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Catalytic Cyclo-oligomerisation Reactions of Lower Olefins and Alkanes with Formation of Aromatic Hydrocarbons

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The results of studies devoted to the aromatisation of lower (C_2-C_5) olefins and alkanes in the presence of a number of metal oxide and oxide catalysts are examined. The type of aromatisation discussed constitutes a new potential source of benzene and its nearest homologues, the need for which has been rapidly increasing.
The bibliography includes 70 references.

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I. INTRODUCTION

The requirement for benzene and its derivatives is at present very great[1-3]. According to Fick[2], the consumption of benzene in the USA will exceed by 1985 the total 1965 requirement by a factor of two for the manufacture of ethylbenzene alone. The overall consumption in 1985 will double compared with the 1976 level, which corresponds to an average annual increment of 7.5%. The great practical value of theoretical and technical developments directed towards the creation of novel processes and the discovery of new possibilities for the synthesis of valuable aromatic hydrocarbons is therefore evident. The important problem of expanding the raw materials base for the manufacture of aromatic hydrocarbons is related to these tasks.

New possibilities for synthesising aromatic hydrocarbons by the dehydrocyclo-oligomerisation of C_2–C_5 light olefins and alkanes[4-15], and in a number of subsequent communications, are of undoubted interest. A characteristic of the cyclo-oligomerisation of C_2–C_3 hydrocarbons is that their aromatisation results in the preferential formation of benzene and toluene[7,11]. It is known that benzene is the primary starting material among aromatic hydrocarbons for industrial organic synthesis and is used to synthesis styrene, cyclohexane, caprolactam, phenol, maleic anhydride, and intermediates for the manufacture of detergents and dyes. Toluene is the starting material for the manufacture of benzene, phenol, benzyl chloride, and various types of varnishes, dyes, and resins.

The synthesis of aromatic hydrocarbons by the dehydrocyclo-oligomerisation of lower olefins and alkanes can be arbitrarily divided into two groups of reactions—non-oxidative and oxidative. The first group includes the conversion of lower (mainly C_2–C_4) olefins into benzene and other aromatic hydrocarbons in the presence of metal-containing and certain oxide catalysts. These reactions have been discussed in the literature under similar names—dehydrocyclo-oligomerisation, cyclodimerisation, cyclotrimerisation, and also aromatisation of lower olefins and alkanes. A distinctive feature of the above group of reactions is that they occur without the supply of gaseous oxygen to the reaction zone and without the participation of oxygen which forms part of the oxide catalyst. In the present review these reactions of lower olefins and alkanes will be referred to as non-oxidative cyclo-oligomerisation. The second groups of reactions includes different versions of the oxidative aromatisation of lower hydrocarbons, which occurs in the presence of various oxide catalysts at 500–600 °C.

The present state of studies on the cyclo-oligomerisation of olefins and the dehydrocyclisation of lower alkanes with formation of benzene and its homologues, mainly in the presence of metal oxides and a number of oxide catalysts, in the non-oxidative and oxidative versions of the reaction is briefly assessed below.

II. DEHYDROCYCLODIMERISATION OF C_3–C_5 OLEFINS AND ALKANES IN THE PRESENCE OF VARIOUS METAL-CONTAINING AND CERTAIN OXIDE CATALYSTS

The first data on the dehydrocyclo-oligomerisation of lower C_3–C_4 olefins with formation of aromatic hydrocarbons were published by Soviet workers[4,5,16-19].

It has been shown[4] that n-butene gives rise to olefins in the presence of an aluminosilicate catalyst at 370 °C; following an increase of temperature to 450–500 °C, aromatic hydrocarbons (benzene, xylenes, and trimethylbenzenes) are formed together with olefins. The polymerisation of isobutene in the presence of an alumina–molybdenum oxide catalyst has been investigated[5] and isomeric xylenes have been detected in the reaction products (400 °C) and isolated. It has been shown[16,17] that aromatic hydrocarbons can be the main products of the conversion of propene over zinc chloride. The polymerisation and aromatisation of propene in the presence of molybdenum/alumina and platinum/alumina catalysts has also been studied[18,19].

The aromatisation of lower C_3–C_5 alkanes in the presence of a number of metal oxides and oxide catalysts was first described by Csicsery in a series of papers[6-10] published in 1969–1970. The dehydrocyclodimerisation of lower alkanes has been studied most thoroughly in relation to butane (and butenes) on platinum/alumina and certain oxide catalysts[6,8,9].

The dehydrocyclodimerisation of propane and propene in the presence of platinum/alumina catalysts, alumina, and mixed oxide catalysts containing bismuth, tin, and nickel oxides as well as a number of others has been studied by Usov and coworkers[20-25].

The dehydrocyclodimerisation of lower C_3–C_5 alkanes takes place at relatively high temperatures. As a rule, the reaction takes place above 430–450 °C. Thus the equilibrium

constants of the reaction 2isobutane ⇌ p-xylene + $5H_2$ at 427° and 527 °C are respectively 16.23 and 1.22×10^4.[6] The reaction takes place successfully in the presence of bifunctional catalysts with the optimum combination of dehydrogenating and acid properties, i.e. having a fairly high dehydrogenating activity and active in acid–base reactions.

A large series of metal oxide and oxide dehydrocyclodimerisation catalysts have been tested[6–10]. Among oxide catalysts, vanadium and chromium oxides are the most active in the reaction discussed; among metals, platinum has proved most successful. The usual overall content of the dehydrogenating component is 0.6–3.0% (for metal oxide catalysts) and 0.3–35% (for complex oxide catalysts) relative to the mass of the carrier. Alumina has been used successfully as the carrier, particularly alumina promoted with a halogen. In addition, amorphous and crystalline aluminosilicates, magnesium oxide, and silicon–magnesium oxides have been used as carriers for catalysts of the dehydrocyclisation of lower alkanes.

The platinum/alumina catalyst proved to be the best of the metal oxide catalysts of the dehydrocyclodimerisation of lower alkanes investigated by Csicsery[6]. Fig.1 shows how the platinum content in the platinum/alumina catalyst affects the degree of conversion of isobutane into aromatic hydrocarbons and the yield of the latter in the dehydrocyclodimerisation reaction. It follows from the results that the active surface of platinum in the catalyst employed (0.5–2.5% Pt/Al_2O_3) is approximately proportional to the platinum content in the catalyst. With increase of the platinum content, the yield of aromatic hydrocarbons falls as a consequence of the considerable intensification of the cracking and coke forming reactions. The author[6] therefore concluded that, under the conditions investigated (the carrier, temperature, space velocity, etc. employed), the optimum concentration of platinum in the catalyst is ~0.8 wt.% or a little less.

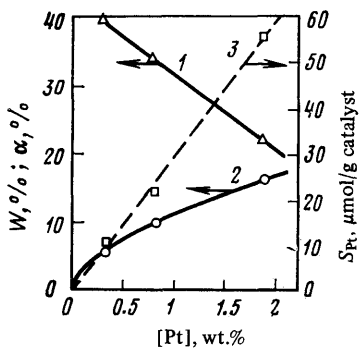


Figure 1. The influence of the concentration of platinum in the Pt/Al_2O_3 catalyst on the dehydrocyclodimerisation of isobutane to aromatic hydrocarbons (560 °C): 1) the yield of aromatic hydrocarbons W; 2) the degree of conversion α of iso-C_4H_{10}; 3) the adsorption capacity of the catalyst[6].

In the presence of this catalyst at 560 °C, C_3–C_5 alkanes undergo a whole series of reactions[6,7]: cracking with formation of methane and other hydrocarbons having a lower molecular weight than the initial compound; dehydrogenation; dehydrocyclodimerisation with formation of aromatic hydrocarbons; coke formation. The yield of aromatic hydrocarbons increases in the sequence propane < butane < pentane and is 9–15, 18–22, and 34–37 wt.% respectively. The main aromatic hydrocarbon obtained as a result of the dehydrocyclodimerisation of propane is benzene[7] the main aromatic compounds obtained as a result of the transformation of butanes are xylenes and toluene; benzene and C_9–C_{10} aromatic hydrocarbons have been detected in much smaller amounts[6]. Pentane gives rise to appreciable amounts of toluene and benzene and also to hydrocarbons with higher molecular weights such as naphthalene, indene, and other condensed compounds[7].

The dependence of the composition of the products of the reaction of isobutane on its contact time with 0.8% Pt/Al_2O_3 has been studied[6]. It follows from Fig.2 that, with increase of contact time, there is a sharp acceleration of the dehydrogenation process accompanied by the formation of butenes, whose amount passes through a definite maximum. The concentration of aromatic compounds in the reaction products increases more gradually. The yield of coke and cracking products increases approximately linearly with increasing contact time. Analysis of the shape of the curves describing the increase of the content of butenes and aromatic compounds led the author[6] to the conclusion that the dehydrocyclodimerisation of isobutane is a consecutive reaction on the assumption that butenes are intermediates in the formation of aromatic hydrocarbons. Rapid skeletal isomerisation was also noted. For longer contact times, the ratio isobutenes: :n-butene approaches the equilibrium value (0.73 at 560 °C). Special experiments showed[6] that the xylenes and ethylbenzene, formed as a result of the dehydrocyclodimerisation of isobutane, undero dealkylation with increase of contact time and are converted into toluene and benzene.

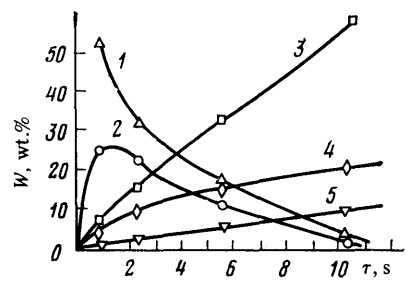


Figure 2. The influence of contact time on the composition of the isobutane dehydrocyclodimerisation products at 560 °C in the presence of 0.8% Pt/Al_2O_3: 1) C_4H_{10}; 2) the sum of C_4H_8 hydrocarbons; 3) the overall yield of C_1 and C_2 hydrocarbons; 4) the sum of aromatic hydrocarbons; 5) coke[6].

An important factor influencing the degree of dehydrocyclodimerisation of lower alkanes and the composition of the aromatic component of the catalytic reaction mixture is the acidity of the catalyst. The latter depends on many factors, including the nature and method of preparation of the carrier, the composition of the compound containing the active component, the method of its deposition, the presence of acid or alkaline additives, etc. Some of these parameters have been varied[6]. An increase of acidity tends to increase the yield of aromatic hydrocarbons.

In the presence of strongly acid catalysts isobutane and n-butane give rise to reaction products with a very similar composition of aromatic hydrocarbons. The latter is apparently due to the fact that the more acid catalyst promotes

the greatest approach of the composition of the initial mixture of isobutenes and n-butenes to the equilibrium composition under the reaction conditions. A definite dependence of the activity of the catalyst in the dehydrocyclodimerisation of isobutane on the acidity of the catalyst has been observed[6], a change in acidity being reflected in the isobutenes:n-butenes ratio in the reaction mixture. Furthermore, in the presence of weakly acid catalyst, n-butane gives rise mainly to ethylbenzene and styrene, while isobutane forms *p*-xylene. At the same time, in the presence of strongly acid catalysts both C_4 alkanes give rise to products with the same composition of the aromatic hydrocarbons.

Interesting data have been published[6] on the reactions of isobutane under dehydrocyclodimerisation conditions over three catalysts: Pt/Al_2O_3; $Pt/Al_2O_3 + Al_2O_3$; $Pt/Al_2O_3 + Al_2O_3 - SiO_2$. In the case of the last two catalysts, used in the form of a mechanical mixture of 0.8% Pt/Al_2O_3 and the "acid component", an appreciable (by a factor of ~2) increase of the yield of aromatic hydrocarbons and a clear decrease of the amount of the products of dehydrogenation of butenes and butadienes were observed.

Csicsery[9] put forward and tested the hypothesis that there is a definite relation between the acidity of the catalyst and its oligomerising activity. It was assumed that olefins are dimerised mainly on acid surface centres. To test this hypothesis, *trans*-but-2-ene was passed over various acid catalysts without a metal. In the presence of alumina and aluminosilicate the butene readily isomerised to a mixture of *cis*-but-2-ene and but-1-ene. A proportion of the butenes were converted into liquid products consisting of linear and cyclic oligomers and also of aromatic hydrocarbons. The concentration of the latter in the catalytic reaction mixtures was appreciably lower than in the presence of corresponding platinum-containing catalysts—Pt/Al_2O_3, and $Pt/Al_2O_3-SiO_2$.

Consequently catalysts not containing the hydrogenating–dehydrogenating component successfully initiate the aromatisation reactions of linear dimers, the disproportionation of polyalkylbenzenes, cracking reactions, etc. but nevertheless to an appreciably small extent than the corresponding metal-containing catalyst. The important role of the acidity of the catalyst has been demonstrated in the study of the reactions of *trans*-but-2-ene over aluminosilicate to which various alkali metals have been added. With increase of the concentration of sodium in the catalyst, the rates of dehydrocyclodimerisation, skeletal isomerisation of olefins, cracking, and coke formation appreciably decreases.

The degree of dehydrocyclodimerisation of butane decreases significantly when the initial hydrocarbon is diluted with hydrogen. It is apparently due to the appreciable acceleration of the hydrogenolysis; in the presence of Pt/Al_2O_3 at 560 °C up to 85% of the butene was converted into methane during the first 10 minutes of the experiment and the main bulk of the aromatic hydrocarbons were demethylated to benzene[6]. In the absence of hydrogen, an increase of the hydrocarbon pressure in the system in the range from 1 to 50 atm entailed an increase of the rate of dehydrocyclodimerisation of the alkane and to a lesser extent an increase of the rate of cracking. Since the dehydrocyclodimerisation of alkanes led to the evolution of a large amount of hydrogen (5 moles of H_2 for 2 moles of the alkane), it is recommended that the initial alkane be diluted with an inert gas.

The question of regeneration of the catalysts of the dehydrocyclo-oligomerisation of lower hydrocarbons has so far been inadequately elucidated. The relatively extensive coke formation on these catalysts necessitates regular and frequent regenerations. Compared with platinum catalysts, the oxide catalysts containing variable-valence elements are much more stable under the conditions of frequent regeneration. It is therefore useful to employ catalysts containing Group V–VII transition metal oxides, which can be usually repeatedly regenerated without significant loss of activity. Vanadium, molybdenum, chromium, tungsten, and manganese oxides deposited on alumina have been investigated[8]; the highest conversion of n-butane was observed in the presence of the first two oxides.

The influence of temperature on the degree of dehydrocyclodimerisation of n-butane in the presence of chromium oxide/alumina catalyst prepared by the method of Pines and Haag[26] has been studied[8], the experiments being performed in the range 490–593 °C. The highest yield of aromatic hydrocarbons was reached at 593 °C. With increase of temperature, an increase of the yields of methane, ethane, ethylene, and coke was noted. The maximum yield of aromatic hydrocarbons, evaluated taking into account the recirculation of the C_3-C_5 hydrocarbons, was observed at 250 °C.

As in the presence of metal-containing catalysts, the acidity of the carrier plays the major role in the case of oxide catalysts. A series of chromium oxide–potassium oxide/alumina catalysts (0.1 wt.% K) with different acid carriers have been studied in relation to the dehydrocyclodimerisation of n-butane[8]. The yield of aromatic hydrocarbons is higher in the presence of catalysts containing η-Al_2O_3 or fluorinated Al_2O_3 (on the latter, the yield of coke is minimal).

The dehydrocyclodimerisation of propane and isobutane on an industrial platinum/alumina catalyst and also the dehydrocyclodimerisation of propene in the presence of alumina specimens of different acidity have been studied in detail[20–25]. The behaviour of propane, propene, and isobutane in the presence of the platinum/alumina catalyst[21,22] and of propene and C_6 hydrocarbons on alumina[23,24], as well as the influence of pyridine and ammonia on the dehydrocyclodimerisation of propane and propene[21,23] have been investigated; finally, alumina specimens of different acidity have been studied by spectroscopic methods[23]. The results enabled the authors to put forward a series of well-founded hypotheses concerning the mechanism of the dehydrocyclodimerisation of propane in the presence of the platinum/alumina catalyst. In particular, it has been shown that, under pulsed conditions in the presence of an industrial platinum/alumina catalyst in the temperature range 560–620 °C, propane undergoes far-reaching transformations in cracking, dehydrogenation, and aromatisation reactions. Depending on the experimental conditions, the yield of aromatic hydrocarbons then amounts to between 0.4 and 17% relative to the propane passed through the system.

The results enabled the authors[21,22] to suggest that propene is an intermediate in the dehydrocyclodimerisation of propane to aromatic hydrocarbons. A similar behaviour has been noted in the reactions of isobutane. The role of olefins in the aromatisation of lower alkanes has been studied in greater detail in relation to the reactions of propene. It was found that in the presence of platinum/alumina catalysts, propene undergoes more far-reaching transformations than propane, particularly with formation of aromatic hydrocarbons.

The same workers[25] described catalytic reactions of the propane–butane fraction of the gas associated with petroleum in the presence of the platinum/alumina catalyst. The transformation of the propane–butane fraction is a complex process consisting of a series of consecutive-parallel reactions, the principal of which are dehydrogenation and cracking of propane and butanes. The olefins formed in the dehydrogenation process subsequently undergo oligomerisation with formation of C_6 and C_8 dimers. The formation of aromatic C_8 and C_9 hydrocarbons, in the first place benzene and toluene, takes place as a result of the C_6-dehydrocyclisation of linear oligomers with the corresponding composition and structure. At the same time benzene (and toluene) are formed as a

result of the demethylation of homologues with a higher molecular weight, as shown by the increase of the concentration of aromatic C_6–C_9 hydrocarbons with increase of temperature and contact time.

In order to elucidate the role of the carrier in the bifunctional platinum/alumina catalyst in the dehydrocyclodimerisation of propane, a study has been made[23,24] of the reactions of propene in the presence of halogenated and alumina not promoted with a halogen. Starting from 250 °C and up to 475 °C, propene dimerises and the concentration of C_6 olefins increases from 3.6 to 16.8%. In the range 520–620 °C propene undergoes far-reaching transformations on fluorinated alumina, the principal reaction being aromatisation.

With increase of the acidity of the catalyst in the sequence γ-Al_2O_3 < γ-Al_2O_3(Cl) < γ-Al_2O_3(F), the overall degree of conversion of propene increases and the yield of aromatic hydrocarbons also rises. In the presence of γ-Al_3O_3(F) isobutene undergoes far-reaching transformations under similar conditions, mainly with formation of aromatic C_8 hydrocarbons.

It has been shown by the pulsed poisoning of fluorinated alumina with ammonia or pyridine that both bases suppress the aromatisation of both propene and C_6 hydrocarbons. It was therefore postulated[23,24] that the dimerising, dehydrocyclising, and dehydrogenating functions of alumina are associated with its acidity. It has been suggested that the first, slowest stage of the conversion of propene is its dimerisation, which can take place on protic acid centres of the catalyst via the carbonium ion mechanism or with participation of Lewis centres via a radical mechanism. The subsequent reactions of the dimers are apparently much faster and involve the formation of five- and six-membered cyclo-olefins and aromatic hydrocarbons and also cracking.

The aromatisation of lower olefins over alumina, aluminosilicates, and activated carbon has been studied[27,28]. The results confirmed that the aromatisation of lower olefinic hydrocarbons is a complex process leading to the formation not only of aromatic hydrocarbons but also of gaseous and liquid aliphatic products and naphthenes. With increase of the number of carbon atoms in the olefin molecule, the degree of conversion of the initial hydrocarbon also increases and the content of aromatic hydrocarbons in the liquid catalytic reaction mixture rises.

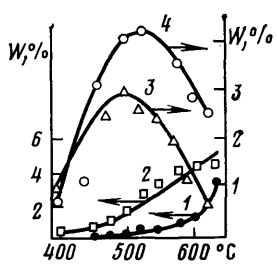


Figure 3. The influence of temperature on the yield of aromatic hydrocarbons W in the aromatisation of C_3H_6 in the presence of Al_2O_3.F: 1) C_6H_6; 2) $C_6H_5CH_3$; 3) aromatic C_9–C_{11} hydrocarbons; 4) xylenes[28].

The data obtained in the presence of fluorinated alumina are presented in Figs.3 and 4. It follows from the results that an increase of the temperature of the dehydrocyclodimerisation of propene and isobutene in the presence of alumina from 300° to 625 °C is accompanied by an increase of the degree of conversion of the initial olefins; aromatic hydrocarbons are formed appreciably only above 500 °C. The greatest selectivity in relation to aromatic hydrocarbons is reached at 550–625 °C. The increase of contact time is accompanied by an appreciable increase of the degree of conversion of the initial olefins but does not have an appreciable effect on the composition of the liquid reaction products and the selectivity of the reaction in relation to aromatisation.

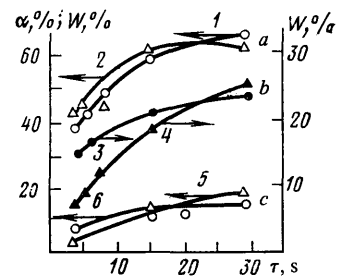


Figure 4. The influence of contact time on the aromatisation of C_3H_6 in the presence of Al_2O_3.F: *a*) the degree of conversion α of C_3H_6; *b*) the yield of aromatic hydrocarbons W relative to C_3H_6 which has reacted; *c*) the yield relative to the C_3H_6 passed through the system; 1), 3), and 5) 600 °C; 2), 4), and 6) 550 °C.[28]

It was noted above that in his study of the dehydrocyclodimerisation of butanes, Csicsery[6] suggested that the given reaction has a consecutive mechanism. In order to elucidate the role of olefins in the dehydrocyclodimerisation of alkanes, a study was therefore made[9] of the conversion of but-2-ene in the presence of the platinum/alumina catalyst. The higher degree of conversion of butene into aromatic hydrocarbons than for butane under similar conditions was established. The but-2-ene conversion products for short contact times proved to be mainly C_6–C_8 olefins and naphthenes. For longer contact times, a relatively larger amount of aromatic hydrocarbons and a much smaller amount of naphthenes were found in the reaction products. This change in the composition of the catalytic reaction mixture shows, according to the author[9], that the dehydrocyclodimerisation of butenes does indeed proceed via the initial formation of C_6–C_8 olefins and naphthenes.

In his treatment of the mechanism of the dehydrocyclodimerisation of butanes in the presence of bi- and polyfunctional catalysts, Csicsery[10] discusses a consecutive scheme consisting of the following stages: (1) dehydrogenation of alkanes to mono- and di-olefins; (2) dimerisation of olefins on acid centres; (3) aromatisation of unsaturated dimers; (4) isomerisation, transalkylation, and dealkylation of the aromatic hydrocarbons obtained initially with formation of a large number of C_8–C_{10} alkyl- and dialkyl-benzenes.

In order to refine the details of the first stage—the formation of olefinic and diolefinic hydrocarbons—experiments with butenes were carried out[9]. The rate of aromatisation of the latter proved to be 2–2.5 times higher than that of butane; the butene ⇌ butadiene equilibrium is established very rapidly; the cracking of butenes is slower and the rate of coke formation is appreciably higher than for butane. It has

been suggested that olefinic and diolefinic hydrocarbons are formed on dehydrogenating catalyst centres:

$$C_4H_{10} \xrightleftharpoons{-H_2} C_4H_8 \xrightleftharpoons{-H_2} C_4H_6 .$$

The second stage—catalytic dimerisation of unsaturated hydrocarbons—occurs mainly on the surface of acid centres on the carrier.

The mode of the third stage—aromatisation of dimerised olefins and diolefins—depends primarily on the experimental conditions and the catalyst. An increase of temperature accelerates the aromatisation of dimers and at the same time favours dealkylation. The latter is apparently responsible for the increase of the yield of benzene and toluene relative to C_9–C_{10} aromatic hydrocarbons. An increase of contact time leads to an increase of the yield of aromatic hydrocarbons compared with naphthenes. Under these conditions, an increase of contact time increases, like the increase of temperature, the contribution of the dealkylation reaction with formation of benzene and toluene. The dimers are aromatised much faster on the dehydrogenating catalyst centres than on the acid centres. However, the latter are also necessary, because, according to the author[9], five-membered naphthenes isomerise to six-membered naphthenes on such centres.

The fourth stage—isomerisation, transalkylation, and dealkylation of primary aromatic hydrocarbons—is accelerated, as noted above, by an increase of the reaction temperature, an increase of contact time, and finally by the acid catalyst centres. As a result of the reactions enumerated above, the n-butane catalytic reaction mixture contains the majority of the possible C_6–C_{10} aromatic hydrocarbons.

With increase of temperature, the cracking and coke forming reactions are accelerated simultaneously. The composition of the butene conversion products suggested[9] that C_3 and C_5 hydrocarbons are formed via the mechanism

$$2C_4H_8 \rightarrow C_8H_{16} \rightarrow C_5H_{10} + C_3H_6 .$$

Above 500 °C, direct cracking of butenes takes place with an appreciable yield:

$$C_4 \rightarrow CH_4 + C_3 \quad \text{or} \quad C_4 \rightarrow 2C_2 .$$

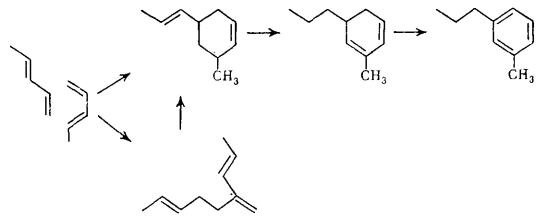
As a result, the following general mechanism has been suggested[10] for the conversion of butanes into aromatic hydrocarbons:

$$C_4H_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_4H_8 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C_8H_{16} \xrightarrow{k_3} C_6H_4(CH_3)_2 ,$$
$$\downarrow k_4 \qquad\qquad \downarrow k_5$$
$$C_3 + CH_4 \qquad\qquad C_3 + C_5$$

Depending on the rate constant ratios for the above reactions, one or other pathway predominates. It follows from the results that the best catalyst of the dehydrocyclodimerisation of alkanes should have the following properties[10]: (a) it should accelerate the dehydrogenation of alkanes more than the dimerisation of olefins on the acid component ($k_1 > k_2$); (b) it should lead to the aromatisation of the dimers on the dehydrogenating component being much faster than cracking and faster than the dimerisation of the acid component: $k_5 \ll k_3 \gg k_{-2}$; $k_3 > k_2$. The formation of dimers and trimers has also been noted[7] in the dehydrocyclodimerisation of n-pentane. The curve relating the yield of aromatic hydrocarbons to the number of carbon atoms has three maxima: for aromatic hydrocarbons containing 7, 10, and 15 carbon atoms (Fig.5).

The dehydrodimerisation of propene and butadiene over the MoO_3–SiO_2 and WO_3–SiO_2 catalysts has been described[29]. These catalysts exhibited a comparatively high activity in the aromatisation of propene. Thus the selectivity in relation to C_6–C_8 aromatic hydrocarbons reached 33% on the MoO_3–SiO_2 catalyst (treated with HCl) for a propene conversion of 71.4%.

The recently published studies[30,31] whose authors investigated the mechanism of dehydrocyclodimerisation and certain other reactions of piperylene in the presence of modified alumina are of undoubted interest. It was shown that piperylene is converted into n-pentenes as well as alkenylcyclohexenes, C_6–C_9 aromatic hydrocarbons and alkenyl and alkyl derivatives of aromatic C_{10} hydrocarbons on $Al_2O_3.K_2O$ at 500 °C:



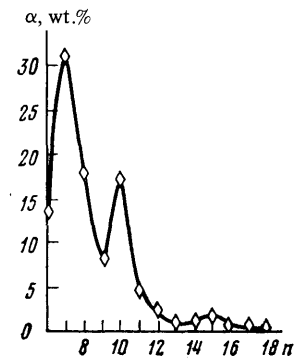


Figure 5. The proportions of aromatic hydrocarbons with different numbers of carbon atoms obtained in the dehydrocyclodimerisation of n-pentane on Pt/Al_2O_3 at 560 °C and for a space velocity of 1.1 h^{-1} (Csicsery[7]); a = overall degree of aromatisation; n = number of carbon atoms in aromatic hydrocarbons.

The activities and selectivities of various oxide catalysts in the dehydrocyclodimerisation of isobutene to *p*-xylene in the non-oxidative version of the reaction have been studied in greatest detail by Japanese workers. Thus the influence of the carrier on the kinetics and mechanism of the vapour-phase dehydrocyclodimerisation of isobutene to xylene over vanadium pentoxide has been studied[32]:

$$2CH_2{=}C\begin{matrix}CH_3\\CH_3\end{matrix} \rightarrow CH_3{-}C_6H_4{-}CH_3 + 3H_2 .$$

In the range 600–800 K at atmospheric pressure the equilibrium constant of this reaction is 4.0–5.4, which corresponds to the equilibrium isobutene conversion in the range 97–100%, i.e. as stated above, the reaction is not limited by the thermodynamic equilibrium.

Together with V_2O_5, the following metal oxides have been used as the active phase: Cr_2O_3, MoO_3, Fe_2O_3, WO_3, and Nb_2O_5 deposited on Al_2O_3 in the atomic proportions M : Al ≅

1 : 19, where M is the metal. Apart from Al_2O_3, the carriers used consisted of SiO_2, Ti_2O_3, MgO, and activated carbon. Data concerning the influence of the nature of the carrier on the catalytic properties of various vanadium oxide catalysts in the dehydrocyclodimerisation of isobutene are presented in Table 1. The V_2O_5/Al_2O_3 catalyst showed the greatest activity under these conditions (at 550 °C the yield of xylene was 27.4% for a selectivity of 54.5%).

Table 1. The influence of the nature of the carrier on the activity and selectivity of vanadium oxide catalysts[32].

Carrier	Conversion, %	Selectivity, %			Yield, %	
		toluene	*p*-xylene	*m*-xylene	iso-octane	n-butane
Al_2O_3 *	49.4	3.2	22.7	31.8	12.0	4.8
SiO_2	25.1	4.0	53.4	5.2	6.5	3.5
MgO	10.8	—	73.2	—	3.0	0.8
Carbon	44.7	2.9	36.9	traces	18.8	—
TiO_2	—	—	—	—	—	—

*Selectivity with respect to benzene 0.6%; yield of *o*-xylene—traces.

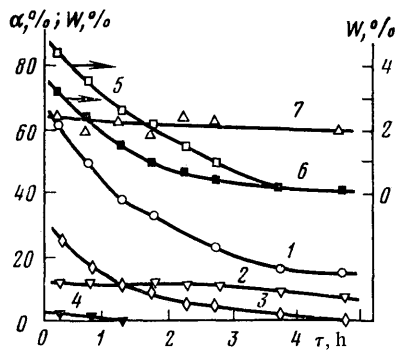


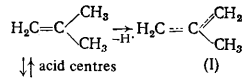
Figure 6. Variation of the degree of conversion α of isobutene (curve *1*) and the yields *W* of *p*-xylene (curve *2*), *m*-xylene (curve *3*), *o*-xylene (curve *4*), but-2-ene (curve *5*), and but-1-ene (curve *6*) as well as the selectivity in the formation of xylenes (curve *7*) in the presence of the V_2O_5/Al_2O_3 catalyst at 550 °C as a function of the duration of the experiment[32].

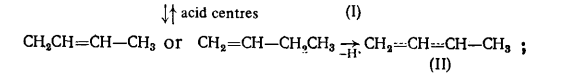
It was established that the catalytic properties of the V_2O_5/Al_2O_3 catalyst change rapidly with time (Fig.6). Thus the *m*- and *o*-xylenes formed in the first hours of the test subsequently disappear and *p*-xylene remains the dominant isomer. The yield of n-butene, formed as a result of the isomerisation of isobutene, also decreases similarly with time, the selectivity of the aromatisation remaining at the same level. Completely different results were obtained in a test of the V_2O_5/MgO catalyst: during the first two hours, the selectivity of the formation of xylene increases from 40 to 75% and remains subsequently at a constant level, the degree of conversion varying only slightly with time and remaining at the level of 10–15%. Skeletal isomerisation does not occur over the catalyst and the only reaction product is *p*-xylene.

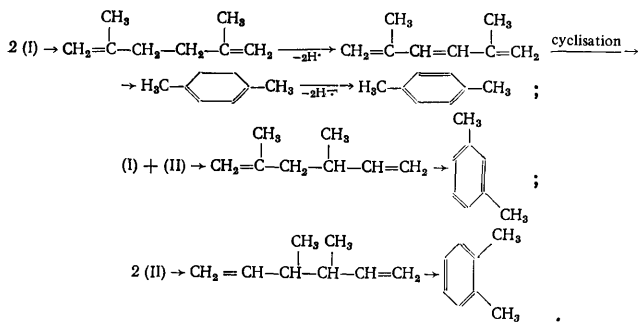
The study of the above oxide carriers for V_2O_5 made it possible to divide them into three groups: (a) aluminium and silicon oxides on which all the xylenes as well as small amounts of benzene and toluene are formed; (b) magnesium oxide and activated charcoal on which only *p*-xylene is formed; (c) titanium dioxide on which an inactive catalyst is obtained.

The virtual absence of the isomerisation of xylenes on the V_2O_5/Al_2O_3 specimens shows that *m*- and *o*-xylenes are not formed as a result of the reactions of *p*-xylene but apparently arise from a parallel reaction involving the isomerisation of isobutene to n-butene and the subsequent dehydrocyclodimerisation of the latter.

A mechanism of the dehydrocyclodimerisation of isobutene has been proposed[32], according to which *p*-xylene is formed via 2,5-dimethylhexa-1,5-diene on V^{3+} centres without the involvement of acid centres; at the same time *m*- and *o*-xylenes are formed on acid centres via 2,4- and 3,4-dimethylhexa-1,5-dienes:







The formation of 2,5-dimethylhexa-1,5-diene and *p*-xylene has been established experimentally. It has been suggested that the intermediates in the formation of *m*- and *o*-xylenes are 2-methylhepta-1,5-diene and octa-2,6-diene. It has been found that in the presence of V_2O_5/MgO the kinetic order of the reaction involving the formation of *p*-xylene is 1.1 with respect to the initial isobutene; the activation energy is 31.4 kJ mol^{-1}. It has been suggested that the rate-limiting stage in the formation of *p*-xylene is apparently the interaction of two adsorbed isobutyl radicals (I).

III. DEHYDROCYCLOTRIMERISATION OF ETHYLENE AND ETHANE TO BENZENE AND OTHER AROMATIC HYDROCARBONS

Together with the dehydrocyclodimerisation of C_3–C_5 olefins and alkanes, the catalytic dehydrocyclotrimerisation of ethylene and ethane with formation of benzene and other aromatic hydrocarbons[11–15,33–35], which has been described comparatively recently, is of undoubted interest. It was shown initially[11,12] that the cyclotrimerisation of ethylene takes place successfully in the presence of Pt/Al_2O_3 in the range 500–670 °C. Subsequently, in the study of catalysts containing other Group VIII metals it was observed that rhodium, ruthenium, iridium, and palladium deposited on alumina (0.5–0.6% of the metal) also catalyse this reaction successfully. In contrast to Pt/Al_2O_3, the cyclotrimerisation of ethylene on these catalysts proceeds at lower temperatures

with appearance of benzene in the reaction products in the presence of the Ru–Ir catalysts already at 450 °C and at 350 °C in the presence of the Rh catalyst.

Thermodynamic calculation showed that the cyclo-oligomerisation of lower olefins, including ethylene, can occur over a fairly wide temperature range[12]. Indeed the equilibrium in the ethylene–benzene system in the range from room temperature to 700 °C and above is almost entirely displaced towards the formation of benzene. Here one should note that the content of benzene in the equilibrium mixture decreases somewhat with increase of temperature. The dehydrocyclo-oligomerisation of other lower hydrocarbons is also thermodynamically feasible over a wide temperature range. Indeed the thermodynamic equilibrium in propene–benzene mixtures at 150–700 °C and in propane–benzene mixtures at 450–700 °C is appreciably displaced towards the formation of benzene. Thus, in the above temperature ranges, the cyclotrimerisation of ethylene as well as the cyclodimerisation of propene and propane are thermodynamically favourable. As regards ethane, its actual aromatisation requires a temperature of ~500 °C. The possibility of the aromatisation of ethane in the presence of platinum and palladium catalysts was demonstrated experimentally by the present author[35].

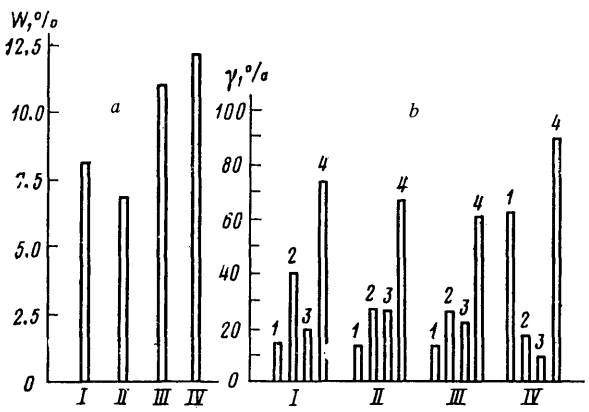


Figure 7. Comparison of the yields (*a*) and selectivities (*b*) in the formation of aromatic hydrocarbons in the presence of a series of catalysts [I) Al_2O_3.F; II) Ru/Al_2O_3.F; III) Pt/Al_2O_3 (AP-56); IV) Rh/Al_2D_3.F] in the cyclotrimerisation of ethylene: 1) benzene; 2) toluene; 3) xylenes; 4) the sum of aromatic C_6–C_8 hydrocarbons; W = overall yield of catalytic reaction products relative to C_2H_4 passed through the system; γ = fraction of aromatic hydrocarbons in the catalytic reaction mixture.

In the course of the study of the cyclotrimerisation of ethylene by a pulsed microcatalytic method platinum/alumina catalysts modified in different ways have been studied in greatest detail[12]. The specimen treated with nitric acid in the course of its preparation proved to be a relatively more active and "low-temperature" catalyst. The yield of aromatic hydrocarbons in its presence reached 9–11% relative to the ethylene passed through the system and 10–14% relative to the ethylene which has reacted. As mentioned above, other Group VIII metals deposited on alumina also exhibited a catalytic activity in the above reaction. The results obtained in the presence of rhodium, ruthenium, and iridium catalysts have been published by Bragin et al.[33] In the course of the application of the first three–four ethylene pulses an increase of the activity of the catalyst was observed; after a definite initiation period the catalytic activity remained close to the maximum in the course of several pulses and then gradually fell.

It has been shown[33,35] that in the presence of M/Al_2O_3 (M = Pt, Ru, Pd, or Ir) catalysts not only ethylene but also ethane undergoes dehydrocyclotrimerisation in the range 550–650 °C with formation of benzene and its homologues. However, the reaction proceeds with somewhat lower degrees of conversion than for ethylene.

The above data refer to the study of the cyclotrimerisation of ethylene under pulsed conditions. Catalysts exhibiting a comparatively high activity and selectivity have also been studied under the conditions of a flow system. Fig.7 presents data[14] referring to the most interesting metal/alumina catalysts. In terms of activity and selectivity, the rhodium- and platinum-containing catalysts proved to be the most effective. The yield of aromatic hydrocarbons in the flow system relative to reacted ethylene reached 18–22%. The presence of C_3–C_6 olefins in the catalytic reaction mixture is striking. It is noteworthy that, in the presence of the rhodium catalyst, cyclotrimerisation takes place at a temperature lower by 80–100 K than on other catalysts; the Rh/Al_2O_3 catalyst has yet another important quality—it exhibits the highest selectivity with respect to the formation of benzene.

It follows from the results of Bragin et al.[14] that in the presence of the 0.6% Rh/Al_2O_3 catalyst the benzene content in the catalytic reaction mixture was 63% and the sum of C_6–C_8 aromatic hydrocarbons was 91%. Specimens with another rhodium content are somewhat less active and are less selective by a factor of 1.5 with respect to the formation of benzene. Nevertheless they are 3–8 times more selective than other metal/alumina systems and Al_2O_3 itself. The distinctive properties of rhodium catalysts discussed above are apparently primarily related to the catalytic properties of rhodium itself, because it is well known that rhodium-containing catalysts are widely used for the demethylation of alkylbenzenes to benzene.

A rhodium/alumina catalyst with a relatively high catalytic activity has been studied by X-ray photoelectron spectroscopy[13]. The state of the metal in the Rh/Al_2O_3 specimen containing 3.5 wt.% of rhodium was investigated as a function of the conditions of the preliminary treatment and the catalytic reaction. It was established that the spectroscopic characteristics of rhodium in the initial non-reduced specimens and in catalysts after oxidative regeneration correspond to the Rh^{3+} state. In the latter case line broadening was observed, which apparently indicates a stronger interaction of rhodium with the carrier.

When the catalyst is treated with hydrogen and also in a hydrocarbon medium, Rh^{3+} is almost completely reduced to zerovalent rhodium. This transition is accompanied by a shift of the spectrum towards lower energies by 3 eV. It has also been noted that the spectrum of reduced rhodium is somewhat broadened compared with that of metallic foil. An important factor is the positive charge observed in the Rh–Al_2O_3 system, appearing when the catalyst interacts with ethylene and its reaction products. It was noted that, under the influence of the reaction medium, the rhodium catalyst is activated in the dehydrocyclotrimerisation of ethylene and that the electronic state of rhodium is then altered. In the course of the activation of the catalyst a positive charge arises on the Rh clusters (formally rhodium passes to the +1 oxidation state); the subsequent decrease of the catalytic activity is accompanied by the return of rhodium to a nearly zerovalent state.

Comparison of the results presented above with the literature data suggested that under certain conditions ethylene can be converted into aromatic hydrocarbons not only in the presence of metal/alumina catalysts but also on alumina itself. Indeed experimental data[33] confirmed this hypothesis. Experiments performed on different γ-Al_2O_3 specimens with different specific activities and also on specimens with and without halogen showed that the cyclotrimerisation of ethylene takes place successfully in the range 500–650 °C. The yield of aromatic hydrocarbons on catalysts with a high acidity is then appreciably higher, which is consistent with the results of a study[23] devoted to the aromatisation of propene in the presence of alumina. Apart from aromatic hydrocarbons, considerable amounts (>25%) of unsaturated aliphatic C_3–C_6 hydrocarbons were detected in the ethylene catalytic reaction mixture. This finding is important for the understanding of the mechanism of the cyclo-oligomerisation of ethylene in the presence of alumina and the above metal oxide catalysts. Studies performed with different alumina specimens free from metal showed that, under the conditions of a flow system, the best results are obtained at 550 °C in the presence of the γ-Al_2O_3 specimen containing 3.4% of fluorine and having a specific surface of 180 $m^2\ g^{-1}$.[33]

The problems of the stability and regeneration of catalysts of the cyclotrimerisation of ethylene merit special attention. An attempt has been made[14] to obtain certain data on the stability of catalysts in a flow system and to determine the conditions for their regeneration. It has been observed that treatment of the catalyst with air for 2 h at 400–450 °C restores its initial activity and selectivity. The catalyst treated periodically in this way after being used for 4–5 h retains its initial activity in the course of 20–30 h. However, it was noted that not all the catalysts investigated are sufficiently stable. Thus the Rh/Al_2O_3 and Pt/Al_2O_3 catalysts are the most stable, while Al_2O_3 itself and Ru/Al_2O_3 are much less stable and somewhat less active after regeneration. The mechanism of the regeneration of catalysts of the cyclotrimerisation of ethylene is so far obscure, but, in conformity with the literature[14,36], one can assume that the regeneration of the metal/alumina catalysts with air consists in burning off and removing from their active surfaces carbon deposits formed on the catalyst in contact with ethylene at 450–550 °C. However, one cannot rule out the possibility that the regeneration of the metal oxide catalyst with air is also associated with a change in the valence state of the active metallic phase.

The mechanism of the formation of aromatic hydrocarbons from ethylene is apparently fairly complex. One of the possible variants is a two-dimensional termolecular reaction on the surface of the catalyst in which a single benzene molecule is formed from three ethylene molecules. An alternative pathway is one in which the formation of aromatic hydrocarbons is preceded by a series of preliminary stages and the cyclotrimerisation reaction is a complex consecutive process. The final answer to these questions is as yet impossible, although the results obtained already constitute definite evidence in support of the second pathway.

The first indication of the course of the reaction is provided by the set of products, indicated above, formed as a result of the cyclotrimerisation of ethylene. Virtually all the catalytic reaction mixtures contain propene and C_4–C_6 aliphatic hydrocarbons; the amount of the latter increases with temperature and with increase of contact time, which is particularly notable on passing from a pulsed to a flow system. Special series of experiments with the initial propene showed that propene is one of the possible intermediates in the aromatisation of ethylene. The yield of aromatic hydrocarbons increased by a factor of ~1.5 when ethylene was replaced by propene[12]. A still more distinctive picture was obtained in a study of the cyclo-oligomerisation of ethylene–butene mixtures (Fig.8) containing 0, 12.5, 25, 50, and 100% of butene in the presence of platinum on fluorinated alumina as the catalyst.

Fig.8 shows that initially the yield of aromatic hydrocarbons, in the first place benzene and toluene, increases appreciable when ethylene is partly replaced by butene, which shows that the formation of butene is apparently an intermediate stage in the cyclotrimerisation of ethylene. The extremum in the dependence of the yields of benzene and toluene on the composition of the reacting gas is consistent with this hypothesis. Presumably, when butene greatly predominates in the initial gaseous mixture, it is converted mainly into xylenes and hydrocarbons with higher molecular weights.

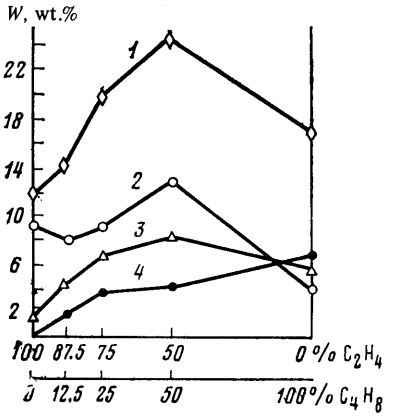


Figure 8. The results of the dehydrocyclo-oligomerisation of ethylene, butene, and their mixtures in the presence of 0.6% Pt/Al_2O_3.F at 559 °C: 1) the overall yield W of aromatic C_6–C_8 hydrocarbons; 2) benzene; 3) toluene; 4) xylenes.

Thus the results support the hypothesis of the preliminary linear oligomerisation of ethylene with formation of C_6 and higher fragments, which is followed by their cyclisation and aromatisation. The proposed mechanism of the cyclotrimerisation of ethylene is also supported by the results obtained independently in a study of the interaction of hydrocarbons with different structures on the surface of fluorinated Al_2O_3 with the aid of diffuse reflectance spectra[37]. Al_2O_3.F, which the present author used previously both as an independent catalyst and as a carrier for various metal/alumina catalysts (M = Pt, Rh, and others) in the cyclotrimerisation of ethylene, was applied. The nature of the spectra and particularly the appearance of a band in the region of 354 nm lead to the hypothesis that surface compounds with conjugated double bonds are formed on alumina. This hypothesis is consistent with the dimerisation of lower olefins on the Al_2O_3 surface with simultaneous evolution of hydrogen known from the literature[38]. These data can be accounted for by the formation of a linear dienyl carbonium ion on the surface; for example, in the case of propene we have

$$H_2C=CH-CH_3 + CH_3-CH=CH_2 \rightarrow H_2C=CH-\overset{+}{C}H-CH_2-CH= = CH_2 + \overline{H} + H_2 .$$

The above results permit the conclusion that linear and cyclic oligomerisation of lower olefins, preceding their aromatisation, take place on the surface of Al_2O_3 and even

more so on metal/alumina catalysts. According to this concept, one can assume that the cyclotrimerisation of ethylene consists of a series of consecutive reactions; one of these is the formation of butene and also propene, which undergo oligomerisation, codimerisation, C_5- and C_6-cyclisation, cracking, disproportionation, etc. At the same time one must emphasise that all the above evidence in support of the consecutive ethylene cyclotrimerisation mechanism does not rule out other reaction pathways which apparently make a smaller contribution to the overall ethylene aromatisation process under the conditions which we investigated. The C_6-dehydrocyclisation of long-chain ethylene oligomers formed in the course of the reaction as well as the termolecular catalytic formation of benzene from ethylene, already mentioned above, may be indicated as possible parallel pathways.

Depending on the experimental conditions (and in the first place on the catalyst used), the benzene and its homologues formed in the cyclotrimerisation of ethylene can undergo further reactions For example, a proportion of the toluene and xylenes detected in the catalytic reaction mixture are obtained by the methylation of benzene. The latter can be obtained in its turn by the catalytic demethylation of toluene and xylenes. This possibility has been tested[13] in relation to the platinum and rhodium catalysts as well as Al_2O_3.F and has been confirmed experimentally.

At the same time one can put forward certain considerations also concerning cyclotrimerisation catalysts. As shown above, metal/alumina catalysts, and in the first place those containing platinum and rhodium, proved to be the most effective. The results obtained, and particularly the occurrence of cyclotrimerisation on the surface of alumina itself, indicate a significant influence of the carrier on specific stages of the reaction. Indeed, on the basis of studies of both catalytic and spectroscopic properties of Al_2O_3, one can postulate that the dimerisation and oligomerisation of lower olefins proceed mainly on the acid centres of alumina. These centres are apparently responsible for isomerisation, polymerisation, and also may be partially responsible for coke formation.

Table 2. The results of the conversion of propene on various metal phosphate catalysts.[41]

Catalyst	Conversion of propene (%) with formation of different products		
	CO_2	C_3H_4O	C_6H_6
$Ca_3(PO_4)_2$	17.1	0	0
$CrPO_4$	5.2	0	0
$FePO_4$	31.9	8.5	0
$Co_3(PO_4)_2$	4.8	0	0
$Ni_3(PO_4)_2$	1.7	0.2	0
$Cu_3(PO_4)_2$	39.6	5.1	0
$Zn_3(PO_4)_2$	4.6	0.2	0
$CePO_4$	2.5	0.4	0
$BiPO_4$*	51.0	5.7	23.1
$BiPO_4$**	19.3	19.2	4.5
$2Bi_2O_3 \cdot P_2O_5$	45.0	0	35.4

*Obtained at a high temperature.
**A type of monazite.

It is known that, when fluorine is introduced into Al_2O_3, the catalytic activity of the latter increases in a whole series of reactions, which is as a rule attributed to the appearance of strong protic centres on the Al_2O_3 surface[39]. It is also known that Al_2O_3 (particularly "acid" alumina) exhibits an appreciable catalytic activity in the cyclisation of olefins and dienes with formation of the corresponding cyclanes and cyclenes. Furthermore, Al_2O_3 is also a dehydrogenating agent albeit a relatively weak one. The dehydrogenation reaction on Al_2O_3 is apparently associated with its aprotic centres, capable of abstracting H atoms from the hydrocarbon molecule. The trienes formed as a result of the consecutive dehydrogenation can then undergo further thermal cyclisation.

At the same time the main dehydrogenating component in the metal/alumina catalysts used is undoubtedly the metal and in the first place platinum. Evidently vigorous dehydrogenation of olefins to dienes and of cyclenes to aromatic hydrocarbons respectively takes place on metallic centres. Furthermore, the metallic centres of the catalyst promote a more far-reaching and more selective dehydrocyclisation. The introduction of a metal (platinum and particularly rhodium) into the catalyst increases the hydrocracking properties of the latter. This is apparently the reason (the formation of smaller "fragments" from aliphatic compounds and dealkylation of alkyl- and polyalkyl-benzenes among aromatic hydrocarbons) why the selectivity of the reaction with respect to the formation of benzene and toluene increases appreciably.

IV. OXIDATIVE DEHYDROCYCLODIMERISATION OF LOWER OLEFINS AND ALKANES

This section deals with the second type of dehydroaromatisation of lower olefins and alkanes—the oxidative version with participation of atmospheric oxygen or oxygen forming part of the catalyst. Various compounds, particularly bismuth phosphate, arsenate, and antimonate, as well as the binary mixture of the oxides Bi_2O_3 and SnO_2 are used as catalysts of the oxidative dehydroaromatisation of olefins in the presence of oxygen[40-42]. Instead of the last oxide, one can also use magnesium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, zirconium, niobium, silver, silicon, or lead oxides[41,43]. Alkali metal compounds in the form of oxides, hydroxides, or weak acid salts are used as promoting agents. The above oxides can also be employed as deposited catalysts on alumina, carborundum, silica, pumice, graphite, etc. as carriers.

Oxygen-containing and aromatic compounds are formed in the oxidative catalytic dehydroaromatisation of olefins with participation of oxygen in the range 300–600 °C. Propene is then converted into acrolein and benzene; this is accompanied by the formation of CO_2 as well as small amounts of CO, acetaldehyde, and hexa-1,5-diene. Butene gives rise to 2,5-dimethylhexa-1,5-diene, CO, and CO_2; isobutene and butadiene are converted mainly into *p*-xylene.

The oxidative dehydrodimerisation and aromatisation reactions have been used successfully not only in reactions involving olefins but also in those with their functional derivatives, particularly halogenoalkanes, unsaturated amines, cyanides, and alcohols[44]. The reactions can occur in both oxidising and reducing media. The process is usually carried out in a reducing medium when the required products are olefin dimers. We may note that, with increase of the partial pressure of oxygen in the mixture of reacting compounds, the selectivity in the formation of linear and cyclic olefin dimers is appreciably reduced.

The dehydroaromatisation of propene has been studied[41] in the presence of various metal phosphates. Table 2 presents the results of these experiments carried out at 500 °C with a mixture of 9% of propene 18% of oxygen. It is seen from the data in Table 2 that the activities of various phosphates differ markedly. The highest degrees of conversion of propene were achieved in the presence of Bi^{3+} ions. The maximum

yield of aromatic hydrocarbons was reached for the Bi:P = 2:1 ratio; at 500 °C and for the oxygen:propene ≅ 2:1 ratio, ~36% of propene is converted into benzene.

Different temperatures and catalysts apparently have different effects on the selectivity of the reaction. Thus at 300–450 °C in the presence of bismuth arsenate and basic bismuth sulphate, propene gives rise mainly to acrolein while in the range 400–550 °C benzene predominates. Bismuth phosphate, arsenate, and antimonate as well as bismuth titanate and sulphate exhibit a relatively high selectivity with respect to the formation of benzene, while bismuth molybdate is more selective in the reaction involving the conversion of propene into acrolein.

The influence of basic promoting agents on the catalytic properties of tin oxide is significant in the oxidative dehydroaromatisation of propene. Thus oxides with basic properties increase the yield of benzene, while modification of the catalysts by acid oxides favours the formation of acrolein with a simultaneous decrease of the overall activity. The influence of various oxide additives on the catalytic activity of tin oxide in the oxidative dehydroaromatisation of propene at 550 °C has been studied[41].

The study of binary oxide systems such as $Bi_2O_3 + P_2O_5$, $Bi_2O_3 + As_2O_5$, and $Bi_2O_3 + TiO_2$ showed[41] that weakly acid catalysts promote the formation of benzene, while strongly acid catalysts promote the formation of acrolein. The latter include, for example, bismuth molybdate. The following mechanism of the aromatisation of propene has been proposed for the bismuth phosphate catalytic system[40]:

$$2CH_3{=}CH{-}CH_3 \xrightarrow[-2H]{} \underset{(A)}{2CH_2{=}CH{-}CH_2} \xrightarrow[-4H]{} C_6H_6 ,$$

where (A) is an intermediate π-allyl complex. This mechanism is consistent with data[45–47] according to which acrolein and hexa-1,5-diene are also formed (from propene on the acid Bi–P catalyst, Cu_2O, and Ag) via an intermediate π-allyl complex adsorbed on the surfaces of the above catalyst.

The oxidative dehydroaromatisation and dimerisation of propene have also been investigated in other studies[48,49]. The conditions for the dimerisation and aromatisation of propene and isobutene in the presence of the In_2O_3/pumice catalyst in the range 440–550 °C have been described[48] and it has been shown[49] that the dehydrodimerisation of propene to diallyl on lead oxides depends on the composition of the reaction mixture and takes place in a reducing medium. In a reducing medium lead oxides are unstable and they are reduced during the period of the experiment. The reduction of the oxide has a positive effect on the process selectivity. The highest selectivity is shown by the catalyst consisting of PbO and metallic lead in the stationary state.

The metal oxides investigated in the oxidation reactions of lower olefins have been divided[43,50] into four conventional groups. They are represented below by series with decreasing activities:

(1) oxides favouring the formation of acrolein:

$$MoO_3 > Sb_2O_3 > V_2O_5 > TiO_2 = Fe_2O_3 > SiO_2 > WO_3, Al_2O_3;$$

(2) oxides favouring the formation of benzene or hexa-1,5-diene:

$$ZnO > Bi_2O_3 > In_2O_3 > SnO_2 > CdO;$$

(3) oxides favouring the formation of CO_2:

$$CuO = Co_3O_4 > NiO > Cr_2O_3 > MnO_2 = GeO_2;$$

(4) oxides weakly favouring the formation of CO_2:

$$CaO, MgO\ GeO_2, PbO_4, Te_2O_3.$$

Within the framework of this classification, it was noted that the majority of the oxides of the first and second groups are *n*-type semiconductors, while those in the third group are *p*-type semiconductors.

The $Bi_2O_3–Al_2O_3$ catalyst mainly promotes the linear dimerisation of propene and isobutene at 540 °C; the addition of $Cr_2O_3–Al_2O_3$ to the above catalyst promotes the dehydrocyclisation of the dimers formed initially, giving rise to aromatic hydrocarbons. The oxidative dehydrocyclodimerisation of propene to benzene on the following catalysts has also been described: $Bi_2O_3–ZnO$, $Bi_2O_3–WO_3$, and $Bi(SnO_3)_3$. It was assumed[43] that hexa-1,5-diene and cyclohexa-1,3-diene are intermediates in the reaction.

Trimm and coworkers[51–53] described the reactions of propene and isobutene in the presence of indium and thallium oxides. In the presence of the above catalysts, propene is converted into acrolein, hexa-1,5-diene, benzene, and carbon dioxide, while methacroleine, 2,5-dimethylhexa-1,5-diene, *p*-xylene, benzene, toluene, traces of *o*- and *m*-xylenes, and carbon dioxide are formed from isobutene. According to the authors[51–53], benzene and toluene are secondary xylene conversion products. The selectivity in the formation of aromatic hydrocarbons hardly changed with increase of temperature from 480° to 530 °C; at the same time the selectivity in the formation of 2,5-dimethylhexa-1,5-diene increased appreciably under these conditions. The yield of aromatic hydrocarbons can be increased by modifying the catalysts with indium and thallium oxides (already mentioned) or by cyclising the diene formed initially in an additional reactor in the presence of a dehydrocyclising catalyst, for example, chromium oxide.

The study of the reactions of propene and isobutene in the presence of indium oxide in the range 420–500 °C for different ratios of the initial olefin and oxygen showed[52,53] that the proportions of the reaction products depend significantly on the ratio of the hydrocarbon and oxygen. The maximum yield of benzene and hexadiene from propene is attained for the molar ratio $O_2 : C_3H_6 \cong 0.2–0.3$. It has been suggested that hexa-1,5-diene can be formed both on the catalyst surface and in the gas phase at a higher temperature. It has been shown that acrolein and hexadiene inhibit the dehydrocyclodimerisation reaction, while benzene does not have an appreciable influence on the reactions of propene. These findings support the view that the adsorption of propene, acrolein, and hexadiene apparently takes place on centres of the same type, while the dehydrocyclisation of hexadiene to benzene occurs on centres of another type[54]. It has been shown[52,53] that the toluene and benzene formed in the reaction of isobutene are the products of the subsequent transformations of dimethylhexadiene and *p*-xylene. The kinetics of the formation of diene and *p*-xylene in the range 460° to 495 °C have been investigated and virtually identical activation energies, amounting to 126–130 kJ mol^{-1}, have been obtained.

It has been established experimentally[52] that hexadiene and acrolein are the primary reaction products in the formation of benzene and carbon dioxide respectively from propene. According to the authors[52], the above reactions can be described overall by the following stoichiometric equations:

$$2CH_3{-}CH{=}CH_2 + 1/2O_2 \rightarrow CH_2{=}CHCH_2CH_2CH{=}CH_2 + H_2O,$$
$$CH_2{=}CHCH_2CH_2CH{=}CH_2 + O_2 \rightarrow C_6H_6 + 2H_2O,$$
$$CH_3CH{=}CH_2 + O_2 \rightarrow CH_2{=}CH{-}CHO + H_2O.$$

The oxidative dehydrodimerisation of isobutene in the presence of indium oxide proceeds, according to Parera and Trimm[53], with formation of an intermediate π-allyl complex, which dimerises to a diolefin with subsequent cyclisation and aromatisation.

The oxidative dimerisation of propene in the presence of bismuth oxide without the supply of oxygen to the reaction mixture has been studied[55]. The starting materials was a mixture of propene and nitrogen in molar proportions of 2 : 1 at an experimental temperature of 475–560 °C. An increase of temperature entails a decrease of selectivity with respect to hexa-1,5-diene and an increase of selectivity with respect to benzene and CO_2. The hypothetical pathways leading to the formation of hexa-1,5-diene and acrolein from propene have been studied using bismuth oxide and molybdate as oxidants[56]. The authors concluded that bismuth oxide forms surface complexes with propene, which then decompose to hexa-1,5-diene and bismuth compounds.

It has been suggested[55] that propene interacts directly with the oxygen of the crystal lattice of the oxide with formation of water and the reduction of the oxide to the metal. The overall equation is as follows:

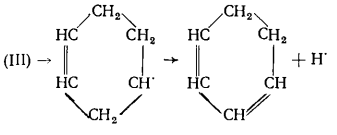
$$2CH_2=CHCH_3+1/2O_2\rightarrow CH_2=CHCH_2CH_2CH=CH_2+H_2O$$

or

$$6C_3H_6\,(g)+Bi_2O_3\rightarrow 3C_6H_{10}\,(g)+2Bi\,(s)+3H_2O\,(g)\,.$$

According to the authors[55], the first stage consists in the formation of a C_3 allyl radical, which then interacts with the oxygen of the lattice after being adsorbed; the subsequent stage involving the dehydrocyclisation of hexa-1,5-diene to cyclodiene takes place with formation of C_6 radicals, which exists in forms (III) and (IV):

$$\underset{\text{(III)}}{CH_2=CH-CH_2-\dot{C}H-CH=CH_2} \rightleftarrows \underset{\text{(IV)}}{\dot{C}H_2-CH=CHCH_2CH=CH_2}\ ;$$



An alternative pathway leading to the formation of hexa-1,5-diene was studied at the same time, taking into account the possibility of the formation of allyl radicals in the pyrolysis of propene. Here two variants are possible (a) the interaction of two allyl radicals on the surface or in the gas phase with formation of hexa-1,5-diene ($2CH_2=CH-\dot{C}H_2 \rightarrow CH_2=CH-CH_2CH_2CH=CH_2$) and (b) the interaction of the allyl radical with propene involving the loss of hydrogen and formation of n-hexenyl or isohexenyl radicals, which then cyclise to methylcyclopentene:

$$CH_2=CH-\dot{C}H_2+CH_2=CH-CH_3\rightarrow\begin{cases}\rightarrow CH_2=CH-CH_2-CH_2-\dot{C}H-CH_3\\ \rightarrow CH_2=CH-CH_2-\underset{CH_3}{CH}-\dot{C}H_2\end{cases}.$$

Analysis of the reaction products enabled the authors[55] to exclude the latter variant of the formation of hexa-1,5-diene, where the allyl radicals adds directly to the propene.

The catalysts of the oxidative dehydroaromatisation of lower olefins (bismuth phosphates) have been studied by X-ray diffraction after their reduction by propene.[57] The main propene reaction products on these catalysts are the same as for the reaction of propene in the presence of oxygen; benzene was obtained in a yield of ~20%. The study of the catalysts showed that after reduction the specimens consist of a mixture of metallic bismuth and bismuth phosphate ($BiPO_4$).

The oxidative dehydrodimerisation and aromatisation of propene in the presence of the individual oxides SnO_2 and Bi_2O_3 as well as the binary oxide system SnO_2–Bi_2O_3 have been recently described[58,59]. The experiments were performed in the absence of oxygen from the gas phase and the oxidative reactions of the hydrocarbons occured with participation of the oxygen in the oxide. It was established that Bi_2O_3 promotes the oxidative dimerisation of propene to hexadiene with a low conversion but with a fairly high selectivity. At the same time SnO_2 exhibits an appreciable catalytic activity in the oxidative dimerisation of propene to hexadiene and the subsequent dehydrocyclisation of hexadiene to benzene in the initial stage of the reduction of the surface of the oxide. The addition of small amounts of one oxide to another increases the oxidising capacity of the catalyst.

The mixed oxide with the ratio Bi : Sn ≈ 1 : 1 exhibits the most effective oxidising properties in the propene dehydrodimerisation and aromatisation reactions. Trimm and Doerr[52] discussed a similar mechanism of the oxidative dimerisation of propene on the SnO_2 surface in terms of the mechanism of the dimerisation of propene in the presence of In_2O_3 on the basis of their experimental data.

The results of a study of the oxidative conversion of propene on a series of individual oxides (copper, nickel, vanadium, cobalt, cadmium, zinc, titanium, iron, antimony, tin, indium, and bismuth oxides) and some of their binary mixtures and also on oxide systems promoted by alkali metal compounds and ammonia have been published[20]. All the above oxides with the exception of Sb_2O_3, SnO_2, and Bi_2O_3 exhibit a high selectivity in the extensive oxidation of propene; copper, nickel, vanadium, cobalt, and iron oxides catalyse the above reactions under the conditions investigated with 100% conversion. On cadmium and antimony oxides, the formation of CO and CO_2 was found to be accompanied by the dehydrodimerisation of propene to diallyl, while on indium oxide propene was dehydroaromatised to benzene, as mentioned above. Bi_2O_3 and SnO_2 are active in both reactions.

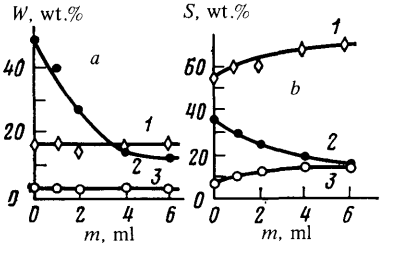


Figure 9. *a*) The influence of the amount of NH_3 (*m*) on the composition of the products (*W*) of the reaction of propene; *b*) the selectivity *S* of the process in the Bi–Ni system at 560 °C; 1) benzene; 2) CO + CO_2; 3) hexa-1,3-diene[20].

In the study of the promoting effect of ammonia and alkali metal compounds on the activity of the bismuth–nickel catalyst it was shown that basic additives appreciably suppress the extensive oxidation reaction and increase the selectivity in the formation of benzene and hexa-1,5-diene. The highest selectivity with respect to benzene is observed when the catalyst is promoted by sodium and rubidium compounds and that with respect to hexa-1,5-diene is attained in the presence of lithium and potassium compounds. Ammonia hardly affects the concentration of benzene and hexa-1,5-diene in the catalytic reaction mixture, but tends to increase appreciably the selectivity in their formation, which rises with increase of the amount of ammonia in the reaction zone with a simultaneous decrease of the amounts of carbon monoxide and dioxide (Fig.9).

Thus it follows from the data presented above that, in the region of the oxidative dimerisation and aromatisation of C_3–C_4 olefins, the reactions of propene and isobutene on indium and bismuth oxides have been studied in greatest detail and most completely and a high activity of the binary oxide catalysts has been discovered. The oxidative conversion of olefins under the conditions of a reducing medium, the influence of promoting additives on the activity of catalysts and the selectivity of their action, and the mechanism of the action of promoting agents have been studied in much less detail.

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During the preparation of the review for the press, a series of studies by foreign[60–65] and Soviet[66–70] workers, devoted to the aromatisation of hydrocarbons (including lower hydrocarbons) in the presence of high-silicon ZSM zeolites, were published. The zeolites, which exhibit a high activity and selectivity in the given process, constitute a new promising generation of zeolite-containing catalysts of the reactions of hydrocarbons and many of their functional derivatives.

REFERENCES

1. G.N.Maslyanskii, E.B.Tsyrkin, and G.L.Rabinovich, Khim.i Tekhnol.Topliv i Masel, 1977(11), 36.
2. J.E.Fick, Hydrocarbon Processing, 1976(7), 50.
3. T.C.Ponder, Hydrocarbon Processing, 1977(6), 19.
4. G.N.Maslyanskii and M.V.Veltistova, Zhur.Obshch. Khim., 1946, **16**, 2132.
5. I.B.Rapoport, R.M.Flid, and K.Lis, Dokl.Akad.Nauk SSSR, 1957, **116**, 244.
6. S.M.Csicsery, J.Catal., 1970, **17**, 207.
7. S.M.Csicsery, J.Catal., 1970, **17**, 216.
8. S.M.Csicsery, J.Catal., 1970, **17**, 315.
9. S.M.Csicsery, J.Catal., 1970, **17**, 323.
10. S.M.Csicsery, J.Catal., 1970, **18**, 30.
11. O.V.Bragin, A.V.Preobrazhenskii, and A.L.Liberman, Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 1205.
12. O.V.Bragin, A.V.Preobrazhenskii, and A.L.Liberman, Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 2751.
13. O.V.Bragin, T.V.Basina, A.V.Preobrazhensky, and A.L.Liberman, "New Approach to Catalysis", Preprints of Papers for the Fourth Japan-Soviet Catalysis Seminar, Tokyo, 1977, Prepr.19.
14. O.V.Bragin, T.V.Vasina, A.V.Preobrazhenskii, V.N.Lutovinova, and A.L.Liberman, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2282.
15. O.V.Bragin, A.V.Preobrazhenskii, T.V.Vasina, and K.D.Erokhina, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 2061.
16. L.I.Antsus and A.D.Petrova, Neftekhimiya, 1962, 2, 28.
17. L.I.Antsus, A.D.Petrov, and O.I.Shcheulina, Izv. Akad.Nauk SSSR, Ser.Khim., 1964, 1866.
18. B.V.Erofeev, G.V.Isagulyants, and I.I.Urbanovich, Izv.Akad.Nauk Beloruss.SSR, Ser.Khim., 1967, 28.
19. V.I.Karzhev, N.V.Shavolina, and V.Z.Zlotnikov, Neftekhimiya, 1968, **8**, 46.
20. Yu.N.Usov, I.M.Bolotov, N.I.Kuvshinova, and V.I.Kitaev, Neftekhimiya, 1975, **15**, 242.
21. Yu.N.Usov, N.I.Kuvshinova, and I.M.Bolotov, Izv. Vys.Ucheb.Zaved., Ser.Neft' i Gaz, 1975(2), 59.
22. Yu.N.Usov, I.M.Bolotov, and N.I.Kuvshinova, Symposium, "Kataliticheskie Prevrashcheniya Ugledovorodov" (Catalytic Reactions of Hydrocarbons), Irkutsk, 1976, p.191.
23. I.M.Bolotov, Yu.N.Usov, and N.I.Kuvshinova, Symposium, "Vsesoyuznaya Konferentsiya po Mekhanizmu Geterogenno-Kataliticheskikh Reaktsii" (All-Union Conference on the Mechanisms of Heterogeneous Catalytic Reactions), Mosocw, 1974, Preprint No.113.
24. I.M.Bolotov, Yu.N.Usov, and N.I.Kuvshinova, Symposium, "Prevrashcheniya Uglevodorodov na Kislotno-Osnovnykh Geterogennykh Katalizatorakh. Trudy Vsesoyuznoi Konferentsii" (The Reactions of Hydrocarbons on Acids–Base Heterogeneous Catalysts. Proceedings of the All-Union Conference), Groznyi, 1977, p.143.
25. Yu.N.Usov, N.I.Kuvshinova, and I.M.Bolotov, Izv. Vys.Ucheb.Zaved., Ser.Khim.i Khim.Tekhnol., 1975, **18**, 457.
26. H.Pines and W.O.Haag, J.Amer.Chem.Soc., 1960, **82**, 2471.
27. D.A.Kondrat'ev, T.N.Bondarenko, A.A.Dergachev, and E.N.Savost'yanov, Izv.Akad.Nauk SSSR, Ser. Khim., 1976, 1068.
28. D.A.Kondrat'ev, T.N.Bondarenko, A.A.Dergachev, and E.N.Savost'yanov, Izv.Akad.Nauk SSSR, Ser. Khim., 1978, 628.
29. F.Janowski, A.Sophianos, and F.Wolf, React.Kinet. Catal.Letters, 1978, **8**, 443.
30. K.M.Gitis, V.I.Kadentsev, M.I.Rozengart, and O.I.Mokrinskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 633.
31. G.V.Isagulyants, M.I.Rozengart, K.M.Gitis, A.A.Greish, L.I.Kovalenko, S.Yu.Antonova, and N.I.Kolpakova, Symposium, "Vsesoyuznaya Konferentsiya po Mekhanizmu Kataliticheskikh Reaktsii" (All-Union Conference on the Mechanisms of Catalytic Reactions), Izd.Nauka, Moscow, 1978, Vol.2, p.75.
32. M.Akimoto, E.Echigoya, M.Okada, and Y.Tomatsu, in "Proceedings of the VIth International Congress on Catalysis, London, 1976", Vol.2, p.872.
33. O.V.Bragin, A.V.Preobrazhenskii, T.V.Vasina, and A.L.Liberman, Izv.Akad.Nauk SSSR, Ser.Khim., 1975, 1649.
34. T.V.Vasina, A.V.Preobrazhenskii, Z.Engels, M.Vilde, N.M.Zaidman, and O.V.Bragin, Symposium, "Nanesennye Metallicheskie Katalizatory Prevrashcheniya Uglevodorodov. Trudy Vsesoyuznoi Konferentsii" (Deposited Metallic Catalysts of the Reactions of Hydrocarbons. Proceedings of the All-Union Conference), Novosibirsk, 1978, p.291.
35. O.V.Bragin, A.V.Preobrazhenskii, and A.L.Liberman, Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 1670.
36. C.L.Thomas, "Catalytic Processes and Proven Catalysts" (Translated into Russian), Izd.Mir, Moscow, 1973.
37. G.N.Asmolov, O.V.Krylov, O.V.Bragin, and D.B.Furman, Kinetika i Kataliz, 1977, **18**, 730.
38. G.N.Asmolov, V.N.Korchak, and O.V.Krylov, Kinetika i Kataliz, 1976, **17**, 192.
39. K.Tanabe, "Solid Acids and Bases" (Translated into Russian), Izd.Mir, Moscow, 1973, p.60.
40. T.Sakamoto, M.Egashira, and T.Seiyama, J.Catal., 1970, **16**, 407.
41. T.Seiyama, M.Egashira, T.Sakamoto, and I.Aso, J.Catal., 1972, **24**, 76.
42. T.Seiyama, T.Uda, I.Mochida, and M.Egashira, J.Catal., 1974, **34**, 29.
43. S.Nowak, H.-G.Vieweg, K.Anders, R.Feldhaus, and M.Gruia, Revista de chimie, 1976, **27**, 98.
44. T.Uda, M.Egashira, and T.Seiyama, J.Chem.Soc. Japan, Chem.Ind., 2973, 853.

45. A.S.Vaabel', L.M.Kaliberdo, L.B.Dubenkova, and P.R.Kuvakina, Neftekhimiya, 1974, **14**, 598.
46. V.G.Mikhal'chenko, V.D.Sokolovskii, A.A.Filippova, and A.A.Davydov, Kinetika i Kataliz, 1973, **14**, 1253.
47. V.B.Dorogova and L.M.Kaliberdo, Zhur.Fiz.Khim., 1971, **45**, 2890 [Russ.J.Phys.Chem., 1971(11)].
48. N.S.Figoli and D.L.Trimm, Rev.Fac.ing.quim.Univ. nac.Litoral, 1973, **40—41**, 165; Ref.Zhur.Khim., 1974, 5N106.
49. B.V.Timashkova, L.A.Vdovina, F.A.Mil'man, V.P.Latyshev, and L.A.Gaivoronskii, Neftekhimiya, 1973(4), 523.
50. T.Saiyamo, Symposium, "I Sovetsko-Yaponskii Seminar po Katalizu" (The Ist Soviet-Japanese Seminar on Catalysis), Novosibirsk, 1971, Preprint 7.
51. D.L.Trimm and L.A.Doerr, Chem.Comm., 1970, 1303.
52. D.L.Trimm and L.A.Doerr, J.Catal., 1972, **26**, 1.
53. N.S.Parera and D.L.Trimm, J.Catal., 1973, **30**, 485.
54. J.Haber, Z.Chem., 1973, **13**, 241.
55. H.E.Swift, J.E.Bozik, and J.A.Ondrey, J.Catal., 1971, **21**, 212.
56. J.Haber and B.Grzybowska, J.Catal., 1973, 28, 489.
57. M.Egashira, S.Urabe, and T.Seiyama, J.Chem.Soc. Japan, Chem.Ind., 1972, 261.
58. F.Solymosi and F.Bozso, in "Proceedings of the VIth International Congress on Catalysis, London, 1976", Vol.1, p.365.
59. F.Solymosi, F.Bozso, and I.Tombacz, Magyar kem. folynrat, 1977, **83**, 304.
60. J.R.Anderson, K.Foger, T.Mole, R.A.Rajadhyaksha, and J.V.Sanders, J.Catal., 1979, **58**, 114.
61. I.Wang, T.-J.Chem., K.-J.Chao, and T.-C.Tsai, J.Catal., 1979, **60**, 140.
62. P.Iru, L.Kubelkova, J.Novakova, Z.Tvaruzkova, and B.Wichterlova, Symposium, "Vsesoyuznaya Konferentsiya po Mekhanizmu Kataliticheskikh Reaktsii" (All-Union Conference on the Mechanisms of Catalytic Reactions), Izd.Nauka, Moscow, 1978, Vol.I, p.25.
63. A.J.Perrotta, C.Kibby, B.R.Mitchell, and E.R.Tucci, J.Catal., 1978, **55**, 240.
64. D.H.Olson, W.O.Haag, and R.M.Zago, J.Catal., 1980, **61**, 390.
65. R.Le Van Mao, U.Bellistri, R.Covini, and E.Morette, Chimica e Industria, 1979, **61**, 661.
66. O.V.Bragin, B.K.Nefedov, T.V.Vasina, T.V.Alekseeva, V.N.Lutovinova, and Kh.M.Minachev, Izv.Akad. Nauk SSSR, Ser.Khim., 1979, 2639.
67. Kh.M.Minachev, D.A.Kondrat'ev, B.K.Nefedov, T.N.Bondarenko, A.A.Dergachev, and T.V.Alekseeva, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 2646,
68. Kh.M.Minachev, D.A.Kondrat'ev, B.K.Nevedov, A.A.Dergachev, T.N.Bondarenko, T.V.Alekseeva, and T.B.Borovinskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 2509.
69. O.V.Bragin, B.K.Nefedov, T.V.Vasina, V.N.Lutovinova, T.V.Alekseeva, A.V.Preobrazhenskii, and Kh.M.Minachev, Dokl.Akad.Nauk SSSR, 1980, **255**, 103.
70. K.G.Ione, Kinetika i Kataliz, 1980, **21**, 1220.

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