$2N_2O \rightarrow 2N_2 + O_2$$

is catalysed by type Y and L zeolites and mordenite containing transition metal cations[76–79]. CuNaY and CoNaY are more effective than NiNaY, while the atomic catalytic activity of NiKL is higher than for the NiNa–mordenite and NiNaY systems, in which the degrees of exchange of $Na^+(K^+)$ for $Ni^{2+}$ are similar.

*In the reduction of $SO_2$ with hydrogen sulphide (the Klaus reaction),*

$$2H_2S + SO_2 \rightarrow 2H_2O + 3/n\,S_n$$

the activity of the NaX and NaY zeolites is comparable to that of an industrial catalyst ($Al_2O_3$), while the activity of NaX impregnated with 2% NaOH is higher[80,81]. The reaction is of zero order with respect to $SO_2$ and of 0.5 order with respect to $H_2S$. It has been established by infrared spectroscopy that $H_2S$ dissociates heterolytically on the surface of the catalyst ($H_2S \rightleftharpoons HS^- + H^+$), which is consistent with an order of 0.5 with respect to hydrogen sulphide. According to George and Tower[81], the reaction proceeds on basic centres and not on the $H^+$-acid centres.

New evidence for extensive possibilities in the application of zeolitic catalytic systems to a wide variety of chemical reactions has thus been obtained.

## 3. Zeolites in Pyrolytic Processes

Pyrolytic processes constitute a promising field of application of zeolite-containing catalysts (ZCC). Thus the maximum yield of ethylene in the thermal decomposition of the propane fraction (40 wt.%) is attained at 850 °C, while in the presence of ZCC such yield is reached at 715 °C, i.e. at a temperature lower by 135 K, the yield of ethylene at 760 °C being 49.5 wt.%.[82] Furthermore, the selectivity of the process in relation to the formation of the desired product increases greatly under the influence of ZCC.

Similar results were obtained in pyrolytic processes involving low-quality petrols in the presence of zeolites and ZCC.[83,84] According to Minachev et al.[83], in the presence of the cationic forms of mordenite it was possible to obtain olefins in higher yields than on the NaA, NaX, and NaY zeolites, chabazite, or K, Na-erionite. The activity of the catalysts and the selectivity of their action depend significantly on the nature of the exchangeable cation $M^{n+}$. Table 3 shows that the greatest amount of gaseous products and $C_2$–$C_4$ alkenes are produced by Ni-mordenite and Co-mordenite. Among the Mn-, H-, and MnH-forms of the zeolite, for which the yields of gaseous products are similar, the decationated specimen has an outstanding selectivity in relation to the formation of olefinic hydrocarbons. These differences can probably be accounted for by the different locations of the $Mn^{2+}$ cations in the Mn- and MnH-mordenites and by the different acid characteristics of the catalysts. The gasification of polyethylene in the presence of the CaX zeolite has also been achieved[85].

These initial studies laid the foundations of the important field involving the utilisation of zeolitic catalysts in pyrolytic processes, whose development is closely related to the synthesis of and research into new thermostable materials.

## 4. Zeolites as Catalysts and Adsorbents

We believe that a great future awaits the application of zeolites in catalytic processes as adsorbents (or as catalysts and adsorbents). This concerns the utilisation of the molecular sieve properties of zeolites for the selective adsorption of one of the reaction products and the displacement of the equilibrium in chemical reactions. The efficiency of this approach has been demonstrated in relation to the synthesis of esters of carboxylic acids and alcohols with the removal of water by the KA, NaA, and CaA molecular sieves[86–89], the transesterification of esters, $RCOOR^1 + ROH \rightleftharpoons RCOOR^2 + R^1OH$, with selective adsorption of $R^1OH$,[90–92] and in the synthesis of acetals and ketals[93,94]. The desired products were thus obtained in yields ≥90% (and in many instances in quantitative yields) even in the case of sterically hindered reactants. The adsorbent can be suspended in the reaction mixture or placed in the cartridge of the Soxhlet apparatus[90]. Comparison of the methods for the removal of $H_2O$ or $R^1OH$. .($CH_3OH$) by azeotropic distillation and adsorption on zeolites showed that in the latter case higher yields of products are obtained in a shorter time[7].

Table 3. Pyrolysis of high-quality petrol (O.N. = 42) on cationic forms of mordenite[83] ($T$ = 600 °C, $v$ = 1 $h^{-1}$).

| Cationic form of zeolite | $c_1$, % | $[C_2-C_4]$, % | $\alpha$ | $c_2$, % |
|---|---|---|---|---|
| Li | 25.0 | 57.2 | 1.44 | 8.1 |
| Na | 78.7 | 47.5 | 1.16 | 5.5 |
| K | 49.5 | 38.2 | 0.8 | 5.7 |
| H | 55.0 | 57.3 | 1.39 | 7.2 |
| Co | 80.0 | 66.6 | 3.37 | 7.0 |
| Ni | 81.2 | 68.8 | 2.63 | 6.0 |
| Mn | 40.6 | 51.7 | 1.29 | 6.6 |
| MnH | 50.4 | 75.9 | 3.6 | 5.7 |

Notation: $c_1$ and $c_2$ are the yields of gas and coke respectively, $[C_2-C_4]$ is the content of olefins in the gas, and $\alpha$ = olefin : paraffin ratio.

The use of zeolites as catalysts and adsorbents simultaneously (either of the same type or of different types and compositions in the two cases) is of special interest. Table 4 presents data[94] obtained for the synthesis of the diethyl acetal of cyclohexanone in the presence of the $M^{n+}$NaY zeolites as catalysts and the CeNaY and KA zeolites as adsorbents. Evidently, the reaction with KA goes to completion and at the same time the period during which cyclohexanone undergoes a quantitative conversion is shortened; KA is a more effective adsorbent than CeNaY.

## 5. Industrial Applications of Zeolitic Catalysts

Considerable advances have been made in recent years in industrial catalysis on zeolitic systems. New catalysts have been developed for the cracking[14,95–102], hydrocracking[18,103], and selective hydrocracking ("selecto-forming")[17,18,104–107] of petroleum fractions, the isomerisation of aromatic $C_8$ hydrocarbons ("octafining")[108,109], and the isomerisation of $n$-paraffins[110,111], in which zeolite-containing compositions have already been used. The scale of the manufacture and utilisation of catalysts has increased and their assortment

has been expanded. It has become possible to process new types of raw materials.

*Catalytic cracking* is the process involving the largest-scale consumption of catalysts. At the present time 220000 tonnes of zeolite-containing cracking catalysts are produced annually in the capitalist countries of which 200000 tonnes are employed in fluidised bed apparatus[18]. Catalysts have been devised which diminish the amounts of coke and gas formed and of the sulphur oxides discharged from the regenerator[98,99] and promote the oxidation of carbon monoxide in the smoke gases present in the fluidised bed cracking regenerators—this is achieved by introducing small amounts (<0.001%) of noble metals[95,96]. Compositions have been developed which are effective in the processing of heavy raw materials, are resistant to poisoning by metals, and increase the octane numbers (O.N.) of the fuels obtained[14,18,99]. They are all based on type Y zeolites, which are used in the ultrastable lanthanide (LnY) and magnesium-lanthanide modifications (MgLnY). Polyzeolitic systems incorporating, together with faujasites, also zeolites of other types (ZSM, mordenite, erionite, and ferrierite), which permit a finer control of the composition of the product formed, in particular they make it possible to increase the yields of propene and butenes, have been proposed recently[18]. Further developments in this field will evidently tend to increase the stability of the catalyst in relation to various influences, including the influence of admixtures in the raw material, to improve the selectivity of the catalyst, and to promote the maximum utilisation of these possibilities.

**Table 4.** Synthesis of cyclohexanone diethyl acetal using zeolitic catalysts and adsorbents[94].

| Catalyst | $t_a$, °C | Adsorbent | $\tau_{50\%}$, min | $\eta$, % | $\tau$, min |
|---|---|---|---|---|---|
| 0.62 CeNaY | 200 | — | 180 | 52 | 240 |
| 0.62 CeNaY | 200 | CeNaY* | 14 | 71 | 60 |
| 0.62 CeNaY | 200 | KA | 13 | 99.9 | 45 |
| 0.61 LaNaY | 200 | KA | 19 | 99.9 | 60 |
| LnY | 200 | KA | 34 | 99.9 | 120 |
| SK-500 (LnHY) | 200 | KA | 11 | 99.9 | 45 |
| 0.67 $NH_4$NaY | 340 | KA | 20 | 99.9 | 105 |
| 0.68 MgNaY | 400 | KA | — | 3.1 | 150 |
| 0.75 CaNaY | 400 | KA | 90 | 99.9 | 250 |

Note. A mixture of cyclohexanone (0.05 mol) and ethanol (0.2 mol) in n-hexane (75 ml) was stirred with the catalyst (4 g) and powdered KA (10 g) at 0 °C; $t_a$ is the catalyst activation temperature, $\tau_{50\%}$ the time of attainment of 50% conversion of cyclohexanone and $\eta$ the final conversion of cyclohexanone.

*In this case 14 g of the 0.62 CeNaY zeolite was taken in order to accelerate the reaction and displace the equilibrium.

*Hydrocracking* is the second process in which zeolitic catalysts are used on a wide scale (the annual consumption exceeded 1000 tonnes; approximately 50% of the starting material subjected to hydrocracking is processed with their aid[18]). They are all based on type Y zeolites and the hydrogenating components are Co, Mo, W, Pt, and Pd. The application of the catalysts is expanding continuously in a varied manner[103,112,113]. Radchenko et al.[103] described in greater detail the existing hydrocracking processes in the USSR and abroad, in which zeolite-containing catalysts are employed, as well as processes developed and designed for industrial use.

*The selective hydrocracking (selectoforming)* of n-paraffins (mainly $C_5$–$C_9$ paraffins) in mixtures with isoparaffins and aromatic hydrocarbons is designed to improve the quality (increase the O.N.) of reforming petrols with simultaneous formation of liquefied petroleum gas (a mixture of propane and butane). A catalyst exhibiting a molecular-sieve activity is used in this process. It is prepared from natural erionite (this is so far the only example of the industrial application of a catalyst made from a natural zeolite)[17,18] or from its synthetic analogue[104,105] and a metal (Ni or Mo). The possibility of employing also catalysts based on a narrow-pore synthetic mordenite has been demonstrated[114,115]. The selective hydrocracking of catalytic reforming petrol, refined petrol, and their mixture on a metal-zeolitic catalyst can yield a basic component with O.N. = 95, which on treatment with ≤15% of isopentane is converted into the non-ethylated petrol AI-93.[106] As a result of the involvement of low-octane refining products in the processing, the consumption of the straight-chain starting material is reduced (by ~20%) in the manufacture of AI-93 petrol[106].

*The isomerisation of n-alkanes* (the pentane–hexane fractions of petroleum and gaseous and light petrols) yields high-octane components of motor fuels—isoparaffinic hydrocarbons. According to Simoniak et al.[116], the complete isomerisation of normal paraffins in the fraction with a terminal boiling point of 71 °C in combination with catalytic reforming increases the O.N. of petrol by 20 points and yields a product balanced with respect to the O.N. of narrow fractions. A zeolitic isomerisation catalyst (H-mordenite containing a small amount of a noble metal) has been used since 1970 (the high isomer process[117]); at the present time it is already used in tens of different types of apparatus[18]. Various modifications of the Pt–zeolite Y catalysts[111] have also been developed and applied in industry. The Leuna-catalyst 8852 with the composition $Pt/LnCaY/Al_2O_3$ was introduced in 1980.[111]

*The isomerisation of aromatic $C_8$ hydrocarbons* (industrial mixtures of xylenes and ethylbenzene) is carried out under hydrogen pressure in the presence of metal-zeolitic systems. The Pt–dealuminated H-mordenite–$Al_2O_3$ catalyst has a high activity and stability in this process, whose aim is the maximum synthesis of *p*-xylene[108]. The latest catalysts are based on zeolites of type ZSM-5.[17,18,118] Their characteristic feature is a high ratio of their activities in the isomerisation and disproportionation of alkylbenzenes, which amounts to approximately 1000 (for mordenite catalysts, it is close to 70 and for faujasite catalysts it is 10–20).[118] This ensures the formation of *p*-xylene in hitherto unattainable yields and a diminution of the principal side reactions.

The industrial applications of zeolites and zeolite-containing catalysts in many of the other processes described below has begun.

*In the alkylation of benzene by ethylene*, designed to synthesise ethylbenzene which is converted into styrene and the latter is used in the manufacture of plastics and synthetic rubbers, aluminium chloride has been used as the catalyst hitherto. The problems associated with the application of $AlCl_3$ are generally known. Studies designed to replace $AlCl_3$ by solid catalysts which at the same time meet current requirements including those concerning the protection of the environment and the improvement of health conditions in the relevant industries, have been prosecuted for many

years. Many zeolitic catalysts have also been proposed[1,2,5,8]. However, it was not until 1977 that ethylbenzene was synthesised on an industrial scale in accordance with the technology of the "Badger" company using a catalyst based on the ZSM-5 zeolite developed by the Mobil Oil Corporation[119-121]. This catalyst does not cause corrosion of the equipment, is inert with respect to admixtures in the starting material, and does not require special storage conditions. The process does not involve the formation of harmful atmospheric and aqueous waste.

According to the results presented in Ref.121, the overall productivity of the existing and planned plant reaches 335000–465000 tonnes of ethylbenzene annually.

*The catalytic deparaffination of distillates and oils* is carried out on bifunctional metal-zeolitic systems and is used to prepare low-setting fuels and basic oils[122-125]. The best catalysts of the deparaffination of petroleum crude are platinum- or palladium-containing dealuminated H-mordenites[124]. They convert effectively only paraffinic hydrocarbons with normal or slightly branched structures, while sulphur and nitrogen compounds in aromatic hydrocarbons are changed little. Here it is important that predominantly the cleavage of alkanes with formation of gaseous products (principally propane, butane, and pentane), and not their isomerisation, takes place on the $M^0$/H-mordenites.

A process for the catalytic deparaffination of heavy distillates, whose application makes it possible to produce diesel and boiler fuels from heavy gas-oils, has been developed[122, 123]. The process is carried out on a stationary catalyst (based on the ZSM-5 zeolite) at 260–427 °C, a pressure of 21–42 atm, and with circulation of the hydrogen-containing gas. Fractions with setting points ranging from 6.7° to 54.4 °C and containing up to 50 wt.% of n-paraffins can be deparaffinated (by the selective hydrocracking of normal or weakly branched paraffins). The catalyst is resistant to the action of sulphur and nitrogen compounds, whose content in the starting material can reach 3 and 0.1 wt.% respectively. The period between the oxidative regenerations of the catalyst is 0.5–2 years. The yield of product which begins to boil at 165 °C is 54–91 vol.% with respect to the starting material and its setting point is greatly reduced[122]. The completion of the construction at the refinery of the Mobil Oil Corporation in Wilhelmshaven (Federal Republic of Germany) of a plant for the catalytic deparaffination of heavy gas-oil with output of 600000 tonnes per year has been reported[125]. The process is designed for the synthesis of furnace fuel (FF). Petrol and gas in the proportions FF : petrol : gas = 86 : 7 : 7 are formed together with the furnace fuel (400 °C, 40 atm). The application of this process increases the yield of the intermediate distillates from petroleum by ~5%.[125]

*The synthesis of propane from butane*[126] is based on the reaction $3C_4H_{10} + H_2 \rightarrow 4C_3H_8$. The catalyst (its composition is not reported) is a zeolite with a low content of an alkali metal, which exhibits hydrogenating properties although hydrogenating components are not specially introduced. The process conditions are as follows: temperature at the inlet to the reactor with a stationary catalyst bed 315–450 °C, pressure 12–23 atm, space velocity of liquid $C_4H_{10}$ 1–3 $h^{-1}$, and the molar ratio $H_2 : C_4H_{10} = (3–6) : 1$. The highest yield of propane is obtained for a conversion of butane of ~90%. The industrial plant yielded 88.8% of propane and 12.8% of fuel gas for a hydrogen consumption of 1.6 wt.%.[126] The process makes it possible to overcome the shortage of propane and to smooth out the seasonal variations in the manufacture of individual hydrocarbons.

*The disproportionation of toluene* in the manufacture of benzene and xylenes can be achieved in the presence of various catalysts. When a lanthanide zeolite Y is used, the process is carried out in the liquid phase at 260–316 °C, 45 atm, and a weight velocity of the starting material of 1.5 $h^{-1}$. The degree of conversion of toluene per pass is ~45%, the yield of benzene is 19.7%, and the yield of xylenes is 23%. The life of the catalyst is 1.5 years[127]. The catalyst, based on the ZSM-5 zeolite, is highly selective and makes it possible to obtain disproportionation products enriched in *p*-xylene[17,18,118].

A series of catalysts for *the hydropurification of petroleum fractions*, based on the GO-115, GO-116, and GK-35 zeolites, have been developed[128-130]. Some results of the employment of the GK-35 catalyst on an industrial plant have already been examined[129].

*The reduction of nitrogen oxides by ammonia* is so far the only inorganic catalytic process in which zeolitic catalysts have found an industrial application. It is designed to make harmless the waste gases from a number of chemical industries (factories producing $HNO_3$, etc.). The H-forms of mordenite are effective catalysts of the reaction of $NO_x$ with $NH_3$ to form $N_2$ and $H_2O$.[64,65] The Zeolon-200H catalyst is used in the USA and Canada in several types of plant. A new, cheaper, and more active NC-300 catalyst, having the following chemical composition (wt.%) has been developed recently: 72–80 $SiO_2$, 17–22 $Al_2O_3$, 1–4 $Fe_2O_3$, and <1.5 $K_2O$; its characteristic feature is the possibility of carrying out the process under milder conditions and in the presence of $SO_2$ as well as large amounts of water[64,65].

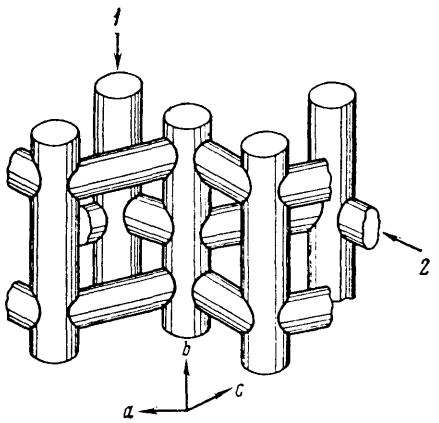
*The conversion of methanol into petrol* is included by some workers[17,18] among the industrial processes in which zeolitic systems are used. Such synthesis of motor fuel has been proposed by the Mobil Corporation[131-133]. Methanol is converted into a mixture of hydrocarbons having the following typical composition (wt.%): 1.7 $C_1$–$C_2$, 6.0 $C_3$, 16.4 $C_4$, 19.0 $C_5$, 16.4 $C_6$, 13.0 $C_7$–$C_9$, and 27.5 $C_6$–$C_9$ (aromatic); $C_n$ with $n \geq 11$ are hardly formed, so that the composition (and characteristics) are close to those of petrol obtained from petroleum. This process has attracted attention as the final stage in one of the procedures for the synthesis of motor fuel from solid mineral fuels (or natural gas) in accordance with the scheme coal → synthesis gas ($CO + H_2$) → methanol → petrol. Its development has advanced to the stage involving the sale of licenses and demonstration plant is operating[17,134]. In November 1979 the government of New Zeland decided to manufacture petrol in accordance with the technology of the Mobil Corporation (the output of the plant is 1500 tonnes in 24 h).[17,134] Methanol can be obtained from natural gas. The design of the plant incorporates reactors with a stationary catalyst bed. The construction of a plant for the production of petrol from methanol in a fluidised bed is planned in the Federal Republic of Germany[134]. However, there is as yet no information as to whether the process is being applied on an industrial scale.

Thus the search for new applications of zeolites in catalysis is being prosecuted in several directions.

## III. CATALYTIC SYSTEMS BASED ON ZEOLITES OF NEW TYPES

Hitherto approximately 150 structural types of zeolites have been described[135]. The catalytic activity has been studied only for certain types: A, X, Y, L, mordenite, erionite, chabazite, omega, clinoptilolite, offretite[1,2,5,6,8,10,12,15], and

ferrierite[136,137]. In recent years much attention has been devoted to zeolites of the pentasil family[138,139]: ZSM (the Soviet analogues are referred to as TsVK, TsVM, and ultrasil) and silicalite. These zeolites have an unusual structure[138–142], in which the dimensions of the windows and channels are intermediate between those of the windows and cavities in narrow- and wide-pore zeolites (see Figure), which ensures their unusual molecular-sieve properties; the zeolites are characterised by a high thermal stability, resistance to acids, and hydrophobic properties (combined with a low Al content); all these factors are responsible for the unusual nature of their interaction with various substances[141–144]. The $SiO_2/Al_2O_3$ ratio in the zeolites of the given families varies within wide limits, from approximately 20 to several hundreds and even thousands (specimens with $x = 8660$ have been investigated[144]); silicalite contains virtually no aluminium. Certain characteristics of ZSM-5 and silicalite are compared in Table 5.




Model of the porous structure of the ZSM-5 zeolite and silicalite: 1) linear channel with an elliptical cross-section (5.7 × 5.1 Å) formed by ten oxygen atoms; 2) zig-zag channel with a nearly circular cross-section (5.4 Å in diameter) formed by ten oxygen atoms.

**Table 5.** Comparison of the properties of the ZSM-5 zeolite and silicalite[46,139].

| Property | ZSM-5 | Silicalite |
|---|---|---|
| Chemical composition | $Na_2O \cdot Al_2O_3 \cdot x\ SiO_2$ ($x = 20 \div 1000$) | $SiO_2$ |
| Number of Si and Al atoms in unit cell | 96 | 96 |
| Ion-exchange properties | Present | Absent |
| Crystal structure | Orthorhombic; $a = 20.1$ Å; $b = 19.9$ Å; $c = 13.3$ Å | Orthorhombic; $a = 20.6$ Å; $b = 19.80$ Å; $c = 13.36$ Å |
| Porous structure | Shown in Figure | Shown in Figure |
| Sorption of $H_2O$ | Low in the presence of high $SiO_2$ content | Low |
| Thermal stability | Increases with increasing silicon content | High |

During a short period, the catalytic properties of systems based on pentasils have been investigated in many reactions: in the cracking of hydrocarbons[143–149], in the oligomerisation[150–155] and aromatisation of $C_2$–$C_4$ olefins[143,152,153,155–159], in the dehydration of alcohols and other oxygen-containing compounds[160–163], in the conversion of methanol into petrol[17,131–133], olefins[49–57], and aromatic hydrocarbons[143,148,153,156,162,164], in the alkylation of aromatic compounds[145,153,165,166], in the chlorination of benzene[38], in the dehydrogenation of ethanol[161], in the synthesis of a wide variety of compounds from CO and $H_2$,[45,47,167,168] in the aromatisation of alkanes and cycloalkanes[169,170], in the disproportionation of aromatic hydrocarbons[165,171], in the selective hydrocracking of n-paraffins and methyl-substituted paraffins in mixtures of hydrocarbons of different compositions[122,123], in the isomerisation of n-alkanes[172,173], in the hydrolysis of ethyl acetate[174], and in others[15,138]. Detailed examination of the results is outside the scope of this review. We shall consider certain features of the catalytic action of systems incorporating pentasils.

In contrast to H-mordenite[175], in the presence of the H-form of TsVK n-pentane undergoes mainly hydrocracking and disproportionation with formation of $C_1$–$C_4$ alkanes and hexanes and not isomerisation (Table 6). The introduction of palladium into zeolites leads to catalysts in the presence of which isopentane is obtained with high yields and selectivity. Since the concentrations and strengths of the protic acid centres in H-ZSM-5 and H-mordenite are similar[16], the different behaviour of the H-TsVK and H-mordenite catalysts in the conversion of n-pentane can be accounted for by the different distributions of the active centres in the crystal structures of the zeolites and also by the characteristics of their structure.

**Table 6.** The conversion of n-pentane on catalysts based on TsVK zeolites of different compositions[173] [$p = 30$ atm, $v = 1\ h^{-1}$, $H_2 : n\text{-}C_5H_{12} = 3.2 : 1$ (moles)].

| Catalyst | $SiO_2/Al_2O_3$ (moles) | $t$, °C | Conversion of $n\text{-}C_5H_{12}$, % | Yield, wt. % | | |
|---|---|---|---|---|---|---|
| | | | | iso-$C_5H_{12}$ | $C_1$–$C_4$ alkanes | $\Sigma C_6H_{14}$ |
| H-TsVK | 33.3 | 250 | 42.7 | 9.0 | 27.0 | 6.7 |
| H-TsVK | 33.3 | 300 | 55.0 | 9.9 | 41.4 | 3.7 |
| H-TsVK | 83.0 | 250 | 37.2 | 10.0 | 21.9 | 6.3 |
| 0.5% Pd/H-TsVK | 33.3 | 310 | 64.8 | 60.0 | 3.9 | 0.9 |
| 0.5% Pd/H-TsVK | 83,0 | 330 | 61,8 | 59,5 | 1,4 | 0,9 |

Since the dimensions of the windows leading to the channels in the structure of pentasils are greater than in the wide-pore zeolites and smaller than in the narrow-pore zeolites, pentasils manifest a specific molecular sieve selectivity. Thus, according to Rabo[172], the isomerisation of n-hexane on the 0.5% Pt/H-silicalite catalyst yields mainly methylpentanes, while 2,2-dimethylbutane is formed only in insignificant amounts (Table 7). On the other hand, in the presence of the Pt/zeolite Y catalyst the fraction of 2,2-dimethylbutane in isohexanes is approximately 19%. Evidently, the fairly large molecules of 2,2-dimethylbutane (critical diameter $d_{cr} = 6.2$ Å) cannot be desorbed from the channels of silicalite (the latter also does not sorb substances whose molecular dimensions are close to $d_{cr}$ for the neopentane, 2,2-dimethylbutane, and other molecules[172]). We may note that only methane and ethane were obtained from n-hexane in the presence of catalysts based on the H-forms of narrow-pore zeolites[172].

The hydrophobic properties of the ZSM specimens with a high $SiO_2$ and silicalite content combined with marked organophilic properties makes it possible to employ such catalysts

in reactions carried out in aqueous solutions, as shown in relation to the hydrolysis of ethyl acetate in the presence of H-ZSM-5 ($x = 93.2$).[174] This cannot be done for the majority of other zeolites.

Table 7. Isomerisation of n-hexane on the 0.5% Pt/vapour-stabilised zeolite Y and 0.5% Pt/silicalite catalysts at 15.3 atm and $H_2 : C_6H_{14} = 3:1$ (Rabo[172]).

| Catalyst | 0.5% Pt/zeolite | | 0.5% Pt/silicalite | | |
|---|---|---|---|---|---|
| $t$, °C | 272 | 262 | 327 | 339 | 351 |
| Conversion of n-$C_6H_{14}$, % | 81.44 | 77.39 | 74.74 | 75.58 | 76.88 |
| $c_1$, % | 55.42 | 56.53 | 68.26 | 66.22 | 64.41 |
| $c_2$, % | 18.97 | 14.84 | 0.64 | 2.0 | 3.67 |

Note. The silicalite contained 0.6 wt.% of $Al_2O_3$ as an impurity; it was converted into the H-form with a moderate acidity by ion exchange with $NH_4^+$ and subsequent heat treatment. The contents of methylpentanes ($c_1$) and 2,2-dimethylbutanes ($c_2$) in the $C_6$ product are quoted.

An important property of pentasils as catalysts and components of catalytic systems is their ability to retain a high activity for a long time (under certain operating conditions), which is significantly higher than for mordenites and other zeolites. Such ability is probably a consequence of the low degree of coke formation when pentasils are employed[16,143,145]. Indeed, using the tracer atom method, it has been established[176] that in the case of mordenite the "yield" of coke is higher by two orders of magnitude than for H-ZSM-5. It has been suggested[16,143,145] that mainly aromatic polyalkylhydrocarbons are a source of coke. They cannot be formed in the limited volume of the channels of pentasils, which limits the "yield" of coke. However, it is noteworthy that the stability of catalysts based on the ZSM, TsVK, and TsVM zeolites depends significantly on their composition and the conditions under which they are employed as well as on the nature of the reactants[143,167]. As a rule, the activity of the catalysts is maintained for a longer period the smaller their residual $Na^+$ content and the higher the $SiO_2/Al_2O_3$ ratio; process temperatures greater than or equal to 350 °C are favourable, so that the stability of the pentasil system is apparently determined not only by the rate of formation of coke but also by other factors.

The above examples (see also, the specific nature of the catalytic action of the type ZSM zeolite and silicalite in the chlorination of benzene[38] and a number of studies[46,57,143–145,159,166,167,170] described in Section I) demonstrate the likely usefulness of a comprehensive study of high-silica materials belonging to the pentasil family and others. Among the latest crystalline aluminosilicates, the Fu-1 and Nu-1 zeolites, obtained in systems involving tetramethylammonium compounds[177,178], and TsKF zeolites synthesised in the Na, Rb-, Na, Cs-, K, Rb-, and K, Cs-systems merit attention[179].

## IV. CATALYSIS ON POLYZEOLITIC SYSTEMS

A natural development of studies involving different zeolites was the synthesis of polyzeolitic systems and the study of their catalytic properties. Such systems have been investigated in greatest detail in the cracking process[18,101,102]. It has been shown that, in the cleavage of a mixture of hydrocarbons on zeolite-containing compositions incorporating zeolites of the mordenite, erionite, ferrierite or ZSM types together with lanthanide or ultrastable faujasite Y, it is possible to achieve a fine control of the composition of the product formed, in particular the yields of propene and butenes as well as the octane number of the resulting petrol can be increased[18].

By combining the properties of different crystalline aluminosilicates, it is possible to "construct" a wide variety of polyfunctional catalysts of a new type. An example of the latter is provided by the bizeolitic alkylation catalysts which we investigated[180]. They consist of mixtures of zeolites, one of which is active only in the dimerisation of ethylene (NiNaA, NiNaX) and the other is active only in the alkylation of benzene by olefins (for example, CaNaY). In the presence of these catalysts the main product of the interaction of $C_6H_6$ with $C_2H_4$ is s-butylbenzene and both single- and two-bed systems are active. Their properties can be regulated by altering the contents of the individual components in the mixture[180]. The polyzeolitic compositions can include the crystallites of both a single type and different types. This application of zeolites in catalysis is very promising and merits further consideration.

## V. POLYFUNCTIONAL CATALYSIS ON ZEOLITIC SYSTEMS

Catalysts with polyfunctional activity, which accelerate simultaneously several reactions coupled in a single process, make it possible to carry out in a single stage complex syntheses, including those which are difficult or impossible to achieve with the aid of monofunctional systems[181,182]. Their theoretical and practical importance is enormous. Special attention was devoted to this problem already in the first studies of Rabo and coworkers[183,184] and Minachev and coworkers[1,185,186], carried out during the initial period of the development of catalysis in the presence of synthetic zeolites. Subsequently new catalysts were devised for the hydrocracking and hydroisomerisation of hydrocarbons[6], the hydroalkylation of benzene to phenylcyclohexane[187], the isomerisation of ethylbenzene to xylenes[6,108,109], the hydrocondensation of carbonyl compounds[6,34], the single-stage synthesis of cyclohexane from toluene and $H_2$,[188] s-butylbenzene from $C_6H_6$ and $C_2H_4$ (see our earlier review[189]), and others[6,8].

The effective catalysts for hydropurification processes[128,129], the synthesis of aliphatic hydrocarbons from CO and $H_2$,[190–193], of olefins from CO and $H_2$ [45,46] or methanol[53–57], and of aromatic hydrocarbons from $C_1$–$C_5$ alkanes[168,194,195] and also from CO and $H_2$,[44] the disproportionation of paraffinic hydrocarbons[196], and other syntheses[168] were developed in recent years.

In the course of this research, a series of important data were obtained concerning the characteristics of zeolites of different types as components of polyfunctional catalysts, the formation of a wide variety of catalysts, the mechanism of their action, and the method and possibilities of the regulation of their activity, selectivity, and stability, etc. It has been shown[193], in particular, that the use of zeolite-containing systems makes it possible to obtain from CO and $H_2$ products containing larger amounts of high-molecular-weight hydrocarbons (ceresin) than those obtained on the industrial CO–MgO–$ZrO_2$–kieselguhr catalyst. On the other hand, it has been observed[192] that the structure of the zeolite can limit the growth of the hydrocarbon chain length. Thus mainly $C_1$–$C_9$ hydrocarbons have been obtained on the Ru/NaY ion-exchange catalyst reduced at 300 °C, while in

the presence of $Ru/SiO_2$ a mixture of $C_nH_m$, in which paraffins and $\geq C_{12}$ olefins predominated (60%), was obtained under the same conditions of the synthesis [250 °C, molar ratio $CO:H_2 = 3:2$, contact time (with respect to CO) 0.4 s].

The range of catalytic systems with polyfunctional activity has been expanded. It has been established that not only compositions of the metal/zeolite type in the form with $H^+$ acidity (the commonest catalyst[6]) can exhibit polyfunctional properties. In the alkylation of benzene and its homologues with ethylene, NiY faujasites and $NiO-H^+$–zeolite systems behave as bifunctional catalysts (the interaction of $RC_6H_5$ with $C_2H_4$ in their presence proceeds mainly with formation of the s-butylderivatives $RC_6H_4-C_4H_9$ [189]). Alkaline cationic modifications of zeolites X and Y containing Group VIII metals exhibit only a single function in the reactions of hydrocarbons, determined by the metal, catalysing the hydrogenation, dehydrogenation, or oxidation of $C_nH_m$.[6] On the other hand, they behave as bifunctional systems in the reaction of butyraldehyde with $H_2$, accelerating simultaneously the crotonic condensation and the hydrogenation of carbonyl compounds coupled in a single process (Table 8); here 2-ethylhexanal and iso-octyl alcohol are obtained in a single stage[32].

Table 8. Hydrocondensation of n-butyraldehyde on metal-zeolitic catalysts[32] (150 °C, $\nu = 1\ h^{-1}$, $C_4H_8O:H_2 = 1:1.5$).

| Catalyst | Conversion of n-butyraldehyde, % | | | | |
|---|---|---|---|---|---|
| | into butanol | into 2-ethyl-hexenal | into 2-ethyl-hexanal | into 2-ethyl-hexanol | Overall |
| 0.5% Pt/NaX | 16.8 | 10.8 | 13.0 | 6.1 | 51.0 |
| 0.5% Rh/NaX | 8.4 | 4.9 | 29.2 | 2.8 | 46.0 |
| 0.5% Pd/NaX | 1.6 | 1.6 | 58.8 | 1.9 | 67.0 |
| 1.0% Pd/KNaX | 1.4 | 1.0 | 61.6 | 1.5 | 69.5 |
| 0.2% Pd/0.65 RbNaX | 1.5 | 4.8 | 58.0 | 0.5 | 65.0 |
| 2.0% Ni/HNaX | 21.8 | 1.1 | 16.1 | 7.3 | 47.0 |
| 2.0% Co/HNaX | 21.5 | 22.2 | 20.5 | 2.7 | 72.0 |

Note. The content of the Group VIII metal is expressed in wt.%.

In the presence of Pd/CaY, it is possible to synthesise from $C_6H_6$ and $H_2$ either cyclohexane, by altering the temperature (to 200 °C), i.e. by merely hydrogenating benzene, or methylcyclopentane and cyclohexane (at 260–320 °C), i.e. benzene is made to undergo hydroisomerisation and as well as hydrogenation[186]. Thus a catalyst having the same composition can behave as monofunctional and polyfunctional depending on the nature of the reactant and the conditions under which it is employed. This leads to new research fields.

It is becoming increasingly obvious that the possibilities in the application of zeolites in catalytic polyfunctional systems have been by no means fully elucidated. The studies and developments in this field will undoubtedly continue.

## VI. ZEOLITIC METAL COMPLEX CATALYSTS

Yet another promising application of zeolitic materials in catalysis has been established—as a matrix for transition metal complexes (TMC) and components of hydrogenised metal complex catalysts. Such systems can be obtained by introducing the prepared complexes into crystallites having the appropriate composition or by synthesising the required compounds within the zeolite cavities (here it is necessary to distinguish cationic complexes and complexes of zerovalent metals[197–199]). The method involving the interaction of dehydrated zeolites containing transition metal cations with the corresponding compounds in the gas phase or solution is most common. It is used, in particular, in the synthesis of phthalocyanine[200], ethylenediamine[201,202], nitrosyl[197–199,203], carbonyl[204–207] and trimethylphosphine[208] transition metal complexes in zeolites X and Y. Catalysts of the TMC–zeolite type can also arise in the interaction of crystalline aluminosilicates with the components of the reaction mixture, as shown for the rhodium-[209–211] and iridium-zeolitic[16,212] catalysts for the carbonylation of methanol with carbon monoxide. The matrices are usually zeolites X and Y, which have the widest pores, ensuring the accommodation of the complex within the structural cavities and the possibility of the coordination of the reactant molecules.

Some characteristics of TMC and zeolites have already been considered[197–199,213]. Important results have been obtained[214–217]; it has been shown with the aid of X-ray photoelectron spectroscopy that the phthalocyanine complexes of nickel and cobalt in faujasite Y are formed mainly in the large cavities of the lattice, being uniformly distributed throughout the volume of the aluminosilicate crystals[214]. With increase of the degree of exchange of $Na^+$ for $M^{2+}$, the degree of binding of the cations to the phthalocyanine increases and reaches ~80% for 0.6 MNaY. The photoelectron spectra led to the conclusion that the zeolite behaves not only as a matrix but also as a ligand for complex formation, causing a charge redistribution over the nitrogen and meso-atoms in the phthalocyanine molecule[214,216].

The catalytic properties of TMC–zeolite systems have already been investigated in a fairly wide range of reactions, some of which are listed in Table 9. A number of characteristic features of the catalytic action of these systems have been discovered. According to Gusenkov et al.[225], in the presence of CuY the decomposition of epoxycyclohexane takes place non-selectively with vigorous coke formation. On the other hand, in the presence of copper-phthalocyanine in the zeolite, $C_6H_{10}O$ undergoes dehydration with formation of cyclohexadiene (100% selectivity). In the presence of the ethylenediamine complex of copper in faujasite, only benzene is obtained, i.e. the mode of reaction is determined by the nature of the ligand environment of the transition metal in the TMC in the zeolite[225]. Another example of an appreciable influence of the formation of complexes by $M^{n+}$ in crystalline aluminosilicates on the selectivity of the corresponding catalysts may be provided by the dimerisation of propene in the presence of phosphine complexes of $Ni^{2+}$ in zeolites X, namely $[R_3P.Ni]X$.[40] Depending on R, the main reaction products obtained are methylpentenes or 2,3-dimethylbutenes (when R is large; see Table 2); this is the result of the steric influence of the ligand $PR_3$, which determines the type of orientation of the π-bonded propene molecule in the olefin dimerisation stage. Thus new interesting possibilities have arisen for the regulation of the activity and selectivity of catalysts.

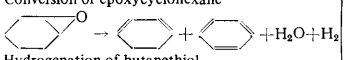
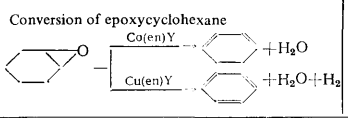
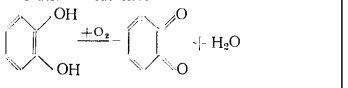
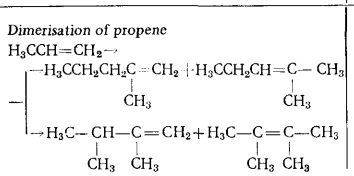
## VII. MODIFICATION OF ZEOLITIC CATALYSTS

In view of the polyfunctionality and "universality" of the catalytic action of zeolites, there exists the acute problem of the controlled alteration of the selectivity of zeolitic catalytic systems and in particular of increasing their stability.

There are several ways in which the catalytic properties of zeolites can be regulated. The simplest and most frequently employed method involves varying the composition and conditions of the preliminary treatment of the catalyst[19].

The composition can be altered in the course of the synthesis of the zeolite by substituting the exchangeable cations, by extracting some of the aluminium atoms (dealumination) or silicon atoms from the skeleton, and by other procedures.

Table 9. Catalytic reactions in the presence of TMC–zeolite systems.

| Complex, zeolite | Reaction | References |
|---|---|---|
| $[Cu(NH_3)_4]^{2+}$ $[Co(NH_3)_2]^{3+}$ in type Y zeolite | $NH_3+O_2\rightarrow N_2+H_2O$<br>$NO+NH_3\rightarrow N_2+N_2O+H_2O$ | [217]<br>[218] |
| Rhodium carbonyl complexes in type Y zeolite | Hydroformylation of olefins<br>$RCH{=}CH_2 + CO + H_2\rightarrow RCH_2CH_2CHO + RCHCHO$ (CH$_3$) | [206] |
| Phthalocyanine complexes of Ni, Co, Fe, and Cu in type Y zeolites | Dehydrogenation of cyclohexane<br>Dehydrogenation of isopropyl alcohol<br>$NO+H_2\rightarrow N_2+NH_3+H_2O$<br>$CO+O_2\rightarrow CO_2$<br>Oxidation of cysteine<br>Conversion of epoxycyclohexane<br><br>Hydrogenation of butanethiol<br>$C_4H_9SH+H_2\rightarrow C_4H_{10}+H_2S$ | [219–222]<br>[220–222]<br>[74]<br>[223]<br>[224]<br>[225]<br>[226] |
| Ethylenediamine complexes of $Co^{2+}$, $Mn^{2+}$, $Cu^{2+}$, and $Ni^{2+}$ in type Y zeolites | Conversion of epoxycyclohexane<br> | [225] |
| | Oxidation of catechol<br> | [201] |
| $[Co^{3+}(NH_3)_nNO]^{2+}Y$, $[Co(en)_2]^{3+}Y$, $[Co(trien)]^{3+}Y$* | $NO+NH_3\rightarrow N_2+N_2O+H_2O$ | [227] |
| $[Ru(NH_3)_x(OH)_y(CO)_z]^{n+}$ in type X and Y zeolites | $CO+H_2O\rightarrow CO_2+H_2$ | [47] |
| Phosphine complexes of $Ni^{2+}$ in type X zeolites: $[R_3P.Ni]X$ | Dimerisation of propene<br> | [40] |

Notation: en = ethylenediamine and trien = triethylenetetramine.

In the studies, carried out in recent years, many of these methods were developed further. In particular new methods were proposed for the dealumination of aluminosilicate zeolites, which make it possible to obtain high-silica materials with high chemical and thermal stability. One of these is based on the repeated ion exchange of the initial aluminosilicate with $NH_4^+$ ions and the hydrothermal treatment of the product in combination with the extraction of non-skeletal aluminium by inorganic acids (HCl or $HNO_3$).[228,229] Specimens of type Y zeolite in the ratio $SiO_2/Al_2O_3 \geq 100$, which retain their structure even after heat treatment at 1150 °C for several hours, were prepared by this method[228].

The method of dealumination with the aid of $SiCl_4$ is of great interest[230]. It is based on the reaction

$$M_{1/n}[AlO_2(SiO_2)_x] + SiCl_4 \rightarrow 1/n\ MCl_n + AlCl_3 + [(SiO_2)_{x+1}],$$

where M is a cation with a charge $n$. The process consists of a single stage and is carried out in the absence of water vapour. The zeolite (NaY, $NH_4Y$, etc.) is dehydrated in a vertical tubular reactor at ~380 °C in a stream of dry nitrogen, after which nitrogen saturated at room temperature with $SiCl_4$ is passed through it, while raising the temperature in the reactor to the specified value (460–560 °C) at a rate of 4 K $min^{-1}$. The treatment is continued for several hours (≥2 h). The aluminium is removed partly in the form of $AlCl_3$ and is partly converted into the complex $M[AlCl_4]$ {$Na[AlCl_4]$ in the case of NaY}, which is washed off with water. The degree of dealumination depends mainly on the reaction time $\tau$ and to a lesser extent on the final temperature of the treatment. In the case of NaY ($x$ = 5.04) for $\tau$ = 2 h and 500–560 °C, products with $x$ ranging from 40 to 100 and distinguished by a high crystallinity were obtained[230].

When $SiCl_4$ is used as the dealuminating agent, direct substitution of Al in the faujasite skeleton for Si is believed[230] to occur. The above method is inapplicable to narrow-pore zeolites, since $SiCl_4$ cannot penetrate into the cavities of the crystal structure[230].

Variation of the chemical composition, the method of preparation, and the type of preliminary treatment are only some of the procedures for the specific alteration of the activity, selectivity, and stability of zeolitic catalysts. "Secondary" modification methods are also used: the addition of various substances to the reaction zone (see the review of Minachev and Isakov[19]), complex formation with the exchangeable metal cations, and others (see below) which have more specific applications. The promoting effect of $NO_2$, $SO_2$, $CO_2$, HCl, $H_2S$, and $Cl_2$ on CaY in the catalysis of the dehydration of isopropyl alcohol[231], of $SO_2$ on the MNaX and MNaY zeolites in the isomerisation of butenes[232–236], and of $H_2S$ on MNaY in the cracking of cumene, the disproportionation of toluene, the cracking and disproportionation of xylene, and the dehydration of isopropyl alcohol[237] has been established. The conclusion[19,238] that the application of systems in the presence of other substances permits not only the intensification of catalytic processes and a change in their selectivity but also a more complete determination and ultilisation of the possibilities of zeolites as catalysts has been confirmed. Valuable information about the nature of their activity and the mechanism of their action is obtained at the same time.

A procedure has been developed for the modification of catalysts comprising the ZSM and TsVK zeolites by phosphorus[17,165,166,171], boron[166,171], magnesium[165,171], antimony[239], and vanadium[159] compounds, whereby it has been possible to increase sharply the selectivity of the processes involving the disproportionation of toluene[17,165,171,239], the aromatisation of $C_2$–$C_4$ olefins[159], and the alkylation of toluene by methanol[166,239] to form $p$-xylene. Table 10 presents data obtained in the conversion of $C_2$–$C_4$ olefins. Evidently, in the presence of the TsVK zeolite without vanadium, the main component of the alkylbenzenes $C_8H_{10}$ is $m$-xylene. The introduction of 5 wt.% $V_2O_5$ into the zeolite lowers the overall degree of conversion of $C_nH_{2n}$ and the yields of the liquid catalytic reaction products and aromatic hydrocarbons (most pronounced in the case of $C_2H_4$) with a simultaneous marked increase of the fraction of $p$-xylene in the mixture of the alkylbenzenes $C_8H_{10}$. The $p$-isomer of ethyltoluene also predominated among the aromatic hydrocarbons $C_9H_{12}$.[159]

The causes of the observed effects have not yet been finally elucidated. It has been suggested[159,165,166] that they are associated with the partial blocking of the channels in

pentasils by the modifying compounds, which entails a decrease in the rate of diffusion of the molecules of *m*- and o-xylenes (in the general case *m*- and o-dialkylbenzenes) from the cavities in the crystal structure to the gas phase. However, the steric hindrance arising under these conditions is apparently not the only factor, particularly since the distribution in the catalysts of modifying agents of various types but inducing similar changes is unknown. According to Hughes[118], the modification of H-ZSM-5 with phosphorus (derived from phosphite) diminishes the strength of the acid centres, which explains the decrease of the activity of the catalyst usually observed[166,171] (see also Table 10), and can make a significant contribution also to their selectivity, for example, by altering the isomerising capacity of the catalysts. It is important to emphasise that the method of modifying the ZSM and TsVK zeolites described leads to the possibility of developing new stereospecific catalytic processes for the synthesis of *para*-substituted aromatic compounds.

Table 10. The influence of the composition of the catalyst on the aromatisation of $C_2$–$C_4$ olefins[159] [500 °C, $v$ = 500 $h^{-1}$, $SiO_2 : Al_2O_3$ (in zeolite) = 70.5 : 1].

| Initial olefin | η, % | W, % | c, % | Aromatic hydrocarbons, % | | | | Composition of $C_8$ alkylbenzenes, % | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $C_6H_6$ | $C_7$ | $C_8$ | $C_9$–$C_{10}$ | *p*-xylene | *m*-xylene | *o*-xylene | ethylbenzene |
| Catalyst-initial TsVK (0.7% $Na_2O$) | | | | | | | | | | | |
| $C_2H_4$ | 84.0 | 44.7 | 97.3 | 12.4 | 57.8 | 27.8 | 2.0 | 12.5 | 65.2 | 13.7 | 8.6 |
| $C_3H_6$ | 86.3 | 40.0 | 79.7 | 7.9 | 33.5 | 46.3 | 12.3 | 22.0 | 50.4 | 19.0 | 8.6 |
| n-$C_4H_8$ | 89.9 | 52.5 | 87.3 | 8.0 | 51.6 | 39.3 | 1.1 | 16.3 | 69.3 | 9.7 | 4.7 |
| iso-$C_4H_8$ | 97.0 | 43.8 | 71.9 | 8.3 | 28.6 | 46.4 | 16.8 | 21.6 | 48.9 | 18.6 | 10.9 |
| Catalyst-TsVk + 5% $V_2O_5$ | | | | | | | | | | | |
| $C_2H_4$ | 23.7 | 7.1 | 91.1 | 5.8 | 34.5 | 48.9 | 10.8 | 78.7 | 6.4 | 0.1 | 14.8 |
| $C_3H_6$ | 68.3 | 24.8 | 60.3 | 4.2 | 40.0 | 37.8 | 18.0 | 75.4 | 9.1 | 3.3 | 12.2 |
| n-$C_4H_8$ | 73.4 | 35.9 | 75.3 | 4.0 | 30.8 | 54.2 | 11.0 | 82.8 | 10.0 | 1.1 | 6.1 |
| iso-$C_4H_8$ | 78.4 | 39.9 | 71.2 | 4.4 | 35.4 | 50.4 | 9.8 | 79.1 | 8.6 | 1.1 | 11.2 |

Notation: η = conversion of $C_nH_{2n}$, $W$ = yield of liquid catalytic reaction products, and c = content of aromatic hydrocarbons in catalytic reaction products.

*The contents of benzene and $C_7$–$C_{10}$ alkylbenzenes are quoted.

In many instances the method involving controlled partial saturation of catalysts with coke has been effective[166,240]. It has been found that this procedure permits a significant increase of the selectivity and stability of catalysts and an increase in their useful life before regeneration. It has been shown, in particular, that the selectivity in the formation of *p*-ethyltoluene in the alkylation of toluene with ethanol increases with increasing degree of saturation of HNaY zeolites with coke[240].

The research in this field is being continued. Hitherto, much art is still involved in dealing with the problem although the contribution of science has become incomparably greater.

## VIII. THE STRUCTURE OF ZEOLITIC CATALYSTS, THE NATURE OF THE ACTIVE CENTRES, AND THE MECHANISMS OF THEIR ACTION

A characteristic feature of the development of catalysis in the presence of zeolites at the present stage is the increasing contribution of studies devoted to a more extensive investigation of the structure, the nature of the active centres, and the mechanism of the action of catalysts using a set of various physical, physicochemical, and theoretical (computational) methods. This is a natural result of the accumulation of extensive experimental data on the catalytic properties of zeolitic systems and the development of methods for the investigation of solids and chemical processes. Many new valuable results have been obtained in studies carried out in recent years. Data concerning the location of the exchangeable cations in zeolites of different compositions not only as regards crystallographic sites but also throughout the bulk of the crystals are of great interest. In particular, it has been established by X-ray photoelectron spectroscopy[216] that, in contrast to NaY and HNaY, for which no significant deviations of the surface $Na^+$ concentrations from those in the bulk phase are observed, the outer layers of the crystals of Na-mordenite and the TsVK and TsVM zeolites are greatly enriched in sodium. The migration of metals, produced on reduction of transition metal ions, to the outer surfaces of zeolite crystals[241] and the formation of alloys in polycationic systems when the latter are treated with hydrogen[241,242] have been demonstrated on many examples. It has been found that the oxidation of the Cu–Ni alloy in the CuNiY zeolite is accompanied not only by the formation of the CuO phase but also by the diffusion of the $Cu^{2+}$ ions within the zeolite structure with appearance of isolated $Cu^{2+}$ cations (as in the initial zeolite before reduction with hydrogen)[242].

Data concerning the influence of zeolites on the electronic state of deposited platinum and palladium have been surveyed[243] and valuable information has been obtained concerning the interaction of the metal with the aluminosilicate in other metal-zeolitic systems[244,245]. The characteristics of the spill over of hydrogen on zeolitic catalysts have been investigated[246]. Quantum-chemical calculations have been made for the OH groups[247,248] and also for the location of cations in faujasites[249]. An inhomogeneous distribution of aluminium in ZSM-5 type zeolites has been established. In their study of 50–200 μm single crystals by scanning electron microscopy and scanning X-ray microanalysis, von Ballmoos and Meier[250] found that aluminium is invariably concentrated at the edge of the crystals, while its content in the bulk of the particles is smaller by an order of magnitude than in the surface layers. The above differences depend on the size of the aluminosilicate crystals and the smaller the crystals the smaller the differences. According to Derouane et al.[251], the distribution of aluminium in the ZSM-5 zeolites depends also on the conditions of their preparation and even on the reactants used in their synthesis. These results lead to the conclusion that, in comparing the properties of zeolites with their composition determined by chemical analysis (the "average" composition), some caution must be exercised.

The above lists of examples is by no means complete and could be extended. The results obtained permit not only a more complete and accurate explanation of the characteristics of the action of catalysts but also promote the development of new approaches to the modification of catalysts and the solution of individual problems in the application of zeolitic systems. They also form part of the foundations of novel ideas concerning the mechanisms of certain reactions occurring on zeolitic catalysts[252].

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Such are the most important trends and the principal directions of development in catalysis on zeolites at the present stage. Zeolitic materials have aroused much promise for the solution of the important problem of the synthesis of artificial liquid and gaseous fuels and chemical products from coal and other mineral fuels. With their aid, much can be done not only in the field of the intensification of the processes and

the saving of energy and raw materials, but also in the solution of ecological and social problems.

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