U.D.C. 542.97:547.31

Catalytic Dehydrogenation of Hydrocarbons

V.K.Skarchenko

A systematic account is given of data on certain problems in the theory of catalytic dehydrogenation relevant to the reaction mechanism and the elucidation of the nature of the active centres. The intermediate products of the hydrogenation reactions, the role of individual elementary stages, the nature of intermediate surface compounds, the side reactions of dehydrogenation catalysts, and modern hypotheses concerning the structure of the active centres are discussed. The bibliography includes 216 references.

CONTENTS

I.	Introduction	997
II.	Intermediate products of dehydrogenation reactions	997
III.	Mechanism of catalytic dehydrogenation	1001
IV.	Varieties of the dehydrogenating effect of catalysts	1004
V.	Modern hypotheses concerning the nature of the active surface of dehydrogenation catalysts	1007

INTRODUCTION

Hydrocarbons of different homologous series are capable of being catalytically dehydrogenated (paraffins, naphthenes, olefins, cyclo-olefins, and alkyl-substituted aromatic hydrocarbons). The reaction results in the elimination of hydrogen and the formation of more highly unsaturated compounds or in cyclisation (dehydrocyclisation). The dehydrogenation catalysts are various metals and oxides. The principal side reactions in catalytic dehydrogenation are cracking, isomerisation, and coke formation. Catalytic dehydrogenation constitutes the basis of one of the most important types of industrial processing of hydrocarbon raw materials. Various aspects of the problem of dehydrogenation of hydrocarbons were examined in previous reviews[1-26].

II. INTERMEDIATE PRODUCTS OF DEHYDROGENATION REACTIONS

1. Olefins as Intermediates in the Aromatisation of Paraffins.

The principal products of the dehydrogenation of $C_{\geqslant 6}$ straight-chain paraffins are aromatic hydrocarbons together with a small amount of olefins. On the basis of the variation of the yield of olefins and aromatic hydrocarbons with contact time (Cr_2O_3, 475°C), Pitkethly and Steiner[27] put forward the hypothesis that heptane is aromatised via the intermediate formation of heptene.

However, a number of objections were raised against this view. Obolentsev and Usov[28] failed to observe maximum yields of olefins as a function of the time of contact under similar conditions. According to Levitskii's thermodynamic calculations[29], in the presence of large amounts of aromatic hydrocarbons the equilibrium yields of olefins are greatly reduced. On this basis, he suggested that olefins and aromatic hydrocarbons are formed simultaneously and the low yields of olefins under the conditions of high yields of aromatic hydrocarbons can be attributed to closeness to equilibrium.

Kazanskii et al.[30], who passed the Synthine fraction over platinised charcoal, failed to detect olefins although aromatisation did occur to a slight extent under these conditions.

Hypotheses concerning the mechanism of the aromatisation of paraffinic hydrocarbons omitting the olefin formation stage were developed for oxide catalysts by Plate[31], Kagan[32], and Kuo Hsie-Shien[33] and for metallic catalysts by Kazanskii, Plate, and Sergienskii[31,34,35]. In connection with this problem, we shall consider certain relations governing the formation of olefins and aromatic hydrocarbons in the catalytic dehydrogenation of paraffins. Shuikin, Timofeeva, and coworkers[36] showed that the olefin/aromatic hydrocarbon ratio greatly increases when the temperature of the dehydrogenation of hexane on an alumina–chromium oxide catalyst and the contact time are reduced. In the present author's studies[37-42], similar relations were established in the dehydrogenation of hexane on chromium oxide–magnesium oxide, chromium oxide–zinc oxide, iron oxide–alumina, and other mixed oxide catalysts and on charcoal.

A decrease in the temperature and in the contact time reduced the total amount of dehydrogenation products. This enabled the author to formulate a more general postulate[43]: a decrease of the conversion of hexane into dehydrogenation products is accompanied by an increase of the olefin/aromatic hydrocarbon ratio in the product. The above relation is valid for catalysts of various chemical compositions and prepared in different ways. Moreover, the olefin/aromatic hydrocarbon ratios and the yields of olefins and aromatic hydrocarbons fit satisfactorily on the curves describing their variation with the overall conversion in the dehydrogenation process. One of such relations is presented in Fig. 1.

Similar curves are obtained from the experimental data data of many investigators for the dehydrocyclisation of paraffins, involving straight-chain C_6-C_{10} paraffins, more than 20 catalysts, different ways of preparation of the catalysts, and different reaction conditions (temperatures in the range 450–600°C and space velocities between 0.15 and 160 h^{-1}). Fig. 2 presents the variation of the ratio of olefin yield to aromatic hydrocarbon yield with the overall yield of the dehydrogenation products.

Thus analysis of extensive experimental data shows that the main factors determining the olefin/aromatic hydrocarbon ratio is the degree of conversion of the starting material into the dehydrogenation products and changes in the chemical composition and methods of preparation of the catalyst, temperature, and the contact time are mainly important only insofar as the conversion depends on them.

The relations governing the relative yields of olefins and aromatic hydrocarbons as a function of conversion led the author to the conclusion that aromatic hydrocarbons are formed consecutively via olefins on both oxide and metallic catalysts[43,56,63-65].

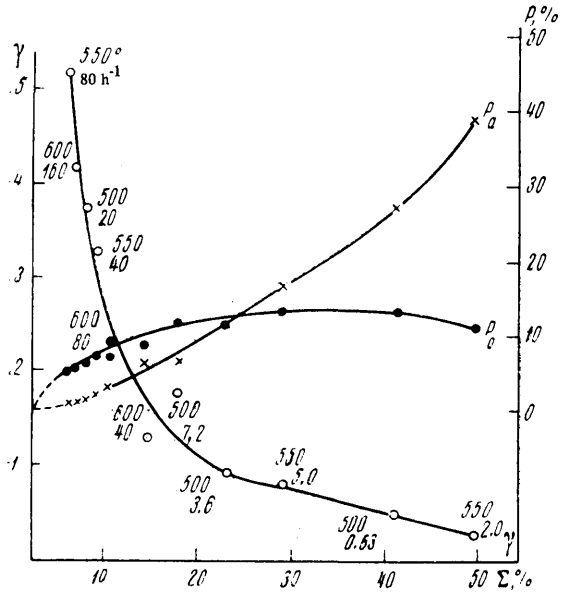


Figure 1. Variation of the yields of the heptane dehydrogenation products—olefins (P_O) and aromatic hydrocarbons (P_a)—and their ratio ($\gamma = P_O/P_a$) with the sum $\Sigma = P_O + P_a$ on the alumina–chromium oxide catalyst at 500–600°C and a space velocity of 0.63–160 h^{-1} according to the experimental data of Mattox[44].

Indeed the curves describing the yields of olefins and aromatic hydrocarbons as a function of their sum may be regarded as related to generalised kinetic curves, used for different experimental data, time having been replaced as the abscissa axis by a quantity which varies proportionately to it. The curves describing the variation of the yields of olefins and aromatic hydrocarbons (Fig. 1) exhibit the distinctive properties of consecutive reactions: the content of the intermediate (olefin) passes through a maximum with conversion and that of the final product (aromatic hydrocarbon) is initially low but increases continuously. The maxima at low yields of olefins can be accounted for by their cracking or closeness to equilibrium[65].

Similar variation of the yields of olefins and aromatic hydrocarbons with the overall degree of dehydrogenation is observed on platinum and oxide catalysts. This shows that, at least on certain metallic catalysts, olefins are also formed as intermediates in the aromatisation of paraffins.

Other data are consistent with this conclusion as well. Thus the rate of aromatisation of mono-olefins is much higher than that of paraffins (Table 1) (which may be regarded as evidence in favour of the intermediate formation of mono-olefins). Addition of hexenes to hexane increases the yields of benzene on the alumina–chromium oxide catalyst[70] and on charcoal[48].

The relative capacity of paraffins to be dehydrogenated to olefins and aromatic products did not change significantly following dilution with hydrogen[66] or on reducing the pressure in the reactor[67]; this should have been the case if the yields of olefins were limited by an equilibrium.

Table 1. Comparative data on the dehydrogenation of straight-chain paraffins and mono-olefins.

Catalyst	Temp., °C	Space velocity, h^{-1}	Yield of aromatic hydrocarbons in dehydrocyclisation, %		Refs
			heptane	heptenes	
Cr_2O_3	450		2.5	16	28
V and Al oxides	480	0.5	6	40	68
Cr, Al, and K oxides	484	0.4	37	52	32
Cr, Al, and K oxides	470	0.8	11	31	69

The conclusion that olefins are formed as intermediates in the aromatisation of paraffins on oxide and non-oxide catalysts is also confirmed by data published in recent years for experiments using tracer atoms (heptane–heptene mixtures at 487°C with contact times in the range 1.1–4 s on the alumina–chromium oxide catalyst[71] and hexane–hexene mixture at 360°C under pulsed conditions in a stream of helium on platinum and nickel[72,73].

Calculations based on Panchenkov's kinetic equation for a heterogeneous-catalytic flow reaction with consecutive stages[74] yields the ratio of the rate constants for the conversion of olefins into aromatic hydrocarbons (k_2) and of paraffins into olefins (k_1): $k_2/k_1 = 7-8$.

2. Dehydrogenation of Lower Paraffins to Mono- and Di-Olefins

In the dehydrogenation of straight-chain butane and pentanes, the products contain a certain amount of diolefins in addition to mono-olefins. The principal factors determining the mono-olefins/di-olefins ratio in the product is the degree of departure from equilibrium. The equilibrium yields of diolefins increase appreciably as the pressure is reduced and the reaction temperature increased[1,7].

Butenes are intermediates in the dehydrogenation of butane to butadiene. The work of Balandin and coworkers on the dehydrogenation of butane–butene mixtures, in which one of the components was labelled with carbon-14, led to this conclusion. The experiments were performed on chromium oxide and on the alumina–chromium oxide catalyst. A 1:1 butane–butene mixture was used in the reaction. The experiments with chromium oxide were performed at 635°C and a 1:9 dilution with water[75].

A quantitative calculation of the ratio of the rates of dehydrogenation of butane to butene (w_1) and butadiene (w_2) and of butene to butadiene (w_3) yielded the following results[76]. Under the above conditions, $w_1 : w_2 : w_3 = 20:1:1000$ for chromium oxide and $w_1 : w_2 : w_3 = 18:1:25$ for the alumina–chromium oxide catalyst (600°C, 250 mmHg), i.e. in both cases butadiene is formed from butane almost entirely via the intermediate formation of butene.

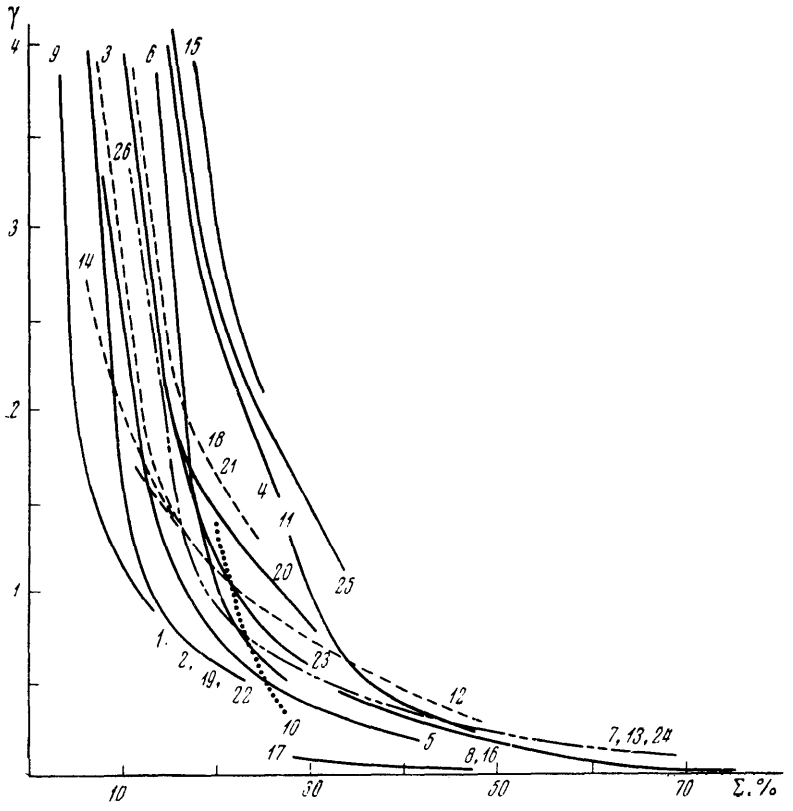


Figure 2. Comparison of the curves relating the ratios γ of olefins to aromatic products with their sum Σ: 1) hexane, Fe, Cr, and Al oxides, 500–525°C, 0.5 h^{-1} [37,39]; 2) hexane, Cr, Mg, and Zn oxides, 425–500°C, 0.5 h^{-1} [40,41]; 3) data from Fig. 1; 4) hexane, $Al_2O_3-Cr_2O_3$, 475–550°C, 0.5–2.1 h^{-1} [36]; 5) heptane, Cr_2O_3, 450–510°C [28]; 6) hexane, Cr, Al, and K oxides, 450–600°C, 9.2 h^{-1} [45]; 7) hexane, $Al_2O_3-Cr_2O_3-K_2O$, 475–527°C, 0.4–0.9 h^{-1} [46]; 8) hexane, $Al_2O_3-Cr_2O_3-K_2O$, 510–550°C, 0.37–2.5 h^{-1} [47]; 9) heptane, V and Al oxides, 450–510°C, 0.5 h^{-1} [48]; 10) heptane, Al, Cr, and Mo oxides, 490°C, 0.15–0.65 h^{-1} [29]; 11) hexane, Al and Cr oxides with Li, Na, K, Rb, Cs, Zn, or Pb additives, 500°C, 0.5 h^{-1} [49]; 12) hexane, Cr, Al, and K oxides prepared in different ways, 500°C, 0.5 h^{-1} [50]; 13) heptane, Al and Cr oxides with Be, Mg, Ca, Sr, Ba, or Zn additives, 530°C, 0.35 h^{-1} [51]; 14) heptane, Cr, K, and P oxides, 450°C, 0.8 h^{-1} [52]; 15) hexane, $Al_2O_3-Cr_2O_3$, some coke deposits, 500°C, 2.1 h^{-1} [53]; 16) heptane, K-162, some coke deposits, 515°C, 0.3 h^{-1} [54]; 17) heptane, Al, Mg, and Mo oxides, 480–530°C, 0.3 h^{-1} [55]; 18) hexane, Al, Mn, and Cr oxides, 400–550°C, 0.5–1.0 h^{-1} [56]; 19) nonane, Fe and Al oxides, 400–550°C, 0.35–1.8 h^{-1} [39]; 20) nonane and decane, Al, Cr, and K oxides, 427–600°C; 0.5–9.2 h^{-1} [45,57,58]; 21) hexane, Pt/charcoal or Al_2O_3, 300–500°C, 0.5 h^{-1} [56]; 22) hexane, MoS_2–silica gel, aluminosilicate, or MgO, 450–550°C, 0.5 h^{-1} [59]; 23) hexane, Cr_2O_3–charcoals, 370–510°C, 0.5–1.5 h^{-1} [42]; 24) hexane, $Pt-Al_2O_3-Na_2O$, 545°C, 0.4 h^{-1} [60]; 25) hexane, $Cr_2O_3-Al_2O_3$ with different porosities, 450–510°C, 0.5–2.5 h^{-1} [61]; 26) hexane, K-5, 450–530°C, 0.3–1.5 h^{-1}, dilution with hydrogen [62].

3. Dehydrogenation of Naphthenes

In the dehydrogenation of six-membered naphthenes, the main products are aromatic compounds. However, sometimes the catalytic reaction mixture contains also a small amount of unsaturated hydrocarbons.

For a long time cyclohexenes were not detected in the products of the dehydrogenation of cyclohexanes on metals. However, in a study of the initial stages of the conversion of cyclohexane on platinum, Block[77] observed by mass spectroscopy not only cyclohexene but also cyclohexadiene in the gas phase. The formation of cyclohexene and cyclohexadiene in the dehydrogenation of cyclohexane on platinum was also established by Paal and Tetenyi[78] by a pulsed technique. Here the curves relating the yields of cyclohexene and benzene to catalyst activity (which corresponds to the degree of conversion) exhibit features characteristic of consecutive reactions.

The intermediate formation of cyclo-olefins is also suggested by data from certain studies on the dehydrogenation of naphthene–cyclo-olefin mixtures by a tracer atom method. Thus cyclohexane on nickel (305–335°C) [79]

and methylcyclohexene on the alumina–chromium oxide catalyst (500°C)[80] are aromatised via an intermediate unsaturated hydrocarbon. However, direct formation of the aromatic hydrocarbon may make a considerable contribution or even predominate. Thus, in the dehydrogenation of cyclohexane on Cr_2O_3 (450°C) and holmium oxide (560°C), only about half the benzene is formed via the intermediate cyclohexene[81], and on the Pd/Al_2O_3 and Re/Al_2O_3 catalysts under reforming conditions benzene is formed almost wholly without the stage involving the intermediate cyclohexene[82].

The dehydrogenation of cyclohexane to benzene without the intermediate formation of cyclohexene can imply that either all the hydrogen atoms are eliminated simultaneously or the ease of conversion of the intermediate surface cyclohexene is much greater than the ease of its desorption. The study of the dehydrogenation of mixtures of hydrocarbons, one of which is labelled with radioactive carbon, as well as kinetic analysis cannot yield information about the stages which occur on the surface without the liberation of the reactants to the gas phase.

In the dehydrogenation of decalin and tetralin, the main product is naphthalene, but in the dehydrogenation of the first compound tetraline is also detected and in that of the second dihydronaphthalene[83]. The yield of tetralin in the dehydrogenation of decalin passes through a maximum as the temperature is increased, while the yield of naphthalene increases in the same temperature range. Dihydronaphthalene can be detected only on catalysts with low activity. Both factors – a decrease of temperature and of the activity of the catalyst—lead to decreased conversion (see Section II, 1). This suggests that the dehydrogenation of decalin proceeds via a stage involving the formation of tetralin and dihydronaphthalene. The main products of the dehydrogenation of ethylcyclohexane are ethylbenzene and styrene. Kinetic data indicate the formation of styrene via ethylbenzene[84].

Table 2. Comparison of the capacities for dehydrogenation of hydrocarbons with different degrees of unsaturation.

Hydrocarbons	Catalysts	References
Heptatriene > heptadiene > heptene > heptane	Chromium and vanadium oxides, Cr_2O_3 — Al_2O_3 — K_2O	28, 32, 68, 69, 85
Cyclohexadiene > cyclohexene > cyclohexane	Cr_2O_3, MoO_3 — Al_2O_3, Pt, Pd, Rh, Ir, Ni, Co, Fe	86–88
Cyclopentene > cyclopentane	Cr_2O_3 — Al_2O_3 — K_2O	9
Tetralin > decalin	Ni, MoO_3 — Al_2O_3	88, 89
Alkyl-substituted aromatic compounds > alkyl-substituted cycloparaffins	Mixed oxide catalyst	90
Cyclohexane > hexane	Cr_2O_3 — Al_2O_3 — K_2O	91
Hex-1-ene > cyclohexane	ditto	92

The rate of dehydrogenation of cyclic hydrocarbons as well as aliphatic hydrocarbons increases with the degree of unsaturation (Table 2), which is consistent with data on the intermediate formation of unsaturated hydrocarbons in the aromatisation of cyclohexanes.

The rate constants for the dehydrogenation of ethylcyclohexane are approximately a power of 10 lower than those for the dehydrogenation of ethylbenzene[90]. Nevertheless considerable amounts of ethylbenzene are formed in the dehydrogenation of ethylcyclohexane and can exceed greatly the yields of styrene. The low yields of styrene under the conditions of the dehydrogenation of ethylcyclohexane are evidently due to closeness to equilibrium in the dehydrogenation of ethylbenzene under the conditions of its formation from ethylcyclohexane[93].

4. Dehydrogenation of Olefins and Alkyl-Substituted Aromatic Hydrocarbons

Small amounts of more unsaturated olefins with the same number of carbon atoms are observed in the catalytic reaction mixtures when $C \geq 6$ straight-chain olefins are aromatised. Data relating the yields of dienes and aromatic hydrocarbons to the contact time and other factors which determine the conversion of mono-olefins (temperature and catalytic activity) on various catalysts (alumina–chromium oxide–potassium oxide, nickel, and platinum) exhibit features characteristic of consecutive reactions[94–96]. Thus one can suppose that the dehydrocyclisation of hexenes and heptenes proceeds via the intermediate formation of dienes.

The relations governing the yields of the products of the aromatisation of hexadienes and heptadienes on the alumina–chromium oxide–potassium oxide and platinum catalysts suggest that direct conversion of the dienes into aromatic hydrocarbons plays a considerable role together with conversion via intermediate trienes[85,97]. In the dehydrocyclisation of C_6 and C_7 trienes, intermediate cyclohexadienes are formed[85,97].

The ratios of the yields of toluene from hept-1-ene, hepta-1,3-diene, and heptatriene on the alumina–chromium oxide–potassium oxide catalyst at 450°C are 1 : 5 : 150,[85] which agrees with the above data concerning the consecutive mechanism of the dehydrocyclisation of olefins.

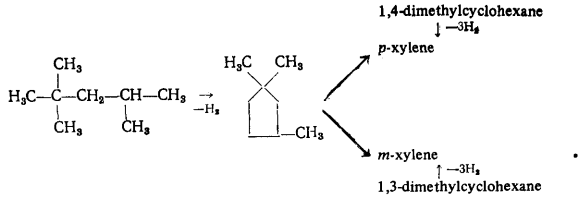
The principal products of the dehydrogenation of diethylbenzene are ethylvinylbenzene and divinylbenzene. The relations governing the yields of these products suggest that ethylvinylbenzene is an intermediate in the formation of divinylbenzene[98]. The dehydrogenation of diethylbenzene is described by the kinetic equation for a heterogeneous-catalytic flow reaction with consecutive stages[74]. On a mixed oxide catalyst at 520–560°C in a 1 : 3 diethylbenzene–water mixture, the rate constant for the dehydrogenation of ethylvinylbenzene to divinylbenzene is approximately twice as high as the rate constant for the stage involving the dehydrogenation of diethylbenzene to ethylvinylbenzene.

5. Naphthenes as Intermediates in the Aromatisation of Paraffins

In the presence of platinum on charcoal or alumina, fairly large amounts of C_5 naphthenes are formed in the paraffin dehydrogenation products. C_5-Dehydrocyclisation of paraffins to naphthenes is promoted by the presence of a five-membered carbon chain and its branching[8].

C_5-Dehydrocyclisation of paraffins is a primary reaction and does not proceed via the formation of olefins, six-membered naphthenes, or isomerisation. This is indicated by many factors[99]. Olefins are more difficult to convert into C_5 naphthenes than are paraffins; C_5-dehydrocyclisation of paraffins with six carbons atoms in the chain proceeds with greater difficulty than for carbon chains with five atoms. In all cases only those cyclopentanes are formed which should arise if the reaction

proceeded without isomerisation at all stages. Thus C_5-dehydrocyclisation of iso-octane yields 1,1,3-trimethylcyclopentane, which is partly aromatised to *m*- and *p*-xylenes under the reaction conditions:

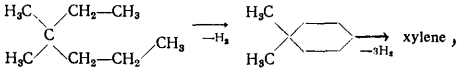


This mechanism of the aromatisation of iso-octane is supported by the following facts. The aromatisation of 1,1,3-trimethylcyclopentane on platinum/charcoal[100] and platinum–alumina[101] catalysts yields the same products (*m*- and *p*-xylenes) as in the aromatisation of iso-octane under the same conditions. On the other hand, in the presence of the alumina–chromium oxide–potassium oxide catalyst the aromatisation of iso-octane has a different mechanism: 1,1,3-trimethylcyclopentane and 2,2,4-trimethylpentane give different aromatic products[101].

In the aromatisation of straight-chain $C_{\geqslant 6}$ paraffins, C_5 naphthenes are formed to a small extent and the fraction of aromatic products formed via C_5 naphthenes becomes insignificant[102].

It has been suggested[22,31,102] that the aromatisation of unbranched $C_{\geqslant 6}$ paraffins proceeds via the intermediate formation of cyclohexanes although so far the latter could only rarely be detected in the reaction product and only in trace amounts. The difficulty of detecting cyclohexane in the dehydrocyclisation of straight-chain hexane cannot be accounted for by its high reactivity. Although cyclohexane is dehydrogenated more readily than hexane, under the usual conditions of the dehydrogenation of cyclohexane it is impossible to achieve a complete conversion [for example, cyclohexane is dehydrogenated with greater difficulty than hex-1-ene (Table 2), which is readily detected in the dehydrogenation reaction products]. In a study of the dehydrogenation of hexane–cyclohexane and hexene–cyclohexane mixtures, where one of the reactants was labelled with carbon-14, Paal and Tetenyi[78] showed recently that cyclohexane is hardly formed as an intermediate in the aromatisation of either hexane or hexene on platinum and nickel.

On the other hand, in the aromatisation of branched hexanes, the intermediate formation of six-membered naphthenes can probably make a fairly considerable contribution. Thus the formation of a conjugated bond in a paraffin containing a quaternary carbon atom is difficult: it can arise only after isomerisation or dimerisation. According to Kazanskii et al.[35], the aromatisation of 3,3-dimethylhexane on a platinum/charcoal catalyst proceeds via the intermediate 1,1-dimethylcyclohexane:



which was detected in the reaction products.

In the aromatisation of paraffins with chain lengths greater than six carbon atoms, account must be taken also of the possible formation of intermediate $C_{>6}$ naphthenes. Thus in the aromatisation of octane on a "non-acid" alumina–chromium oxide catalyst[103], methylcyclopentane, which the authors believed to be an intermediate in the formation of xylenes, was isolated.

The foregoing data show that there is an analogy in the mechanisms of the dehydrogenation of various hydrocarbons. The dehydrogenation reactions accompanied by the removal of two and more hydrogen molecules take place in steps. The intermediate product is as a rule liberated to the bulk phase before further reactions occur. In certain cases (dehydrogenation of cyclohexane to benzene), another type of reaction can predominate—direct conversion into the final product.

$C_{\geqslant 6}$ straight-chain paraffins are formed via olefins, diolefins and (to a lesser extent) triolefins. Cyclisation occurs in later stages of the reaction. This mode of reaction predominates on both oxide and metallic catalysts. The intermediate formation of five and six-membered naphthenes makes a considerable contribution to the formation of an aromatic product apparently only in the dehydrogenation of certain branched hydrocarbons.

III. MECHANISM OF CATALYTIC DEHYDROGENATION

1. Certain Elementary Steps and the Nature of Intermediate Surface Compounds

While the nature of the bulk-phase intermediate dehydrogenation products can be regarded as established in the majority of cases, there are still few data concerning intermediate surface compounds.

The dehydrogenation mechanism can be represented as a sequence of bulk-phase and surface intermediate compounds. For example, in the aromatisation of an olefin or naphthene,

$$\underset{n\geqslant 6}{C_nH_{2n}} \rightarrow \underset{0\leqslant r\leqslant 2}{(C_nH_{2n-r})} \rightarrow C_nH_{2n-2} \rightarrow \underset{0\leqslant r_1\leqslant 2}{(C_nH_{2n-2-r_1})} \rightarrow C_nH_{2n-4} \rightarrow \underset{0\leqslant r_2\leqslant 2}{(C_nH_{2n-4-r_2})} \rightarrow C_nH_{2n-6} \qquad (1)$$

(the surface compounds are indicated in brackets). Each stage of mechanism (1) can in turn consist of two or more substages and conversely not all the stages indicated are obligatory and under certain conditions there is a possibility of the simultaneous elimination of more than two hydrogen atoms from the molecule undergoing dehydrogenation or the conversion in certain stages can take place in steps but without the liberation of intermediates into the gas phase.

With increased reactivity of the hydrocarbons dehydrogenated, homogeneous stages acquire a significant importance together with surface reactions. Thus hexatrienes are known to undergo thermal cyclisation to cyclohexadiene at a temperature as low as 360°C[97,104] and at 300°C cyclohexadiene is converted into benzene[105].

According to the multiplet theory, an intermediate surface compound is formed via a two-point (doublet) or six-point (sextet) adsorption of the molecule being dehydrogenated. There must be structural and energy correspondence between the catalyst and the reacting molecule under these conditions[15].

According to Balandin, reactions such as the dehydrogenation of paraffins to olefins, of olefins to diolefins, and of alkyl-substituted to alkenyl-substituted aromatic hydrocarbons, i.e. reactions involving the dissociation of two C–H bonds, take place via a doublet mechanism. The direct dehydrogenation of cyclohexane to benzene, involving the dissociation of six C–H bonds, has a sextet mechanism. According to Liberman[99], C_5 dehydrocyclisation of paraffins to naphthenes has a sextet–doublet mechanism, in contrast to other dehydrogenation reactions:

the doublet reaction is preceded by adsorption involving a sextet mechanism.

Some data on the nature of the intermediate surface compounds of hydrocarbons were obtained recently by studying the chemisorption of hydrocarbons on catalysts by infrared and ESR spectroscopy, etc. According to modern concepts, the following types of adsorption of olefins on a metal are possible[106]:

Adsorbed at two points via σ-bonds:

$$R_aCH{=}CHR_b + 2M \rightarrow R_a\overset{M}{C}H{-}\overset{M}{C}HR_b \ ; \qquad (A)$$

associatively adsorbed via a π-electron mechanism:

$$R_aCH{=}\underset{M}{C}HR_b \ ; \qquad (B)$$

a dissociatively adsorbed olefin forming compounds of the π-allyl type:

$$R_aCH{=}CH{-}CH_2R_b + M \underset{-H}{\longrightarrow} R_aCH{-}\underset{M}{CH}{-}CHR_b \ . \qquad (C)$$

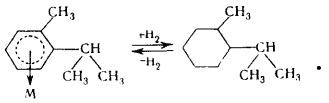
The hypothesis of the formation of an intermediate via one-point absorption does not involve a significant contribution by the geometrical factor of the kind postulated in the multiplet theory.

When an adsorbed olefin in treated with hydrogen, changes occur in the infrared spectrum, indicating the formation of surface alkyl radicals:

$$R_aCH{-}\underset{M}{CHR_b} \ (\text{or } R_aCH{=}\underset{M}{CHR_b}) \underset{-H}{\overset{+H}{\rightleftarrows}} R_aCH{-}\underset{M}{CH_2R_b} \ .$$

The adsorbed alkyl radical is evidently linked to the surface via one σ bond.

The formation of a stable partly hydrogenated form is observed also in the chemisorption of branched cyclic hydrocarbons on nickel, for example[108]:



On the other hand, under the conditions tested (room temperature, residual pressure 10^{-5} mm) the hydrogenation of adsorbed benzene yields cyclohexane, which is readily desorbed from the surface. According to the authors[107], the explanation is that an absorbed unsubstituted six-membered cyclic hydrocarbon is linked to the metal via a π bond which is weaker than a σ bond.

Under conditions approaching more closely those which actually obtain in dehydrogenation (temperatures up to 200°C), the adsorption of cyclohexane involves the formation of a surface cyclohexyl radical. This is indicated by mass-spectrometric data for the ions desorbed from platinum under the influence of a field pulse[77]. Studies of the ESR spectra also established the presence on the surface of nickel of a surface compound with a higher carbon content, which is believed[109] to be an intermediate in coke formation.

When about 10% of the nickel surface has been covered, cyclohexane has an accelerating effect on the ortho–para conversion of hydrogen, the catalytic effect increasing with the temperature of the preliminary adsorption of the hydrocarbon[110]. The acceleration of the ortho–para conversion of hydrogen is evidently related to the radical-like nature of certain surface compounds—products of the partial dissociation of the hydrocarbon molecule.

2. Cyclic Intermediates in the Aromatisation of Paraffins

Some data on the structure of the unstable intermediate compounds can be obtained by studying the dehydrogenation of hydrocarbons containing labelled carbon atoms, i.e. the variation of the product composition and of the reaction rates with the structure of the initial paraffin.

According to the Twigg–Herington hypothesis[111], the cyclisation of a linear molecule requires two-point adsorption via two carbon atoms. For example, the relative probability of the cyclisation of heptane is 4/6, since cyclisation is favoured by 1–2, 2–3, 5–6, and 6–7 adsorption but not 3–4 and 4–5 adsorption.

In a calculation of the relative probability of aromatisation, Kuo[112] began with the hypothesis of one-point adsorption. Then the probability of cyclisation should be equal to the ratio of the number of surface radicals cyclised to their total number. For heptane, the number of semihydrogenated radicals undergoing cyclisation is four, while their total number is seven and therefore the probability of cyclisation is 4/7. Kuo's mechanism, like the Twigg–Herington mechanism, allows the possibility of subsequent isomerisation of the adsorbed hydrocarbon.

According to Raik[113], the probability of cyclisation is determined by the product of the relative number of the possible collisions between the molecule and the catalyst and the relative chemical activity of the atoms. For primary, secondary, and tertiary hydrocarbons, the ratios of the first and second quantities are 3 : 2 : 1 and 1 : 2 : 10. According to this method of calculation, the relative probability of the ring-closure of heptane is 0.54.

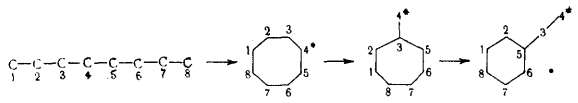
Each of the methods of calculation described explains satisfactorily in many cases the relative rates of dehydrogenation of various hydrocarbons and the composition of the aromatisation products, the differences between them involving a greater or lesser approximation to the experimental data for the individual paraffins. However, nowadays the calculation of the probability of the cyclisation of paraffins requires revision in the light of new data indicating the intermediate formation of open-chain olefins, as a result of which the cyclisation takes place at later stages than the initial adsorption of the original paraffin (see Section II, 1, 4).

The dehydrocyclisation of octane on various catalysts results in the formation of ethylbenzene and all three isomers of xylene[103,111,114–116]. According to the Twigg–Herington mechanism, ethylbenzene may be formed via 1–6 and 3–8 adsorption, and *o*-xylene via 2–7 absorption; *m*- and *p*-xylenes are formed as a result of the isomerisation of the 1–6 or 3–8 cyclic structure with intermediate formation of bicyclic species. One can also postulate isomerisation via the migration of a CH_3 group around the ring in the intermediate 2–7 surface compound[115] or as a result of an octane → iso-octane reaction[116].

However, the cyclisation of an aliphatic hydrocarbon to a six-membered ring is not the only possible pathway leading to the aromatisation of paraffinic hydrocarbons (see Section II, 5 about the formation of an intermediate five-membered ring). The numerous data of Pines and coworkers indicate other possibilities of cyclisation.

Thus one of their studies[103] dealt with the dehydrocyclisation of labelled [4-^{14}C] octane at 522°C on a "non-acid" alumina–chromium oxide catalyst, which is inactive in the isomerisation of hydrocarbons. Experiments showed that ethylbenzene is radioactive in the side chain. The displacement of the radioactive label to

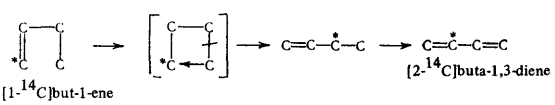
the side chain of ethylbenzene is difficult to account for otherwise than by the formation of an intermediate eight-membered ring:



The side chain contains 5–7.8% of ^{14}C, which corresponds to a 20–31% contribution of the mechanism involving the formation of a surface cyclo-octane. In order to explain the formation of other products, one must also postulate closure to a seven-membered ring and the usual six-membered ring.

Hypotheses concerning the closure of open chains to rings with various numbers of carbon atoms and the isomerisation of intermediate cyclic surface compounds have also been put forward to account for the aromatisation of hydrocarbons containing seven[117–119] and five[120,121] carbon atoms in the chain.

Cyclic intermediates and their isomerisation can play a significant role even in the dehydrogenation of lower hydrocarbons. Thus, according to recent data of Okamoto et al.[122], in the dehydrogenation of [1-^{14}C] but-1-ene over the alumina–chromium oxide catalyst there is a rearrangement involving the migration of ^{14}C from the 1-position in but-1-ene to the 2-position in buta-1,3-diene. The degree of this ^{14}C rearrangement in butadiene at 675°C is 23%. The ^{14}C rearrangement cannot be accounted for by the recombination of C_2 cracking products and indicates the formation of a four-membered ring, for example:



3. The Rate-limiting Stages and Kinetic Equations

There are data showing that the slowest stage in the dehydrogenation of various hydrocarbons is the chemical reaction. The rate of deuterium exchange involving cyclohexene and hence the rates of adsorption and desorption of cyclohexene on Pd/Al_2O_3 and Re/Al_2O_3 are much higher than the rate of dehydrogenation[123]. The same conclusion can also be reached concerning the rates of adsorption and desorption of hydrogen: the para–ortho conversion of hydrogen on Ni–ZnO is much faster than the dehydrogenation of cyclohexane[124]. Calculation of the stoichiometry for the rate-limiting stage in the dehydrogenation of butane on the alumina–chromium oxide catalyst yields a value close to unity[125].

On the assumption that the unimolecular stage of dehydrogenation on a quasihomogeneous surface is rate-limiting and that the adsorption of the reactants is described by the Langmuir isotherm, kinetic equations of the following types were derived[16] for the process under conditions far from equilibrium.

$$w = k\frac{b_i p_i}{1 + \Sigma b_i p_i}, \qquad (2)$$

where b_i are the adsorption coefficients of the reactants. Depending on the relative adsorption coefficients and the ratios of the reactant concentrations, Eqn. (2) yields effective reaction orders ranging from zero to unity with respect to the initial hydrocarbon and from –1 to 0 with respect to the product, in agreement with experiment[16,33,74,124,126–140].

This interpretation of the rate coefficients of the equations has been widely accepted. A fairly large number of determinations have been made of the adsorption coefficients of the reactants on various catalysts, including dehydrogenation catalysts. According to the available data[16,136–138,141–143], the kinetic adsorption coefficients increase in the series paraffins ≃ naphthenes ≤ aromatic hydrocarbons < olefins < diolefins and differ comparatively little on catalysts such as alumina–chromium oxide, alumina–molybdenum oxide, and nickel/Al_2O_3.

The above treatment of rate coefficients involves contradictions in a number of cases and therefore their physical significance is apparently still controversial.

Thus according to the relative adsorption coefficients, the dehydrogenation of paraffins is inhibited by the products (olefins). However, these data are inconsistent with direct measurements of the degree of adsorption. Thus the degree of chemisorption of isopentane proves to be higher than that of isopentene[144]. The hypotheses of intense adsorption of olefins are also apparently inconsistent with, for instance, kinetic dehydrocyclisation data. The consecutive equation for the dehydrocyclisation of straight-chain paraffins is valid only in the form corresponding to the intense adsorption of the product—an aromatic hydrocarbon and not an olefin[74]. At the same time, according to other data (see above), the kinetic adsorption coefficients for aromatic hydrocarbons are lower than those for olefins.

In a study published subsequently[145], it was shown by a chromatographic procedure that the degree of adsorption of hydrocarbons (paraffins and olefins) on the alumina–chromium oxide–potassium oxide catalyst under dehydrogenation conditions is lower than the degree of adsorption of hydrogen. These results make it possible to explain published data on the inhibition of the dehydrogenation of paraffins by olefins within the framework of the mechanism of the inhibition of the reaction by hydrogen[145]. One can add that sometimes in the interpretation of experimental data in terms of equations of type (2) adsorption coefficient $b_i < 0$ are obtained[146]; this is inconsistent with the assumptions made in the derivation of the kinetic equation which must be then regarded as semiempirical or it must be explained in another way. Indeed the hypothesis that the rate of the chemical reaction is limiting can hardly be regarded as universally valid, since the rates of the individual stages can vary markedly depending on the reactant and the state of the catalyst surface.

Kinetic equations analogous to Eqn. (2) or its special forms but with the constants having a different physical significance can also be derived on the hypothesis that the rate-limiting stages are the chemisorption of the initial hydrocarbon (dehydrogenation of cyclohexane on the alumina–chromium oxide catalyst)[147] or the desorption of products (dehydrogenation of methylcyclohexane on $Pt-Al_2O_3$)[148].

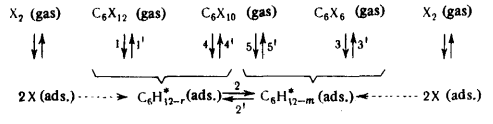
Under the usual conditions of the dehydrogenation of hydrocarbons, transfer processes apparently have a considerable influence and, at a sufficiently high temperature and for small dimensions of the catalyst pores, the rate-limiting stage may be diffusion of reactants.

The present author[61] investigated the effect of the porous structure of the alumina–chromium oxide catalyst on the conversion of hexane. Pore size was varied by

changing the intermicellar liquid. At temperatures above 470°C and for a dominant pore radius in the specimens less than 40 Å (grain size 2–5 mm), the rate of reaction was found to depend on pore size, i.e. transport processes influenced the rate of reaction. At the same time the experimental data are described fairly satisfactorily by the kinetic equation derived on the assumption that there is no diffusion-dependent inhibition.

Diffusion-dependent inhibition has also been noted by other workers: dehydrogenation of butane[7] and dehydrocyclisation of heptane[54] on alumina–chromium oxide catalysts, and dehydrogenation of cyclohexane on platinum deposited on alumina[149].

When dehydrogenation of cyclohexane and deuterium exchange involving it takes place simultaneously on the Ni–ZnO catalyst, the degree of exchange passes through a maximum with increase of temperature from 201° to 298°C, while the degree of hydrogenation increases. According to the scheme proposed by the authors[150],



(where X = H or D), the H–D exchange involving cyclohexane takes place via the intermediate surface compound $C_6H^*_{12}$ - r(ads.) and the dehydrogenation of cyclohexane involves in addition the intermediate surface compound $C_6H^*_{12}$ - m(ads.). Stages 1, 3, 4, and 5 and also the hydrogen adsorption and desorption stages are fast, while stage 2, in which one intermediate surface compound is converted into another, is slow and rate-determining.

The maximum in the rate of isotope exchange can be explained by the effect of the simultaneous occurrence of dehydrogenation on the concentration of $C_6H^*_{12}$ - r(ads.). Exchange reactions do not require the slow stages 2 or 2′ and therefore are fast even at low temperatures. With increase of temperature, the rate of dehydrogenation begins to rise sharply, which leads to a decrease of the degree of exchange. According to this mechanism, when benzene is introduced into the system, the rate of exchange falls but it does not change significantly when cyclohexene is added.

In a cordance with the data presented in Section III, 1, the compounds $C_6H^*_{12}$ - r(ads.) may be dissociatively adsorbed cyclohexene linked via two σ bonds and $C_6H^*_{12}$ - m(ads.) may be a π complex or a series of rapidly interconverted π complexes. The first surface compound may correspond to the edgewise (doublet mechanism) and the second to the planar (sextet mechanism) orientation of cyclohexane on the surface[150].

IV. VARIETIES OF THE DEHYDROGENATING EFFECT OF CATALYSTS

Dehydrogenation catalysts are extremely numerous and have a wide variety of chemical compositions. Thus, the compilation in Plate's book[31], already mentioned 51 elements as active components of catalysts for the aromatisation of paraffins and included the elements of almost all the Groups in the Periodic System, mainly Groups IV–VI. The number of known catalysts and the methods for their preparation are being continuously enlarged.

The same catalyst is capable of dehydrogenating hydrocarbons of various homologous series and structures, provided that it is sufficiently active. Thus fairly high yields of the products of the dehydrogenation of lower C_3–C_5 straight-chain paraffins, the aromatisation of C_6–C_7 straight-chain paraffins and cyclohexane, the dehydrogenation of ethylbenzene, olefins, branched paraffins, five-membered naphthenes, and alkyl-substituted hydroaromatic and other hydrocarbons have been obtained on alumina–chromium oxide–potassium oxide catalysts[9,32,70,91,151,152].

The problem of the effect of the catalyst on the relative yields of various dehydrogenation products is considered below.

1. Side and Secondary Non-dehydrogenation Reactions

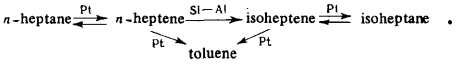
As a rule, there is no parallelism between the hydrogenating activity of catalysts and their activity in cracking and isomerisation reactions[7,31,153–155]. This suggests that the isomerisation and cracking reactions are not caused by the active centres responsible for dehydrogenation.

Numerous facts demonstrating the role of the acidity of the surface of alumina–chromium oxide catalysts in the isomerisation of paraffins have been adduced by Pines and coworkers[156].

The isomerisation of hydrocarbons on a dehydrogenation catalyst may be not only a side reaction but in certain cases may be an important stage in the dehydrogenation processes. Thus the aromatisation of paraffins with a chain length corresponding to not more than five carbon atoms must include the isomerisation stage.

When the alumina–chromium oxide catalyst is poisoned with pyridine or quinoline, there is not only a decrease in isomerising activity but also in the yields of the "abnormal" dehydrocyclisation products of octane (*m*- and *p*-xylenes), which are believed to form via a stage involving the isomerisation of octane to iso-octane or via intermediate cyclic compounds[116] (see also section III, 2).

On the other hand, under reforming conditions (hydrogen pressure, "bifunctional" catalysts), dehydrogenation may be one of the stages in the isomerisation of the hydrocarbon. Thus when heptane is brought into contact with an aluminosilicate or platinum deposited on alumina, isoheptanes are not formed. On the other hand, in the presence of these catalysts, the yield of isoheptanes is 24%. Toluene is also formed[157]. The isomerisation probably proceeds via intermediate dehydrogenation-hydrogenisation stages:



2. Dehydrogenation of Cyclohexane to Cyclohexene and Benzene

According to the multiplet theory, the dehydrogenation of cyclohexane with intermediate formation of bulk-phase cyclohexene proceeds on doublet centres, like the dehydrogenation of paraffins to olefins, and the direct dehydrogenation of cyclohexane to benzene, on sextet centres.

In early studies it was postulated that the doublet centres are characteristic of oxide catalysts and the sextet centres of metallic catalysts. Recently, with improved

experimental techniques for the investigation of catalytic reactions, an increasing number of facts have been observed, showing the intermediate formation of cyclohexene and cyclohexadiene in the presence of metallic catalysts (see Section II, 3)₹ On the other hand, Balandin and coworkers established that cyclohexane is dehydrogenated on oxide catalysts (α-Cr_2O_3), the process showing properties characteristic of sextet reactions. Therefore it is now recognised that doublet and sextet reactions can occur on both oxides and metals[15,16].

Another reason for the presence or absence of an intermediate unsaturated product in the bulk phase can probably be the capacity of the catalyst to form different types of metal–adsorbed hydrocarbon π or σ-bonds (see Section III, 1). For example the rates of desorption of cyclohexene linked to the surface by a single π bond or two σ bonds can differ markedly, as a result of which cyclohexene is evolved into the bulk phase in one case but not in the other.

3. Aromatisation and Formation of Olefins

It has been frequently postulated in the literature that the dehydrogenation of paraffins to olefins and their aromatisation on oxide catalysts take place on different active centres[31,53,158]. The fact that the olefin/aromatic hydrocarbon ratio varied within wide limits when catalysts of different chemical compositions were tested and the poisoning of an active aromatisation catalyst led mainly to decreased yields of the aromatic hydrocarbons and had much less influence on the yields of mono-olefins has been frequently put forward as the main evidence for the above hypothesis.

Thus, when the alumina–chromium oxide catalyst is poisoned with furfural or cyclopentadiene, the content of benzene in the catalytic reaction mixture in the dehydrogenation of hexane diminishes from 8–9 to less than 1% and that of alkenes from 18–19 to 6–7% (at 500°C)[53]. A similar situation was observed also in the coking of an aromatisation catalyst during the experiment[31] and when a dehydrocyclisation catalyst was poisoned with ethylene[158].

Since the dehydrogenation of higher paraffins to olefins was a more difficult problem than their aromatisation, the above concepts led to a large-scale development of studies on the choice of selective catalysts for the dehydrogenation of $C_{\geqslant 6}$ paraffins to olefins, which would be at the same time inactive in the aromatisation reaction. Various workers obtained catalysts which yielded olefins with high olefin/aromatic compound ratios or the product was altogether free of aromatic hydrocarbons[37-42,49,50,159-163]. For example, the dehydrogenation of hexane on a Cr_2O_3–AG-5 charcoal specimen at 430°C and a space velocity of 1.5 h^{-1} gave a yield of hexenes of about 10% for a selectivity of 90–95%, the yield of benzene being less than 1%.[42]

However, as pointed out for the first time by the present author[43], a high selectivity of catalysts for the formation of olefins is associated primarily with their low activity. The increase of the olefins/aromatic hydrocarbons ratio with decrease of the conversion of the starting material into dehydrogenation products is a common property of the process under consideration regardless of the causes responsible for the decrease of conversion, i.e. it is unimportant whether the decrease is a result of the deactivation of the catalysts or a change in temperature or in the contact time. Low conversions constitute a general condition for improved yields of intermediates such as olefins in the dehydrocyclisation of a paraffin.

Therefore in order to account for the experimental data on the poisoning of dehydrocyclisation catalysts as well as other data for the dependence of the relative yields of olefins and aromatic hydrocarbons on the chemical composition of catalysts, there is no need to resort to the hypothesis of the existence of two types of dehydrogenation active centres.

Previously, it was suggested[31,34] that aromatisation on oxide catalysts takes place via a doublet mechanism and on metals via a sextet mechanism. It was then believed that on oxide catalysts the dehydrocyclisation of paraffins takes place via the intermediate formation of olefins and on metals there is a direct conversion into aromatic hydrocarbons. These hypotheses were based mainly on the results of one of the early studies[30], according to which paraffinic hydrocarbons in the Synthine fraction are converted on a platinum/charcoal catalyst into aromatic hydrocarbons without the formation of olefins, the addition of which poisoned the catalyst for the aromatisation reaction.

However, subsequent studies on the aromatisation of individual hydrocarbons yielded numerous data indicating an analogy between the reactions of paraffins on oxide and non-oxide catalysts. Thus the present author's investigations[56,64,65] showed that the relative ability of platinum and also molybdenum sulphide and catalysts containing charcoals to promote dehydrogenation to olefins and aromatic hydrocarbons is almost indistinguishable from that of oxide catalysts (Fig. 2). The dehydrocyclisation of hexane on platinum and nickel as well as on oxide catalysts proceeds via the intermediate formation of olefins (Section II, 1,5). This suggests that one should not draw a distinction between metallic and oxide catalysts as regards the nature of active centres in dehydrocyclisation reactions.

The olefin/aromatic hydrocarbon ratios plotted against the sum of olefins and aromatic hydrocarbon yields on the basis of the results of different investigations give rise to a family of curves (Fig. 2) instead of a single curve as would have been expected in the ideal case if the overall conversion into dehydrogenation products constituted the only factor determining the yields of olefins and aromatic hydrocarbons. The divergence of the curves in Fig. 2 reflects the fact that the ratio of olefins and aromatic hydrocarbons in the products is influenced, apart from the overall conversion, by certain other factors. One of the principal causes of the divergence of the $P_O/P_a-(P_O+P_a)$ curves in Fig. 2 is probably the difference between the experimental methods employed in different studies or series of experiments[65]†.

In order to solve the problem of the effect of chemical composition on the relative capacity of catalysts to promote dehydrogenation to olefins and aromatic hydrocarbons (not associated with a change in activity), additional data are required which allow for other factors which may be important (for example secondary thermal reactions of the products, the presence of impurities in the raw material, etc.).

We shall consider from this point of view the results of one of the latest studies by Timofeeva[164] on the dehydrocyclisation of hexane and nonane on alumina–chromium

† This must be taken into account in the interpretation of experimental data. Otherwise, instead of the curves relating P_O, P_a, and P_p/P_a to P_O+P_a, more or less broad bands would have been obtained and the objection[164] against the use of the method in the study of theoretical problems would have been justified.

oxide catalysts promoted in different ways, represented by plots of the olefin/aromatic hydrocarbon ratio against the sum of olefins and aromatic hydrocarbons (Fig. 3).

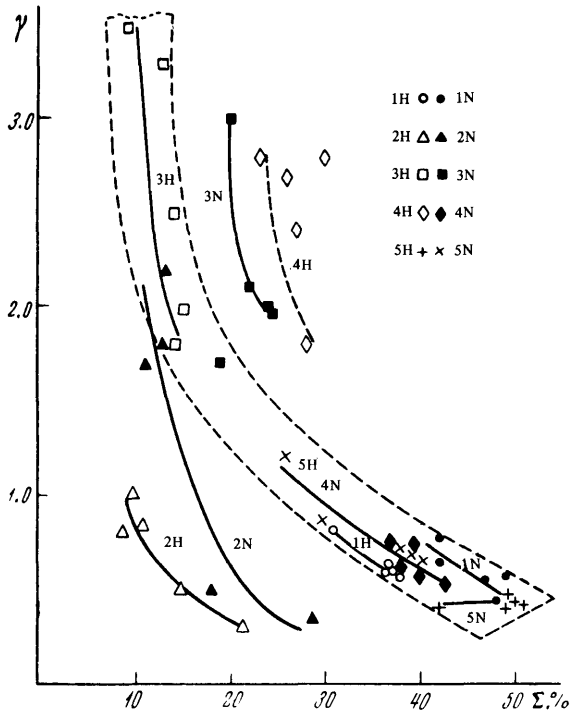


Figure 3. Plots of the ratios γ against the sum Σ of olefins and aromatic hydrocarbons based on Timofeeva's experimental data[164]; H—hexane; N—nonane: 1) $Al_2O_3-Cr_2O_3-Na_2O$; 2) K-16; 3) K-5; 4) $Al_2O_3-Cr_2O_3$; 5) $Al_2O_3-Cr_2O_3-K_2O$.

The majority of experimental points lie within a single narrow band, $P_o/P_a = f(P_o + P_a)$, in which two groups of points are distinguished: one of them refers to specimen *2* (K-16) with respect to hexane and nonane and the other to specimens *4* (alumina–chromium oxide catalyst) with respect to hexane and *3* (K-5) with respect to nonane.

Following Timofeeva[164], one could conclude on this basis that specimen *2* is somewhat less selective and specimens *3* and *4* somewhat more selective than specimens *1* and *5* (K and Na alumina–chromium oxide catalysts). However, the present author believes that such a conclusion would be premature. Indeed the results for hexane and nonane on specimens *3* and *4* do not agree. The data for hexane on specimen *4* are inconsistent with other results of the same author's[45,49,50], obtained on alumina–chromium oxide catalysts both with and without alkali metals, which fit satisfactorily on $P_o/P_a = f(P_o + P_a)$ curves (Fig. 2). The discrepancy between the olefin/-aromatic hydrocarbon ratios in Timofeeva's work[164] is probably associated with the method of analysis of the products, which was not the same in all the experiments.

The conclusion that the active centres for the dehydrogenation and aromatisation of paraffins are of the same type is consistent with the experimental data for the catalytic properties of various substances.

The most active catalysts in the dehydrogenation of lower paraffins to olefins and the aromatisation of $C_{\geq 6}$ paraffins are promoted alumina–chromium oxide catalysts and as a rule the additives introduced into the catalyst or the change in the method of preparation or the treatment of the catalyst have similar effects (activation, increase of activity with time of operation, etc.) on both reactions and also on the dehydrogenation of six-membered naphthenes (Table 3).

Table 3. Effect of certain additives on the properties of dehydrogenation catalysts.

Starting material	Additives	Hydrocarbons	Effect on catalytic properties	Refs.
$Cr_2O_3 - Al_2O_3$	Alkali metal oxides	C_3–C_7 paraffins, cyclohexane, isopentenes	Increase of activity	165–175
ditto	CaO, SrO, BaO	Butane, heptane, cyclohexane	Ditto	51, 167, 176, 177
»	Fe oxides	Butane, hexane	Decrease of activity	37, 178
»	Alkali metal oxides	Isopentane, heptane, cyclohexane	Retardation of attainment of steady activity	168, 173, 179
»	K_2O	Butane, heptane	Decrease of coke formation	167, 180
$MoO_3 - Al_2O_3$	K, Rb, Cs, Ce, Nd, and Hf oxides	Hexane, heptane cyclohexane	Increase of activity	179, 181, 182
$Pt - Al_2O_3$	Na_2O	Hexane, cyclohexane	Activity passes through a maximum	183
$Pd-Al_2O_3$ with added HF	Rare-earth oxides	Hexane, cyclohexane, methylcyclohexane	Increase of activity	185

4. Dehydrogenation of Hydrocarbons with and without a Double Bond

On the basis of the product proportions in the conversion of cyclohexane into benzene and methylcyclopentane and of methylcyclopentane into benzene and cyclohexane, Haensel et al.[186] concluded that, on treatment with sulphur-containing compounds, the activity of a fluorinated alumina–platinum catalyst for the stage involving the conversion of cyclohexene and benzene is lost but its activity in the conversion of cyclohexane into cyclohexene is not lost and therefore the above reactions take place on different active centres. The subdivision of catalyst active centres into those which dehydrogenate paraffins and olefins was adopted by Pines[156] and also certain earlier investigators.

However, when the $Pt-F-Al_2O_3$ catalyst is poisoned with thiophen, a sharper decrease of the yield of benzene is observed in the dehydrogenation of cyclohexane than in the dehydrogenation of cyclohexene[187], which is inconsistent with the data of Haensel et al.[186].

The conclusion that there is no sufficient evidence for a subdivision of active centres into those for the dehydrogenation of paraffins and olefins is arrived at by analysing the experimental data on the effect of chemical composition on the activity of the catalyst. As a rule, all active catalysts for the dehydrogenation of paraffins are also active in the dehydrogenation of olefins. That this is so is shown, for example, by data on the intermediate formation of olefins in the aromatisation of paraffins, which would not otherwise have occurred.

A parallelism is observed between the relative reactivities of saturated and unsaturated hydrocarbons on catalysts of different types on the one hand and on the relative activities of various catalysts in the dehydrogenation of these hydrocarbons on the other. Thus the reactivity of hydrocarbons increases with the degree of unsaturation on alumina–chromium oxide and alumina–molybdenum oxide catalysts, platinum, nickel, etc. (Tables 1 and 2). The differences between the specific activities of individual metals in relation to the dehydrogenation of cyclohexane, cyclohexene, and cyclohexadiene reach several powers of 10.[87] If one neglects the comparatively small changes (by a factor of 2–3), the specific activities of metals in the dehydrogenation of all three hydrocarbons can be arranged in the following sequence:

$$Pd \approx Pt \approx Rh \approx Ir > Ni > Ag \approx Cu \approx Co \approx Fe.$$

The hypothesis that the active centres for the dehydrogenation of saturated and unsaturated hydrocarbons are of the same type does not of course imply that the same catalysts should be optimal for both reactions.

The individual characteristics of the hydrocarbons can be reflected in side reactions and secondary transformations of the products. For example, the capacity of butadiene to cause the coking of the catalyst is much higher than that of butane or butene[183]. To reduce coke formation, the dehydrogenation of butene to butadiene is carried out in the presence of water vapour, which poisons alumina–chromium oxide catalysts. Therefore butenes are not dehydrogenated on the alumina–chromium oxide catalyst, but on other catalysts, which are stable in relation to water, for example the ion oxide–chromium oxide–potassium oxide catalyst.

Other factors can of course also be important, for example the ratio of the rates of the individual stages. Thus if the rate-limiting stage in the dehydrogenation of the less reactive of two hydrocarbons being compared is the chemical reaction, then the rate of dehydrogenation of the more reactive hydrocarbon on the same catalyst may be affected also by factors such as the rate of adsorption or of internal diffusion. Therefore the optimum catalysts for the two hydrocarbons should be different.

5. C_5 Dehydrocyclisation

A parallelism is not observed between the activities of various catalysts in relation to the C_5 dehydrocyclisation of paraffins and other reactions involving the dehydrogenation of hydrocarbons. Thus the activity of platinum on charcoal in the C_5 dehydrocyclisation of isooctane to 1,1,3-trimethylcyclopentane is independent of the temperature at which the catalyst is formed in the range between −10° and 40°C but, when the platinum content in the catalyst diminishes from 20 to 5%, its capacity for C_5 dehydrocyclisation falls sharply[189]. On the other hand the activity of the platinum/charcoal catalyst in the dehydrogenation of cyclohexane passes through a maximum in the first case and in the second case remains virtually unchanged.

These data, indicating that the C_5 dehydrocyclisation of paraffinic hydrocarbons to naphthenes takes place on different active centres than the dehydrogenation of cyclohexane, are consistent with the experimental data on the selection of catalysts. It is known that on many active dehydrogenation catalysts—metals (palladium, osmium, and iridium on charcoal, nickel on charcoal and alumina, etc.) and oxides—it has not so far been possible to achieve the C_5 dehydrocyclisation of paraffins, which occurs only on platinum[8,102,190]. This does not apparently apply to the C_5 dehydrocyclisation of olefins, which, in contrast to paraffins, takes place not only on platinum but also on the alumina–chromium oxide catalyst (for example, the C_5 dehydrocyclisation of dimethylpentadiene to dimethylcyclopentadiene[191].

V. MODERN HYPOTHESES CONCERNING THE NATURE OF THE ACTIVE SURFACE OF DEHYDROGENATION CATALYSTS

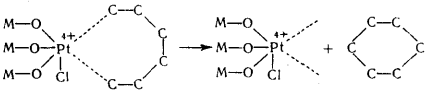
1. Platinum and Certain Metallic Catalysts

The catalytic activity of metals in dehydrogenation reactions is due to their capacity to form chemical bonds with hydrocarbon molecules in the gas phase. According to modern data[106], an olefin (A) adsorbed via two σ bonds on a transition metal is formed by the rehybridisation of the carbon atoms involved in the olefinic bond to sp^3 hybridisation with subsequent formation of two σ bonds between the carbon and metal atoms. In an olefin (B) adsorbed via a π bond, the carbon atoms are in a state of sp^2 hybridisation, the atoms and groups linked to the carbon atoms being located in almost the same plane, parallel to the surface. One surface metal atom is directly involved in the formation of the π bond. The problem of the role of surface chemical compounds formed by the catalyst metal and the carrier of the adsorbed reactant has been widely discussed in recent years. In many cases the role of active reaction centres is attributed to these compounds.

McHenry et al.[192] found in an alumina–platinum catalyst a platinum complex which may be extracted by dilute HF solution or acetylacetone. In the catalyst obtained by impregnating alumina with H_2PtCl_6 solution, the soluble platinum complex may contain also chlorine and a promoting agent—an alkali metal. Platinum may pass into an acid-soluble state not only by forming a complex with aluminium but also as a result of non-stoichiometric absorption of oxygen[193]. Therefore the soluble platinum contained in catalysts is very inhomogeneous in composition.

A partial correlation between dehydrogenating activity and the amount of soluble platinum in the catalyst has been observed in a number of studies.

Bursian et al.[194] attribute to the complex of the alumina–platinum catalyst a structure with a coordination-unsaturated Pt^{4+} ion; its participation in the dehydrocyclisation reaction takes place as shown below (for hexane):



(D)

where M is the cation of the carrier or a structural promoting agent. Thus the catalytic effect of centres containing Pt^{4+} ions is attributed to coordination properties.

A positive aspect of the hypotheses concerning the platinum complex as an active component of the catalyst is that they reflect the common features of metallic and oxide catalysts: the activity of the latter is also attributed to the presence of cations with a definite valence (see below).

However, the soluble complex present in the alumina–platinum catalyst may decompose on reduction of the catalyst to yield metallic platinum, while the activity of the catalyst is fairly high under these conditions[193]. This implies that the presence of the platinum complex is not an essential factor determining the activity of the catalyst. This is also suggested by the catalytic activity of pure metals without a carrier. A specific objection to scheme (D) is that, according to the available data, the initial intermediates in the aromatisation of hexane are hexenes and hexadienes while cyclisation takes place only subsequently and is a rapid step (Section II, 1 and 5). Therefore if the Pt^{4+} ions entering into the complex were effective only in the cyclisation stage of the aromatisation of hexane, they would behave as weak centres and would not play a significant role in catalysis.

The problem of the nature of soluble platinum is closely related to the problem of the degree of its dispersion. Thus, according to Kraft and Spindler[193], platinum dispersed to the maximum extent becomes completely solubilised by treatment with air at 500°C and after the reduction of the catalyst the degree of dispersion of platinum increases still further. The degree of dispersion of platinum and other metals on a carrier can become very high, up to atomic dispersion[195-197].

The structure of the platinum as well as the nature of the carrier were of secondary importance compared with the surface area in tests on the activity of alumina–platinum catalysts compared in different ways and containing different amounts of soluble platinum[193]. Thus the observed correlation between the content of the platinum–aluminium complex and the activity of the catalyst may be accounted for by the fact that the formation and subsequent decomposition of the complex promotes an increase in the degree of dispersion of platinum.

The affect of alkali metal promoting agents in alumina–platinum catalysts consists, apart from supressing the acid centres, in preventing the recrystallisation of platinum because the promoting agent is involved in the formation of a soluble complex.

Hypotheses have been put forward concerning the catalytic role of compounds formed by platinum and the carrier—charcoal ("pseudosandwich" complexes or a combination of platinum crystallites and graphite sextets[198-200]). However, there are still very few data on this problem.

According to Wood[201], adsorbed hydrogen is required for the dehydrogenation of cyclohexane on a metallic catalyst. This conclusion follows from the fact that, under the conditions investigated, the reaction ceased when hydrogen was completely removed from the reactor. The experiments were performed at 125°C and hydrogen was evacuated via a membrane made of the material of the catalyst (a palladium–silver alloy) which is permeable to it. Wood believes[201] that the active centre for the dehydrogenation reaction on the catalyst investigated is an adsorbed hydrogen atom.

2. Chromium Oxide and Certain Oxide Catalysts

According to modern concepts, the hydrocarbon adsorbed on a metal oxide is linked to metal ions and not to oxygen[16,202]. The formation of a bond between the adsorbed hydrocarbon and a transition metal ion takes place via unfilled *d* levels of the metal or via the formation of an *s*–*d* bond.

Some investigators[167,203] established a correlation between the amount of Cr^{6+} contained in the alumina–chromium oxide catalyst and its dehydrogenating activity and in this connection suggested that the hexavalent chromium present in the catalyst acts as a carrier of catalytic activity.

However, this hypothesis is not adequately justified, since under the reaction conditions the reduction of Cr^{6+} and other possible compounds in which the valence of chromium is greater than 3 takes place very rapidly[204], while the activity of the alumina–chromium oxide catalysts persists for a long time. In the regeneration of the alumina–chromium oxide catalyst in a stream of carbon dioxide, higher chromium oxides are not formed and yet such catalysts are not less active than those regenerated with air[205].

The amount of Cr^{6+} in the catalyst depends on the conditions and duration of oxidation and on the nature of the promoting agent. The correlation between the activity and amount of Cr^{6+} in the catalyst observed in some cases might have been due to the fact that the reduction of higher chromium oxides under the reaction conditions is nevertheless not entirely complete and the residual non-reduced chromium, being a constituent of, for example, a spinel with the aluminate of the added metal, has a promoting effect.

Van Reijen et al.[147] concluded from measurements of the magnetic moments and ESR signals of alumina–chromium oxide catalysts subjected to various types of oxidation–reduction treatment that the higher chromium oxides are reduced in a stream of dry hydrogen, i.e. under conditions favouring the formation of an active alumina–chromium oxide catalyst, not only to tervalent but also to bivalent chromium. The proportions of the bivalent and tervalent chromium oxides are determined by the equilibrium

$$2\,CrO + H_2O \rightleftarrows Cr_2O_3 + H_2\,. \qquad (3)$$

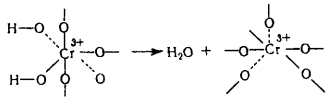
Further experimental evidence for the formation of bivalent chromium in the reduction of alumina–chromium oxide catalysts was obtained by Rubinshtein and coworkers[206]. Thus hydrogen was evolved on treatment of carefully reduced alumina–chromium oxide catalysts with water. When a catalyst reduced with deuterium was treated with water, only protium was detected in the gas. This implies that the hydrogen is formed in the decomposition of water by Cr^{2+} ions, which have reducing properties, and is not evolved as a result of desorption by water.

The amount of Cr^{2+} ions calculated from the volume of hydrogen evolved agreed approximately with the amount of hydrocarbon chemisorbed on the catalyst. On the other hand, the amount of Cr^{3+} ions present in the catalyst was approximately 40 times greater[207].

However, $CrCl_2$ is much less active in the dehydrocyclisation reaction than $CrCl_3$.[208] There are also other data which do not agree with the hypothesis that Cr^{2+} ions behave as dehydrogenation centres. Thus, according to the conditions for equilibrium in reaction (3), Cr^{2+} ions should not be present in the catalyst when the partial pressure of water vapour in the gas is greater than 1.7×10^{-3} mmHg. At the same time, at a water vapour pressure in the reacting gas of 22 mmHg, the alumina–chromium oxide catalyst retains a considerable activity[205]. On the other hand, when the partial pressure of water vapour in the gas was reduced to 3×10^{-4} mmHg, the catalytic activity fell.

The d^3 cationic structure is particularly active in reactions on semiconductors involving hydrogen[209]. The chromium ion in Cr_2O_3 has this electronic configuration. According to Kazanskii and Shvets[210], the active dehydrogenation centres are coordination-unsaturated Cr^{3+} ions.

In specimens containing adsorbed water, all the Cr^{3+} ions are in an octahedral configuration. When one water molecule is eliminated, the coordination is reduced to that of a square pyramid:



and the removal of subsequent molecules can lead to a further decrease of coordination. In order to discover if coordination-unsaturated Cr^{3+} ions present on the surface of catalysts from which water had been desorbed at high temperatures behave as dehydrogenation centres, additional studies are necessary.

Some investigators have suggested that the activity of alumina–chromium oxide catalysts is due to the formation of a specific mixed structure by the components of the catalysts. Krylova et al.[211] observed a maximum styrene content in the catalytic reaction mixture obtained in the dehydrogenation of ethylbenzene and a maximum paramagnetic susceptibility when the chromium content in the catalyst was about 2%. The maximum specific susceptibility at a low chromium content is probably associated with the formation of a Cr_2O_3 δ-phase. As regards the activity of the catalyst, one should bear in mind that chromium oxide is fairly active by itself[7,16] and the mixed alumina–chromium oxide structure would have had to be very active to play a significant role in catalysis.

However, the specimens tested[211] were relatively inactive (the styrene content in the catalytic reaction mixture was only 2–2.5 times higher than in the thermal reaction) and probably their acidity was high. Therefore the decreased yield of styrene observed when the chromium content is increased above 2% may be attributed to the formation of side products. Indeed, in the dehydrogenation of less reactive hydrocarbons (paraffins), a maximum activity was not observed in the presence of amounts of added chromium as low as 2%.[7]

Buyanov et al.[212] attribute the activity of iron oxide–chromium oxide–zinc oxide catalysts in the dehydrogenation of butenes to the presence of a chromium spinel in the catalyst composition. However, iron(III) [38,213] and zinc oxides [214] exhibit a considerable activity in the absence of chromium, let alone chromium oxide itself. Therefore the active centres in iron oxide–chromium oxide–zinc oxide catalysts can probably be the ions of any metal entering into the composition of the catalyst. On the other hand, the formation of solid solutions and mixed structures is more likely to promote the stability of the catalyst, preventing recrystallisation and undesirable chemical transformations of the catalyst, which may be particularly important in the dehydrogenation of butene and other olefins in view of the severe operating conditions of these catalysts.

The available data also do not justify the hypothesis that the dehydrogenating capacity of chromium oxide–magnesium oxide or chromium oxide–silica gel catalysts is due to the formation of mixed active structures[41,215]. The nature of the activating effect of small amounts of water remains obscure. Poorly dehydrated dehydrogenation catalysts are inactive[7]. When the water content in the starting material is increased, the activity of alumina–chromium oxide catalysts passes through a maximum.

One may suppose that water enters into the composition of the active centres of the catalyst and has a promoting effect. The reversible poisoning of the alumina–chromium oxide catalyst by larger amounts of water, can be explained by the blocking of the active centres. Indeed preliminary adsorption of water suppresses the chemisorption of hexane on the alumina–chromium oxide catalyst[216]. In this case there is only physical adsorption of hexane, which is not accompanied by dehydrocyclisation.

---o0o---

The data examined show that the problem of the structure of the active centres remains controversial even for the most thoroughly investigated catalysts. In dehydrogenation reactions, metal atoms (in metallic catalysts) metal atoms or ions (in metallic adsorption catalysts), and metal ions (in oxide catalysts) can behave as carriers of catalytic activity. The composition of the active centres probably includes also chemisorbed atoms or molecules (hydrogen in the case of metallic catalysts and water in the case of the chromium oxide catalyst). The molecule undergoing dehydrogenation can be linked to the surface via one- two-, or multipoint adsorption with different types of chemical bonding (the σ bond or different varieties of coordinate bonds).

Nevertheless only a few types of dehydrogenating effect of catalysts on hydrocarbons have been observed. There is sufficient evidence to suppose that the dehydrogenation and aromatisation of paraffins takes place at the same active centres and probably this can also be said of paraffins, olefins, and naphthenes (except for the direct conversion of six-membered naphthenes into aromatic hydrocarbons).

In all these cases, where there is an analogy in the action of catalysts of different types and in the conversion of hydrocarbons of different homologous series and structures, preference should be given to the model involving an intermediate compound with one- or two-point adsorption rather than multipoint adsorption, and, among the existing hypotheses concerning the structure of the active centres, those which attribute the activity to the material of the catalyst itself and the degree of its dispersion rather than to its various compounds with carriers are to be preferred. Probably an active catalyst, such as, for example, platinum or chromium oxide, retains a considerable dehydrogenating capacity on all carriers of different types capable of ensuring that its degree of dispersion remains stable.

Conversely, the more specific dehydrogenation reactions (C_5 dehydrocyclisation of paraffins, dehydrogenation of naphthenes without an intermediate formation of cycloolefins) can be accounted for by the effect of multipoint active centres or a different type of bonding between the adsorbed molecule and the catalyst surface compared with other dehydrogenation reactions.

REFERENCES

1. K. Kearby, Symposium, "Khimiya Uglevodorodov Nefti" (The Chemistry of Petroleum Hydrocarbons), Gostoptekhizdat, 1958, Vol. 2, p. 189.
2. K. Kearby, in "Catalysis" (Edited by P. H. Emmett), New York, 1955, Vol. 3, p. 453.

3. H. Steiner, Symposium, "Kataliz v Neftekhimicheskoi i Neftepererabotayushchei Promyshlennosti" (Catalysis in the Petrochemical and Petroleum-processing Industry), Gostoptekhizdat, 1959, p. 270.
4. O. B. Livtin and I. L. Fridshtein, Khim. Prom., No. 8, 38 (1955).
5. V. I. Komarewsky, C. H. Riesz, and F. L. Morritz, Symposium, "Kataliticheskie, Fotokhimicheskie i Elektroliticheskie Reaktsii" (Catalytic, Photochemical, and Electrolytic Reactions), Inostr. Lit., Moscow, 1960, p. 133.
6. B. N. Dolgov, Kataliz v Organicheskoi Khimii" (Catalysis in Organic Chemistry), Leningrad, 1959.
7. G. D. Lyubarskii, Uspekhi Khim., 27, 316 (1958).
8. B. A. Kazanskii and A. L. Liberman, Symposium, "5-i Mezhdunarodnyi Neftyanyi Kongress" (The Fifth International Petroleum Congress), Gostoptekhizdat, Moscow, 1961, p. 241.
9. N. I. Shuikin and T. I. Naryshkina, Symposium, "5-i Mezhdunarodnyi Neftyanyi Kongress" (The Fifth International Petroleum Congress), Gostoptekhizdat, Moscow, 1961, p. 261.
10. J. Bradbury, W. Keely, T. O'Hara, and R. Vance, Ind. Eng. Chem., 51, 1111 (1959).
11. H. Connor, Chem. Ind. (London), 1454 (1960).
12. O. Benn, Chem. Tech. (Berlin), 12, 706 (1960).
13. G. F. Hornaday, F. M. Ferrell, and G. A. Mills, Symposium, "Noveishie Dostizheniya Neftekhimii i Neftepererabotki" (Latest Advances in Petrochemistry and Petroleum Processing), Gostoptekhizdat, 1963, Vol. 4, p. 275.
14. C. H. Riesz and F. L. Morritz, Symposium, "Noveishie Dostizheniya Neftekhimii i Neftepererabotki" (Latest Advances in Petrochemistry and Petroleum Processing), Gostoptekhizdat, 1963, Vol. 4, p. 180.
15. A. A. Balandin, "Mul'tipletnaya Teoriya Kataliza" (The Multiplet Theory of Catalysis), Izd. Moskov. Gos. Univ., 1963, Part 1.
16. A. A. Balandin, "Mul'tipletnaya Teoriya Kataliza" (The Multiplet Theory of Catalysis), Izd. Moskov. Gos. Univ., 1964, Part 2.
17. A. D. Sulimov, "Kataliticheskii Reforming Benzinov" (Catalytic Reforming of Motor Fuels), Izd. Khimiya, 1964.
18. I. Ya. Tyuryaev, "Fiziko-khimicheskie i Tekhnologicheskie Osnovy Polucheniya Divinila" (Physicochemical and Technological Principles of the Synthesis of Butadiene), Izd. Khimiya, 1966.
19. V. T. Sklyar, E. V. Lebedev, and V. A. Zakupra, "Vysshie Mono-olefiny" (Higher Mono-olefins), Izd. Tekhnika, Kiev, 1964.
20. J. Reidel, Oil Gas J., 55, No. 45, 166, No. 48, 87, No. 49, 114, No. 50, 110 (1957).
21. L. Nowakowski, Wiadomosci Chem., 17, 553 (1963).
22. H. Hansch, Chem. Rev., 53, 353 (1953).
23. A. Z. Shikhmamedbekova, "Degidrirovanie Izopentenov v Izopren" (Dehydrogenation of Isopentenes to Isoprene), Izd. Azerneshr., Baku, 1963.
24. O. D. Sterligov, T. G. Olfer'eva, and N. F. Kononov, Uspekhi. Khim., 36, 1200 (1967) [Russ. Chem. Rev., No. 7 (1967)].
25. V. K. Skarchenko, Uspekhi. Khim., 37, 3 (1968) [Russ. Chem. Rev., No. 1 (1968)].
26. R. A. Buyanov, "Zakoksovanie i Regeneratsiya Katalizatorov Degidrirovaniya" (The Coking and Regeneration of Dehydrogenation Catalysts), Izd. Nauka, Novosibirsk, 1968.
27. R. Pitkethly and H. Steiner, Trans. Faraday Soc., 35, 979 (1939).
28. R. D. Obolentsev and Yu. N. Usov, Zhur. Obshch. Khim., 21, 1438 (1951).
29. I. I. Levitskii, Izd. Akad. Nauk SSSR, Otd. Khim. Nauk, 425 (1959).
30. B. A. Kazanskii, S. R. Sergienko, and N. D. Zelinskii, Dokl. Akad. Nauk SSSR, 27, 664 (1940).
31. A. F. Plate, "Kataliticheskaya Aromatizatsiya Parafinov" (Catalytic Aromatisation of Paraffins), Izd. Akad. Nauk SSSR, 1948.
32. M. Ya. Kagan, L. A. Erivanskaya, and I. V. Trofimova, Dokl. Akad. Nauk SSSR, 82, 913 (1952).
33. Kuo Hsie-Shien, Sci. Sinica, 11, 1075 (1962).
34. S. R. Sergienko, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 177 (1941).
35. B. A. Kazanskii, A. L. Liberman, and M. I. Batuev, Dokl. Akad. Nauk SSSR, 61, 67 (1948).
36. E. A. Timofeeva, N. I. Shuikin, Yu. N. Plotnikov, and V. M. Kleimenova, Dokl. Akad. Nauk SSSR, 125, 1272 (1959).
37. V. K. Skarchenko, P. N. Galich, I. T. Golubchenko, V. S. Frolova, and V. P. Musienko, Kinetika i Kataliz, 5, 548 (1964).
38. V. K. Skarchenko, P. M. Galich, V. P. Musienko, V. S. Frolova, and I. T. Golubchenko, Symposium, "Neftekhimiya" (Petrochemistry), Izd. Akad. Nauk Turkman SSR, Ashkhabad, 1963, p. 76.
39. V. K. Skarchenko, V. S. Frolova, I. T. Golubchenko, V. P. Musienko, and P. N. Galich, Kinetika i Kataliz, 5, 932 (1964).
40. V. S. Frolova, R. I. Polataiko, V. K. Skarchenko, V. P. Musienko, and P. N. Galich, Neft. i Gaz. Prom., No. 3, 54 (1964).
41. V. P. Musienko, R. I. Polataiko, V. K. Sharchenko, V. S. Frolova, and P. N. Galich, Ukrain. Khim. Zhur., 30, 915 (1964).
42. O. D. Konoval'chikov, P. N. Galich, A. A. Petrov, and V. K. Skarchenko, Kinetika i Kataliz, 5, 561 (1964).
43. V. K. Skarchenko, Dokl. Akad. Nauk Ukrain. SSR, 1058 (1963).
44. W. Mattox, J. Amer. Chem. Soc., 66, 2059 (1944).
45. Yu. N. Plotnikov, V. S. Smirnov, E. A. Timofeeva, V. M. Kleimenova, and N. I. Shuikin, Kinetika i Kataliz, 2, 267 (1961).
46. E. A. Timofeeva, V. S. Smirnov, and Yu. N. Plotnikov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1433 (1959).
47. B. A. Kazanskii, A. Z. Dorogochinskii, M. I. Rozengart, A. V. Lyuter, and M. G. Mitrofanov, Kinetika i Kataliz, 2, 258 (1961).
48. A. F. Plate and G. A. Tarasova, Zhur. Obshch. Khim., 13, 36 (1943).
49. E. A. Timofeeva, N. I. Shuikin, T. P. Dobrynina, Yu. N. Plotnikov, and G. S. Petryaeva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 480 (1960).
50. E. A. Timofeeva, N. I. Shuikin, T. P. Dobrynina, G. S. Petryaeva, and Yu. N. Plotnikov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 292 (1960).
51. B. A. Kazanskii, M. I. Rozengart, and Z. F. Kuznetsova, Dokl. Akad. Nauk SSSR, 127, 1228 (1959).
52. B. A. Kazanskii, M. I. Rozengart, and L. A. Freiberg, Dokl. Akad. Nauk SSSR, 134, 1360 (1960).
53. E. A. Timofeeva, N. I. Shuikin, and T. P. Dobrynina, Kinetika i Kataliz, 2, 574 (1961).
54. M. I. Rozengart and B. A. Kazanskii, Dokl. Akad. Nauk SSSR, 119, 716 (1958).
55. A. I. Adzhieva, Izv. Vys. Ucheb. Zaved., Neft' i Gaz., No. 11, 89 (1959).
56. V. K. Skarchenko and N. S. Kruglikova, Neft. i Gaz. Prom., No. 4, 42 (1967).

57. E. A. Timofeeva, N. I. Shuikin, Yu. N. Plotnikov, and V. M. Kleimenova, Dokl. Akad. Nauk SSSR, 129, 128 (1959).
58. E. A. Timofeeva, V. S. Smirnov and V. I. Zaeva, Kinetika i Kataliz, 1, 300 (1960).
59. R. I. Polataiko, N. S. Kruglikova, V. S. Frolova, P. N. Galich, and V. K. Skarchenko, Neft. i Gaz. Prom., No. 2, 53 (1965).
60. N. R. Bursian, S. B. Kogan, and Z. A. Davydova, Kinetika i Kataliz, 4, 783 (1963).
61. O. D. Konoval'chikov, P. N. Galich, V. P. Musienko, V. K. Skarchenko, and A. A. Petrov, Kinetika i Kataliz, 5, 350 (1964).
62. O. D. Konoval'chikov and P. N. Galich, Symposium, "Neftepererabotka i Neftekhimiya" (Petroleum Processing and Petrochemistry), Izd. Naukova Dumka, Kiev, 1967, No. 2, p. 80.
63. V. K. Skarchenko, Symposium, "Neftekhimiya" (Petrochemistry), Izd. Akad. Nauk Ukrain. SSR, Kiev, 1964, p. 5.
64. V. K. Skarchenko, "Tezisy Dokladov Vsesoyuznogo Soveshchaniya po Glubokomu Mekhanizmu Kataliticheskikh Reaktsii" (Abstracts of Reports at the All-Union Conference on the Detailed Mechanism of Catalytic Reactions), Izd. Akad. Nauk SSSR, Moscow, 1964, p. 61.
65. V. K. Skarchenko, Probl. Kinetiki i Kataliza, 12, 207 (1968).
66. O. D. Konoval'chikov, Candidate's Thesis, Institute of Petrochemical Processes of the Azerbaijan SSR, Baku, 1964.
67. Yu. N. Plotnikov, E. A. Timofeeva, and N. I. Shuikin, Neftekhimiya, 4, 225 (1964).
68. A. F. Plate and G. A. Tarasova, Zhur. Obshch. Khim., 22, 765 (1952).
69. Yu. M. Zhorov, G. M. Panchenkov, and L. G. Rulyk, Neftekhimiya, 7, 868 (1967).
70. A. A. Petrov, Neftekhimiya, 1, 604 (1961).
71. V. G. Lipovich, O. I. Shmidt, M. A. Lur'e, and I. V. Kalechits, Neftekhimiya, 9, 661 (1969).
72. Z. Paal and P. Tetenyi, Kem. Közl., 28, No. 1, 13 (1967); Ref. Zhur. Khim., 6P134 (1968).
73. Z. Paal and P. Tetenyi, Acta Chim. Acad. Sci. Hung., 54, 175 (1968).
74. G. M. Panchenkov, Yu. M. Zhorov, A. S. Kazanskaya, I. M. Kolesnikov, and K. A. Venkatachalam, Trudy Inst. Neftekhim. Gaz. Prom. im Gubkina, 51, 154 (1964).
75. A. A. Balandin, M. B. Neiman et al., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 157 (1957).
76. A. A. Balandin, O. K. Bogdanova, G. V. Isagulyants, M. B. Neiman, and E. I. Popov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 18 (1958).
77. I. Block [tentative spelling], "4-i Mezhdunarodnyi Kongress po Katalizu" (The Fourth International Congress on Catalysis), Moscow, 1968.
78. Z. Paal and P. Tetenyi, Acta Chim. Acad. Sci. Hung., 55, 273 (1968).
79. P. Tetenyi, L. Babernics, and S. Thomson, Acta Chim. Acad. Sci. Hung., 34, 335 (1962).
80. G. V. Isagulyants, E. N. Komarova, and A. A. Balandin din, Dokl. Akad. Nauk SSSR, 164, 1307 (1965).
81. Yu. I. Derbentsev, M. A. Markov, G. V. Isagulyants, Kh. M. Minachev, and A. A. Balandin, Dokl. Akad. Nauk SSSR, 155, 128 (1964).
82. G. V. Isagulyants, M. A. Ryashentseva, Yu. I. Derbentsev, Kh. M. Minachev, and A. A. Balandin, Neftekhimiya, 4, 229 (1964).
83. N. I. Shuikin, T. I. Naryshkina, and Z. A. Rashchupkina, Neftekhimiya, 6, 22 (1966).
84. N. I. Shuikin and I. I. Levitskii, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1003 (1953).
85. M. I. Rozengart, E. S. Mortikov, and B. A. Kazanskii, Dokl. Akad. Nauk SSSR, 166, 619 (1966).
86. G. V. Isagulyants, A. A. Balandin, Yu. I. Derbentsev, and E. N. Komarova, Kinetika i Kataliz, 5, 171 (1964).
87. P. Tetenyi and K. Schachter, Acta Chim. Acad. Sci. Hung., 50, 129 (1966).
88. Yu. N. Usov, E. V. Skvortsova et al., Neftekhimiya, 7, 172 (1967).
89. P. Tetenyi and K. Schachter, Acta Chim. Acad. Sci. Hung., 29, 199 (1961).
90. O. K. Bogdanova, A. A. Balandin, and I. P. Belomestnykh, Dokl. Akad. Nauk SSSR, 133, 841 (1960).
91. E. A. Timofeeva, N. I. Shuikin et al., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 893 (1958).
92. M. I. Rozengart, V. G. Bryukhanov, V. L. Polinin, Yu. G. Dubinskii, and B. A. Kazanskii, Neftekhimiya, 9, 693 (1969).
93. I. I. Levitskii and N. I. Shuikin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1012 (1953).
94. M. I. Rozengart, E. S. Mortikov, and V. A. Kazanskii, Dokl. Akad. Nauk SSSR, 158, 911 (1964).
95. Z. Paal and M. I. Rozengart, Acta Chim. Acad. Sci. Hung., 49, 395 (1966).
96. Z. Paal and P. Tetenyi, Acta Chim. Acad. Sci. Hung., 53, 193 (1967).
97. Z. Paal and P. Tetenyi, Acta Chim. Acad. Sci. Hung., 58, 105 (1968).
98. O. K. Bogdanova, A. A. Balandin and I. P. Belomestnykh, Izv. Akad. Nauk SSSR, Ser. Khim., 2100 (1963).
99. A. L. Liberman, Kinetika i Kataliz, 5, 128 (1964).
100. B. A. Kazanskii, A. L. Liberman, G. V. Loza, and T. V. Vasina, Dokl. Akad. Nauk SSSR, 128, 1188 (1959).
101. G. R. Lester, J. Cat., 13, 187 (1969).
102. Yu. V. Fomichev, I. V. Gostunskaya, and B. A. Kazanskii, Dokl. Akad. Nauk SSSR, 180, 383 (1968).
103. H. Pines, C. Goetschel, and S. Csicsery, J. Org. Chem., 28, 2713 (1963).
104. K. Lewis and H. Steiner, J. Chem. Soc., 3080 (1964).
105. S. Benson and R. Shaw, Trans. Faraday Soc., 63, 985 (1967).
106. G. C. Bond and P. B. Wells, Symposium, "Kataliz. Fiziko-khimiya Geterogennogo Kataliza" (Catalysis. Physical Chemistry of Heterogeneous Catalysis), Izd. Mir, Moscow, 1967, p. 351.
107. A. Palazov, A. Andreev, and D. Shopov, Compt. rend. Acad. bulg. Sci., 18, 1145 (1965).
108. D. Shopov and A. Palazov, Kinetika i Kataliz, 8, 862 (1967).
109. D. Shopov, A. Palazov, and A. Andreev, "4-i Mezhdunarodnyi Kongress po Katalizu" (The Fourth International Congress on Catalysis), Moscow, 1968, Preprint No. 30.
110. N. A. Gaidai, S. L. Kiperman, and M. V. Tikhomirov, Probl. Kinetiki i Kataliza, 14, 135 (1970).
111. F. Herington and E. Rideal, Proc. Roy. Soc., A, 184, 447 (1945).
112. H. S. Kuo, Sci. Sinica, 11, 1237 (1962).
113. S. E. Raik, Probl. Kinetiki i Kataliza, 6, 262 (1949).
114. L. Fogelberg, R. Gore, and B. Ranby, Acta Chem. Scand., 21, 2041 (1967).
115. I. Nicolescu, M. Gruia, A. Papia, and V. Dumitrescu, Rev. Chim. (Roumania), 10, 523 (1965).

116. V. L. Polinin, M. I. Rozengart, and B. A. Kazanskii, Izd. Akad. Nauk SSSR, Ser. Khim., 1435 (1967).
117. J. Mitchell, J. Amer. Chem. Soc., 80, 5848 (1958).
118. H. Pines and C. Chen, J. Org. chem., 26, 1057 (1961).
119. J. Feighan and B. Davis, J. Cat., 4, 594 (1965).
120. F. R. Cannings, A. Fisher, J. F. Ford, P. D. Holmes, and R. S. Smith, Radioisotopes, Phys. Sci. Ind., Proc. Conf. Use, Copenhagen, 1962, Vol. 3, p. 205.
121. H. Pines and M. Csicsery, J. Cat., 1, 313 (1962).
122. Y. Okamoto, J. Happel, and H. Koyama, Bull. Chem. Soc. Japan, 40, 2333 (1967).
123. G. V. Isagulyants, M. A. Ryashentseva, Yu. I. Derbentsev et al., Neftekhimiya, 5, 501 (1965).
124. A. A. Andreev, D. M. Shopov, and S. L. Kiperman, Kinetika i Kataliz, 7, 120 (1966).
125. P. Atkins and D. Heppel [tentative spelling], "4-i Mezhdunarodnyi Kongress po Katalizu, Moskva, 1968, Simpozium. Mekhanizm i Kinetika Slozhnykh Kataliticheskikh Reaktsii" (The Fourth International Congress on Catalysis, Moscow, 1968. Symposium on the Mechanism and Kinetics of Complex Catalytic Reactions), Preprint No. 4,
126. S. Noda, R. Hudgins, and P. Silveston, Canad. J. Chem. Eng., 45, 294 (1967).
127. G. A. Tarasova and B. A. Kazanskii, Neftekhimiya, 4, 561 (1964).
128. H. S. Pan and H. S. Kuo, Acta Foculia Sinica, 3, 179 (1968); Ref. Zhur. Khim., 34 281 (1969).
129. Yu. N. Usov, E. V. Skvortsova, N. I. Kuvshinova, G. A. Raikova, and V. F. Il'in, Kinetika i Kataliz, 7, 809 (1966).
130. V. S. Gadzhi-Kasumov, S. L. Kiperman, G. V. Isagulyants, and A. A. Balandin, Kinetika i Kataliz, 7, 273 (1966).
131. V. S. Gadzhi-Kasumov, S. L. Kiperman, G. V. Isagulyants, and A. A. Balandin, Kinetika i Kataliz, 8, 609 (1967).
132. L. E. Martyshkina, Zh. V. Strel'nikova, and V. P. Lebedev, Vestnik Moskov. Gos. Univ., Ser. Khim., No. 6, 21 (1966).
133. A. A. Andreev and S. L. Kiperman, Kinetika i Kataliz, 6, 869 (1965).
134. A. A. Andreev, D. M. Shopov, and S. L. Kiperman, 7, 1092 (1966).
135. A. V. Sagalovich, A. L. Klyachko-Gurvich, and A. A. Slinkin, Izv. Akad. Nauk SSSR, Ser. Khim., 106 (1968).
136. Yu. N. Usov, E. V. Skvortsova, N. I. Kuvshinova, L. A. Elovatskaya, and G. V. Alferova, Neftekhimiya, 7, 341 (1967).
137. S. Carra and L. Forni, Ind. Eng. Chem. Proc. Des. Dev., 4, 281 (1965).
138. G. M. Panchenkov and I. M. Kolesnikov, Neftekhimiya, 2, 480 (1962).
139. O. V. Bragin and A. L. Liberman, Dokl. Akad. Nauk SSSR, 148, 338 (1963).
140. O. V. Bragin, G. K. Gur'yanova, and A. L. Liberman, Dokl. Akad. Nauk SSSR, 160, 823 (1965).
141. Yu. N. Usov, E. V. Skvortsova, and N. I. Kuvshinova, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 10, 816 (1968).
142. Yu. N. Usov, N. I. Kuvshinova, E. V. Skvortsova, and G. G. Nasledskova, Neftekhimiya, 8, 529 (1968).
143. Yu. N. Usov, N. I. Kuvshinova, and G. G. Nasledskova, Neftekhimiya, 9, 687 (1969).
144. A. M. Rubinshtein, K. I. Slovetskaya, and T. R. Brueva, Kinetika i Kataliz, 2, 584 (1961).
145. K. P. Lavrovskii, A. L. Rozental', and T. A. Denisova, Neftekhimiya, 8, 332 (1968).
146. A. Ya. Rozovskii and E. V. Shchekin, Trudy Inst. Nefti Akad. Nauk SSSR, 10, 275 (1957).
147. L. Van Reijen, W. Sachtler, P. Cossee, and D. Brouwer, "Proceedings of the Amsterdam Congress on Catalysis, 1964", p. 829.
148. J. Sinfelt, H. Hurwitz, and R. Shulman, J. Phys. Chem., 64, 1559 (1960).
149. L. Barnett, R. Weaver, and M. Gilkeson, Amer. Inst. Chem. Engineers J., 7, 211 (1961).
150. A. A. Andreev, B. S. Gudkov, S. L. Kiperman, and D. M. Shopov, Kinetika i Kataliz, 9, 47 (1968).
151. B. A. Kazanskii, O. D. Sterligov, and A. P. Belen'kaya, Symposium, "Nauchnye Osnovy Podbora i Proizvodstva Katalizatorov" (Scientific Principles of the Selection and Manufacture of Catalysts), Novosibirsk, 1964, p. 336.
152. G. N. Maslyanskii and N. R. Bursian, Zhur. Obshch. Khim., 28, 2656 (1958).
153. V. K. Skarchenko, "Alyumosilikatnye Katalizatory" (Aluminosilicate Catalysts), Izv. Akad. Nauk Ukrain. SSR, Kiev, 1963.
154. V. S. Gadzhi-Kasumov, G. V. Isagulyants, and A. A. Balandin, Izv. Akad. Nauk SSSR, Ser. Khim., 921 (1966).
155. A. L. Liberman, K. Kh. Shnabel', and B. A. Kazanskii, Kinetika i Kataliz, 2, 547 (1961).
156. H. Pines and C. Goetschel, J. Org. Chem., 30, 3530 (1965).
157. P. Nix and P. Weisz, J. Cat., 3, 179 (1964).
158. A. Popescu and I. Nicolescu, Annalen Univ. «Parhon», Ser. Stiint. natur., 9, No. 26, 149 (1960).
159. L. Hughes, US P. 3 222 417 (1965).
160. L. Hughes, US P. 3 248 451 (1966).
161. J. Roth, J. Abell, and A. Schaefer, Ind. Eng. Chem. Prod. Res. Dev., 7, 254 (1968).
162. J. McEnen, US P. 3 322 849 (1967).
163. S. R. Sergienko and V. D. Medvedeva, Symposium, "Gazokondensaty i Nefti" (Gas Condensates and Different Types of Petroleum), Izd. Ylym, Ashkhabad, 1968, p. 219.
164. E. A. Timofeeva, Kinetika i Kataliz, 7, 494 (1966).
165. R. Kline and W. Starnes, US P. 3 285 985 (1966); Chem. Abs., 66, 12 744 (1967).
166. L. Nowakowski and M. Taniewski, Przemysl. Chem., 45, 671 (1966).
167. I. L. Fridshtein and N. A. Zimina, Symposium, "Nauchnye Osnovy Podbora i Proizvodstva Katalizatorov" (Scientific Principles of the Selection and Manufacture of Catalysts), Novosibirsk, 1964, p. 274.
168. O. D. Sterligov, N. A. Eliseev, and A. P. Belen'kaya, Kinetika i Kataliz, 8, 141 (1967).
169. B. A. Kazanskii, M. I. Rozengart, and Z. F. Kuznetsova, Dokl. Akad. Nauk SSSR, 126, 787 (1959).
170. S. Nowak and H. Vieweg, Erdölu. Kohle, 18, 618 (1965).
171. Yu. N. Usov, E. V. Skvortsova, N. I. Kuvshinova, and B. A. Elovatskaya, Trudy Groznensk, Neft. Inst., No. 23, 174 (1960).
172. J. Bridges, G. Rymer, and D. McIver, J. Phys. Chem., 66, 871 (1962).
173. V. E. Varshaver, A. Z. Dorogochinskii, and M. I. Rozengart, Trudy Groznensk. Neft. Inst. (Izd. Khimiya, Moscow), 23, 192 (1967).
174. M. Spinzi and M. Gruia et al., Chem. Tech. (Berlin), 20, 759 (1968).

175. B. A. Dadashev, I. G. Sultanova et al., Azerb. Khim. Zhur., No. 3, 17 (1969).
176. A. G. Efendiev, V. E. Smirnova, and Z. G. Zul'fugarov, Azerb. Khim. Zhur., No. 5, 85 (1966).
177. T. A. Agdanskii, S. G. Agaeva, and Z. G. Zul'fugarov, Dokl. Akad. Nauk Azerb. SSR, 20, No. 7, 21 (1964).
178. D. A. Bol'shakov, Khim. Prom., 525 (1961).
179. M. I. Rozengart and Z. S. Kuznetsova, Kinetika i Kataliz, 3, 942 (1962).
180. Ho Che-Chang and Pan Ku-Shan, Acta Fucalia Sinica, 1, 23 (1957); Chem. Abs., 52, 6775 (1958).
181. B. A. Dadashev, S. A. Kasimova, and Z. A. Davydova, Azerb. Khim. Zhur., No. 6, 29 (1964).
182. B. A. Dadashev, Z. A. Davydova, S. A. Kasimova, and A. T. Khudiev, Azerb. Khim. Zhur., No. 5, 33 (1965).
183. N. R. Bursian, S. B. Kogan, and Z. A. Davydova, Kinetika i Kataliz, 6, 744 (1965).
184. M. A. Ryashentseva, Kh. M. Minachev, and Yu. A. Afanas'eva, Neftekhimiya, 2, 41 (1962).
185. M. A. Ryashentseva, Yu. A. Afanas'eva, and Kh. M. Minachev, Izv. Akad. Nauk SSSR, Ser. Khim., 518 (1968).
186. V. Haensel, G. Donaldson, and F. Riedl, "Proceedings of the Third International Congress on Catalysis, Amsterdam", 1964, Vol. 1, p. 294.
187. G. V. Isagulyants and M. A. Ryashentseva, Dokl. Akad. Nauk SSSR, 172, 597 (1967).
188. A. A. Balandin, M. B. Neiman et al., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 270 (1957).
189. A. L. Liberman, K. Kh. Shnabel', T. V. Vasina, and B. A. Kazanskii, Kinetika i Kataliz, 2, 446 (1961).
190. Kh. I. Areshidze, Trudy Inst. Khim. Akad. Nauk Gruz. SSR, 14, 129 (1958).
191. N. I. Shuikin, T. I. Naryshkina, Z. A. Rashchupkina, Neftekhimiya, 2, 44 (1962).
192. K. McHenry et al., "Actes 2e Intern. Congr. Catalyse, Paris", 1960, Vol. 2, p. 2295.
193. M. Kraft [tentative spelling] and H. Spindler, "4-i Mezhdunarodnyi Kongress po Katalizu, Moskva, 1968" (The Fourth International Congress on Catalysis, Moscow, 1968).
194. N. R. Bursian, S. B. Kogan, and Z. A. Davydova, Kinetika i Kataliz, 9, 661 (1968).
195. N. V. Nikicorova, A. K. Potapovich, M. F. Rusak, and B. V. Erofeev, Vestsi Akad. Nauk Beloruss. SSR, Ser. Khim. Nauk, No. 3, 113 (1965).
196. P. Debye and B. Chu, J. Phys. Chem., 66, 1021 (1962).
197. M. M. Zaidman, V. A. Dzis'ko, A. P. Karnaukhov, N. P. Krasilenko, and N. G. Koroleva, Kinetika i Kataliz, 10, 652 (1969).
198. C. Nicolau, Rev. Chem. (Roumania), 10, 923 (1965).
199. K. Kh. Shnabel', Kinetika i Kataliz, 8, 583 (1967).
200. C. Nicolau and K. Schnabel, Nature, 193, 871 (1962).
201. B. Wood, Nature, 11, 30 (1968).
202. B. M. W. Trapnell, "Chemisorption" (Translated into Russian), Inostr. Lit., Moscow, 1958.
203. A. Gremillion and W. Knox, J. Cat., 1, 216 (1962).
204. Yu. I. Pecherskaya and V. B. Kazanskii, Kinetika i Kataliz, 6, 357 (1965).
205. Kh. M. Minachev, Yu. S. Khodakov, G. I. Kalyaev, and V. K. Nesterov, Neftekhimiya, 9, 677 (1969).
206. K. I. Slovetskaya, K. M. Gitis, R. V. Dmitriev, and A. M. Rubinshtein, Izv. Akad. Nauk SSSR, Ser. Khim., 196 (1969).
207. K. I. Slovetskaya and A. M. Rubinshtein, Kinetika i Kataliz, 7, 342 (1966).
208. K. M. Gitis, M. I. Rozengart, and B. A. Kazanskii, Dokl. Akad. Nauk SSSR, 174, 1331 (1967).
209. O. V. Krylov, "Kataliz Nemetallami" (Catalysis by Non-metals), Izd. Khimiya, Leningrad, 1967.
210. V. A. Shvets and V. B. Kazanskii, Kinetika i Kataliz, 7, 712 (1966).
211. I. V. Krylova, O. I. Kozunenko, and N. I. Kobozev, Vestnik Moskov. Gos. Univ., No. 3, 90 (1967).
212. R. A. Buyanov, M. M. Andrushkevich, and L. G. Karakchiev, Kinetika i Kataliz, 6, 1069 (1965).
213. W. Armstrong and J. Wilson, US P. 2 940 940.
214. K. Heise [tentative spelling], Probl. Kinetiki i Kataliza, 14, 231 (1970).
215. I. V. Krylova, O. I. Kozunenko, and N. I. Kobozev. Vestnik Moskov. Gos. Univ., No. 4, 108 (1967).
216. K. I. Slovetskaya, T. R. Brueva, and A. M. Rubinshtein, Kinetika i Kataliz, 7, 566 (1966).

Institute of the Chemistry of
Macromolecular Compounds,
Academy of Sciences of the
Ukrainian SSR, Kiev