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Catalytic conversion of paraffinic hydrocarbons into isoparaffins and olefins

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ABSTRACT. The catalytic isomerisation, disproportionation, and dehydrogenation reactions of the C_4–C_{12}, C_4–C_8, and C_3–C_{18} hydrocarbons respectively are examined. The chemical composition, the methods of preparation of the catalysts, the effect of promoting agents, and the kinetics and mechanisms of the reactions are discussed. The principal characteristics of the existing and likely future processes leading to the synthesis of C_4–C_{12} isoparaffins and C_3–C_{18} mono-olefins are presented.
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I. Introduction

The isomeristion, dehydrogenation, and also disproportionation reactions of paraffinic hydrocarbons are linked together by the application of catalytic systems of the same type and by the existence of common features in their chemistry and technology. These reactions are carried out on heterogeneous catalysts in the presence of hydrogen, using individual paraffinic hydrocarbons or their narrow fractions as the starting materials. The limititation of the degree of conversion by the thermodynamic equilibrium necessitates the isolation and recirculation of the hydrocarbons which have not reacted.

Isomerisation and dehydrogenation constitute traditional methods for the selective conversion of paraffinic hydrocarbons[1,2] and during the last decade these have been the object of vigorous investigation, which is to a significant extent due to the appearance of new highly efficient catalysts.[3,4] The isomerisation and dehydrogenation reactions of lower paraffins are combined in the proposed technological schemes for the processing of hydrocarbons in order to attain the optimum yield of the branched olefins [Bursian (Ref.3, page 99), Zhorov (Ref.4, page 218), Pujado and Vora,[5] and Bursian et al.[6]]. The manufacture of scarce C_4–C_5 paraffinic hydrocarbons can be expanded by employing a new process involving the disproportionation of C_6–C_8 hydrocarbons.[7-9]

The need for isoparaffinic and olefinic hydrocarbons has been increasing continuously owing to the need to solve the general world problem of the pollution of the atmosphere and water. In all countries, the use of ethylated types of automobile petrols has been decreasing, the consequent reduction in the octane number of petrols being compensated for by increasing the amount of isomerisation and alkylation mixtures and oxygen-containing compounds as additives—see Bursian (Ref.3, page 157) and other investigators.[5,6] Ecological requirements are also responsible for the growth in the manufacture of biodegradable surfactants based on higher linear olefins (Refs.10, 11, page 11).

The hydrocarbon composition of the most promising (North Siberian) petroleums of the Soviet Union is distinguished by a fairly high content of C_4–C_{20} paraffinic hydrocarbons (~20 wt.%), the ratio of the iso- and normal hydrocarbons varying within the limits 0.3–0.8 (Ref.12, p.126). Paraffinic hydrocarbons are extracted from petroleum by processes involving fractionation (C_4–C_6 paraffins) and isolation by absorption on zeolites (C_{11}–C_{18} paraffins) (Ref.3, page 7).

The economic efficiency of the processes involving the isomerisation and dehydrogenation of paraffinic hydrocarbons is determined by the low consumption of metals and energy, the high selectivity of the reactions, reaching 97–99%, the technological simplicity, and the waste-free technology.

In particular, platinised alumina containing halogen promoting agents[1-3] and metal-containing zeolites[3,4,13] are used as isomerisation catalysts. Metallozeolite catalysts are extremely effective also in the paraffin disproportionation reactions.[14] Non-acid polymetallic aluminoplatinum catalysts are used for the dehydrogenation of higher paraffins to olefins.[10,15] Catalysts based on chromium oxide have come to be widely used in the preparation of lower olefins by the dehydrogenation of paraffins.[16-18]

A series of large-scale industrial processes are based on the application of isomerisation and dehydrogenation reactions. The catalytic isomerisation of paraffinic C_4–C_{12} hydrocarbons increases the available raw material resources for the manufacture of isoprene rubber, ensures the preparation of high-octane components of AI-93 petrol and of reactive diesel C_3–C_5 paraffinic hydrocarbons—the source of mono-olefins used in the synthesis of monomers for isoprene and butadiene fuels and oils with a low setting temperature,[3] and dehydrogenation of natural rubbers.[16-18] The dehydrogenation of C_8–C_{18} hydrocarbons is used to obtain linear olefins which are necessary for the manufacture of plasticisers and components of surfactants characterised by high biodegradability.[10,15]

II. Isomerisation of paraffinic hydrocarbons

The isomerisation of paraffinic hydrocarbons in the presence of aluminium chloride was discovered in 1933 by Nenitzescu and Dragan. In 1935, Moldavskii demonstrated the possibility of

accelerating the isomerisation of paraffins in the presence of aluminium chloride by adding hydrogen chloride, which resulted in the practical application of this reaction (Ref.19, page 512).

The vapour-phase isomerisation of paraffinic hydrocarbons under hydrogen pressure was subsequently achieved at 350–500 °C in the presence of bifunctional catalysts—the oxides and sulphides of Group VI elements as well as Group VIII metals on carriers with acidic properties (alumina promoted by halogens and aluminosilicates).[1–4]

The fluorine-promoted aluminoplatinum catalyst became the first widely used catalyst of an industrial isomerisation process.[3,4,15,20]

1. Thermodynamics, kinetics, and mechanism

The isomerisation reaction of paraffinic hydrocarbons proceeds without change in volume and the thermodynamic equilibrium depends virtually only on temperature. Theoretical corrections for the non-ideality of the gas[21] under the usual isomerisation conditions do not exceed 1% (Ref.4, page 11). The data on the composition of the equilibrium mixtures of isomeric paraffins are well known.[1–4,22] A common characteristic is the increase in the content of branched isomers as the temperature is reduced.

The form of the kinetic equation and the isomerisation mechanism depend on the type of catalyst and the experimental conditions. At the same time, comparison of the various existing equations (Table 1) shows that the reaction is found in all cases to be of first order with respect to the hydrocarbon and is inhibited by hydrogen. The optimum hydrogen partial pressure is determined by the nature of the catalyst (Ref.3, pages 18–28).

The study of the kinetics of the isomerisation of paraffinic hydrocarbons as well as the mechanism of the poisoning of catalysts by poisons acting on various active centres of bifunctional isomerisation catalysts established that the rate-limiting stage of the reaction is the conversion of the intermediate unsaturated products on acid centres of the catalysts (Ref.3, page 18; Ref.31, page 347; Ref.32, page 38).

In the limiting cases of high and low partial hydrogen pressures, the rate of isomerisation can be limited by the rates of dehydrogenation of paraffins and hydrogenation of olefins on the metallic centres of catalysts respectively (Ref.3, page 28). In contrast to aluminium chloride, in the presence of bifunctional aluminoplatinum catalysts the rate of isomerisation of C_4–C_6 paraffins increases with increase in their molecular weight; the isomerisation of C_7 and higher hydrocarbons takes place non-selectively on all the catalysts investigated with the cracking reaction predominating.[1]

The relative rates of interconversions of hexanes in the presence of metal halide salts and an aluminoplatinum catalyst have been measured in a number of studies (Ref.33–35, page 171; Ref.36, page 99) and it has been established that the migration of the methyl group along the paraffinic hydrocarbon chain takes place at the highest rate.

In the isomerisation of C_5–C_6 mixtures on the platinum/mordenite catalyst, n-hexane is found to have a strong influence on the rate of isomerisation of n-pentane.[28] This effect, which can be explained by the preferential adsorption of n-hexane on the active centres of H-mordenite, is reflected in the inverse dependence of the rate of isomerisation of n-pentane on the partial pressure of n-hexane (Table 1).

The activation energies for isomerisation reactions on various catalysts diminish with increase in the activity of the latter, which is manifested by a decrease in the process temperature (Table 1).

The side reactions involving hydrogenolysis, cracking, and disproportionation accompanying the main isomerisation reaction of paraffinic hydrocarbons leads to a decrease in the selectivity and

Table 1. Kinetics of the n-pentane and n-hexane isomerisation reactions on different catalysts.

Catalyst	p, MPa	T, °C	Kinetic equation	α, mol%	E, kJ mol^{-1}	Refs.
$Pt—Al_2O_3$	0.77–2.77	372	$r=\frac{k(p_{n\text{-}C_5}/p_{H_2})}{1+m(p_{n\text{-}C_5}/p_{H_2})}$	4–18	—	[23]
$Pt—Al_2O_3—F$	3.5	360–485	$r=(k_1 p_{n\text{-}C_5}-k_2 p_{iso\text{-}C_5})/p_{H_2}$	12–56	172	[24]
$Pt—Al_2O_3—F$	0.1	420–480	$r=k p_{n\text{-}C_5} p_{H_2}^{b}$	18–35	—	[25]
$Pt—Al_2O_3—Cl$	0.9–4.1	130–160	$r=\left\{k_{true}\left(\frac{[n\text{-}C_5]_0}{[H_2]}\right)^{0.125}-0.0000197t\right\}\times \times\{K_e[n\text{-}C_5]_0-(K_e+1)[iso\text{-}C_5]\}$	0–20	46	[26]
H—M *	0.5–0.6	200–227	$r=k(p_{n\text{-}C_5}/p_{H_2})$	0–10	129	[27]
Pt—H—M **	0.79–2.17	241	$K_{C_6}=134/(1+0.294p_{C_6})^2 p_{H_2}$	—	148	[28]
»	»	»	$K_{C_6}=366/(1+0.124p_{C_6})^2 p_{H_2}$	—	—	[28]
Pd—Ca—Y	0.1–5.0	300–360	$r=k(p_{n\text{-}C_5}/p_{H_2})$	3–15	—	[29]
$HF—SbF_5$	1.0	from −20 to +20	$r=\{k_1[n\text{-}C_6]-k_2[iso\text{-}C_6]\}\frac{[SbF_5]}{[n\text{-}C_6]}$	—	60	[30]

Notation: α is the degree of conversion, m the adsorption coefficient, r the rate of reaction, k the reaction rate constant, K_e the equilibrium constant, and p the pressure.

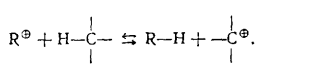
* H–M represents the hydrogen-form of mordenite.

**Isomerisation of the C_5 + C_6 mixture; C_5 content 15–75 mol %.

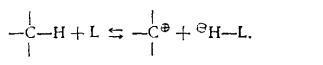
stability of the catalyst. Hydrogenolysis takes place on metallic centres and cracking and disproportionation take place on acid centres.

In order to restrict the side reactions under the conditions of isomerisation on bifunctional catalysts, the optimum ratio of the concentration of the metal and the acidity of the carrier, regulated by the chemical composition of the latter and the selection of the partial hydrogen pressure, is established. The rates of the cracking and disproportionation reactions are maximum in the absence of hydrogen and, with increase in its partial pressure, they gradually diminish to a definite limit and then increase (Ref. 3, page 35).

The principal question concerning the mechanism of the isomerisation reaction is the mechanism of the formation of the carbonium ion. Such ions can be formed as a result of intermolecular hydride transfer:[37]

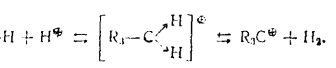


There exists also another view,[35,38] according to which carbonium ions are formed as a result of the abstraction of a hydride ion from the paraffin molecule by a Lewis acid:



In this case the recombination of a proton and a hydride ion can lead to the formation of gaseous hydrogen.

The isomerisation of paraffinic hydrocarbons in superacid media[39,40] proceeds via the protonation of paraffinic hydrocarbons at the σ-bond, whereupon a non-classical carbonium ion with a two-electron three-centre bond is formed and its subsequent cleavage leads to the formation of the usual tricoordinate carbonium ion and hydrogen:



A mechanism according to which the isomerisation proceeds via the formation of cyclic carbonium ions has been proposed.[1,40]

The isomerisation of paraffins on bifunctional catalysts of the aluminofluoroplatinum and metallozeolitic types takes place in accordance with the classical scheme[41] via stages involving the formation of unsaturated compounds on the metallic centres (M) of the catalyst, their further conversion via the carbonium ion mechanism on the acid centres (A) into the corresponding iso-olefin, and the rehydrogenation of the latter on the metallic centres:

$$\text{paraffin} \overset{M}{\rightleftarrows} \text{olefin} \overset{A}{\rightleftarrows} \text{iso-olefin} \overset{M}{\rightleftarrows} \text{isoparaffin}.$$

This scheme was confirmed by numerous experimental studies and mathematical analysis.[42] There exists also a different point of view on the mechanism of the reactions of paraffinic hydrocarbons on bifunctional catalysts, according to which a special role is attributed to the metal (Ref.31, pages 327, 347). The different ideas about the isomerisation mechanism (catalysis by metals, bifunctional catalysis, and catalysis by acids) are not mutually exclusive and their relative contributions depend on the nature of the catalyst and the reaction conditions.

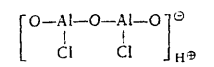
2. Catalysts

As already mentioned, paraffin isomerisation catalysts can be divided into three groups:

(a) platinum on halogenated alumina; (b) Group VIII metals on zeolites; (c) "superacids" (the fluorides of Group V and VI elements).

The study of the isomerisation of paraffinic hydrocarbons on these catalysts established a series of characteristic features. The most important include the dependence of the activity of the catalyst on its acidity. In the case of aluminoplatinum catalysts promoted by halogens, the acidity and activity increase with increase in the amount of fluorine and chlorine up to a certain limit (Ref.3, pages 17, 70). The acidity and activity also increase up to a definite value with increase in the modulus and degree of removal of sodium.[13] The maximum activity and acidity are shown by the SbF_5–HF system among metal fluorides.[43]

There exist a series of hypotheses concerning the structure of the active centres of the isomerisation catalyst promoted by chlorine or fluorine. According to one of them,[1] the acidity of alumina treated with HCl increases if the chloride ion substitutes one of a pair of hydroxy-groups, whereupon the hydrogen of the other hydroxy-group becomes capable of dissociation in the form of a proton by virtue of the presence of the electronegative chlorine atom in its immediate vicinity. The structure of the active centre of chlorine-substituted alumina can be represented by a formula according to which the halogenated alumina is an acid having mobile hydrogen ions:



The enhancement of the acidity when halide ions and hydroxy-groups are accommodated on neighbouring aluminium atoms has been postulated.[44]

The mechanism of the gas-phase activation of the aluminoplatinum catalyst by halogens and organochlorine compounds (especially carbon tetrachloride) in the absence of water has been discussed.[15,45–48] It has been suggested that organochlorine compounds react with the surface hydroxy-groups and the sections of the η-alumina surface generated on dehydroxylation; the oxygen of the oxygen-containing groups is then replaced by chlorine and active centres with the properties of acid Lewis centres are formed.

The interaction of CCl_4 with pairs of dehydroxylated surface sites on the γ-Al_2O_3 surface leads to the formation of centres with an enhanced acidity.[45] The requirements which must be met by the structures of alumina and the chlorinating agent have been formulated (Ref.3, page 66). It has been suggested that the active centres of the chlorinated η-alumina represent complexes whose composition includes chloride, oxygen, and aluminium ions as well as a proton. The chemisorbed hydrogen chloride, whose presence is ensured by the small amounts of water on the catalyst surface, serves as the source of protons. Centres which are active in the isomerisation reaction of paraffinic hydrocarbons are generated when platinised alumina is treated with aluminium chloride as a result of the formation on the surface of aluminium oxide chlorides stabilised by added hydrogen chloride (Ref.3, page 73).

The formation of acid active centres as a result of the introduction of up to 2 wt.% of fluorine into the aluminoplatinum catalyst proceeds via the substitution of the hydroxy-groups on neighbouring aluminium atoms by fluorine;[49] when the content of fluorine is above 2 wt.%, it substitutes isolated hydroxy-groups, which increases

the strength of the existing acid centres without increasing their concentration. The proton centres on the surface of fluorinated alumina can be formed on chemisorption of water.

The influence of fluorine on the isomerising, hydrogenating, and cracking functions of the aluminoplatinum catalyst has been investigated (Figs. 1 and 2) (Ref.3, page 48).

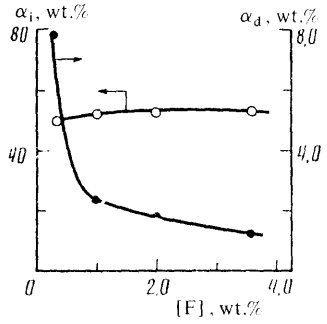


Figure 1. Dependence of the yield of the n-pentane conversion products on the fluorine content [F] in the aluminoplatinum catalyst (Ref.3, page 49); T = 380 °C; p = 3.5 MPa; α_i and α_d are the yields of isopentane and the decomposition products respectively.

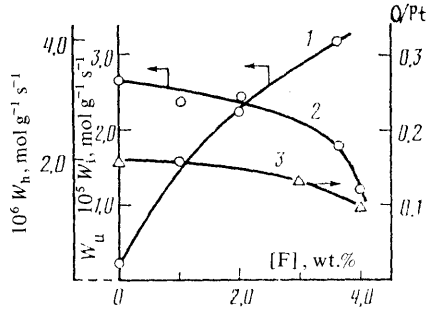


Figure 2. The influence of fluorine on the activity of the aluminoplatinum catalyst in the n-pentane isomerisation (curve *1*) and benzene hydrogenation (curve *2*) reactions and on the chemisorption capacity of platinum (curve *3*) (Ref.3, page 48); W_i and W_h are the rates of isomerisation and hydrogenation respectively.

The increase in the isomerising activity when aluminoplatinum catalysts are promoted by fluorine (Fig. 2) is associated with increase in the Lewis acidity and the appearance of Brønsted acidity. The simultaneous decrease in the activity of the catalyst in the reactions involving the hydrogenation of benzene and the hydrogenolysis of paraffins indicates a change in the state of the platinum, which has been confirmed by an IR spectroscopic study of the adsorption of carbon monoxide (Ref.3, page 49). The fluorination of the catalyst increases significantly the CO vibration frequency, which indicates an increase in the electron deficiency in the platinum. The latter can be explained by the strengthening of the electron-accepting centres of the carrier with which platinum interacts.

The introduction of sulphur into an aluminoplatinum catalyst promoted by fluorine suppresses the hydrogenolysis reaction in the course of the isomerisation of n-pentane without altering the isomerising activity of the catalyst (Ref.3, page 55).

The IR spectroscopic study of the adsorption of CO on the sulphur-treated catalyst showed that the maximum of the band corresponding to the CO adsorbed on platinum undergoes a hypsochromic shift in the presence of sulphur and that its position is independent of the degree of surface coverage of platinum by carbon monoxide (Ref.3, page 49). This finding indicates the inhomogeneity of the platinum in the non-sulphur-treated catalyst. On treatment with sulphur, the latter forms a strong bond with some of the platinum centres (the least electron-deficient centres), while the electron-deficient platinum centres remain free after heat treatment in the presence of hydrogen. The increase in the electron deficiency of platinum as a result of promotion by fluorine and sulphur weakens the Pt–C bond in the chemisorption of hydrocarbons and suppresses the hydrogenolysis reactions, whose rate is determined by the chemisorption stage.

The studies which have been carried out have served as a basis for the selection of the chemical composition of the catalysts of the high-temperature isomerisation of paraffinic hydrocarbons (IP-62, IP-62-M, and IP-82). Their platinum content is 0.45–0.55 wt.%, the fluorine content in γ-alumina is 3.5 ± 0.5 wt.%, and the sulphur content is 0.2 wt.%.[3,4,15,20]

The discovery of a new method for the introduction of chlorine into the carrier by the gas-phase chlorination of the catalyst with organic chlorides is of fundamental importance for the synthesis of bifunctional aluminoplatinum isomerisation catalysts (Ref.3, page 74; Refs.15,20,50,51). The gas-phase chlorination procedure, which consists in treating the aluminoplatinum catalyst at 250 to 300 °C with an inert gas containing carbon tetrachloride, makes it possible to obtain a catalyst whose acid strength approaches that of aluminium chloride, which creates the possibility of carrying out the isomerisation of paraffinic hydrocarbons in the absence of a metal at 50–100 °C. The introduction of platinum ensures the stability of the catalyst.

The isomerisation of paraffins on metallozeolitic catalysts was first described by Rabo et al.[52] and has been widely used by Minachev and co-workers.[13] Faujasite in the calcium- and H-forms and zeolites of the type of mordenite and ZSM in the H-forms are used for this reaction. Catalysts with a high activity, making it possible to achieve the isomerisation at 230–270 °C, can be obtained by maintaining a number of conditions; they must have a definite value of the silicate modulus (not less than 4.5 for faujasite, 12–18 for mordenite, and 40 for ZSM), adsorption capacity, and degree of crystallinity. The required acidity is obtained by removing sodium by ion exchange or de-alumination. H-Mordenite exhibits the highest activity and selectivity in the paraffin isomerisation reactions; the metal is introduced to increase the stability of the catalyst.[53]

The possibility of isomerising paraffinic hydrocarbons on Group V and VI metal fluorides in the presence of HF in hydrogen was first demonstrated by Oeldrik.[54] The reaction takes place at a higher rate and with a high selectivity at 20–50 °C and a hydrogen pressure of 0.5 MPa in the liquid phase in the presence of the MF_5–HF complex. The TaF_5–HF system is the most stable and the SbF_5–HF system is the least stable.

The nature of the active centres on "superacid" catalytic systems of the type of MF_x–HF has been examined.[43] The sharp increase in the acidity of hydrogen fluoride following the addition of SbF_5 is explained by the formation of the more acid ion H_2F^+. The low nucleophilicity of superacids, promoting the stabilisation of carbonium ions, is due to the stablisation of the F^- and FSO_3^- ions as a consequence of the formation of complex anions in which antimony has a coordination number of 6. The instability of the given catalytic system is associated with the formation of polymeric compounds and their dissolution in the catalyst.

The selectivity and stability of the catalytic system depend on the ratio of the rates of formation of carbonium ions and of their alkyl rearrangement and hence are determined to a significant extent by the properties of the initial hydrocarbon. Thus the isomerisation of n-butane can be achieved at an acceptable rate and with an acceptable selectivity in the presence of aluminium chloride and chlorine-promoted aluminoplatinum catalysts. In the presence of fluorine-promoted aluminoplatinum catalysts and metallozeolitic catalysts, it proceeds with a lower selectivity, while it hardly occurs at all in the presence of metal fluorides, with the exception of the MoF_6–HF and AsF_5–HF systems, which nevertheless exhibit some activity.[43] The lack of activity of the SbF_5–HF system in the isomerisation of n-butane can be explained by the fact that the secondary butyl cation can rearrange to a tertiary butyl cation only via the formation of an intermediate carbonium ion with a very high energy (in contrast to the pentyl and hexyl cations, whose rearrangement proceeds via the formation of secondary carbonium ions). The isomerisation of n-butane on the $AlCl_3$–HCl, AsF_5–HF, and MoF_6–HF systems can be explained by the rearrangement of the butyl cation via a preliminary carbonium ion dimerisation stage, where the product rearranges and is cleaved without the formation of primary cations.[33]

High-silica zeolites (H-mordenite, ZSM-5), promoted by Group VI and VIII elements, are the most effective in the isomerisation of higher n-paraffins (Ref.3, pages 63, 118; Ref.4, page 142).

In practice, isomerisation catalysts are always used at an appreciable hydrogen pressure which promotes the desorption of the unsaturated intermediate compounds and ensures high stability.

One of the most important questions associated with the isomerisation of paraffinic hydrocarbons is that of the poisoning of the catalysts as well as the protection of the latter against the action of poisons. Sulphur and nitrogen compounds, carbon oxides, and water are some of the poisons. As a result of the reactions of sulphur and nitrogen compounds in hydrogen on platinum catalysts, hydrogen sulphide and ammonia are formed respectively.

Bearing in mind the bifunctional nature of the isomerisation catalysts, model reactions characterising the functions of the catalyst are selected to investigate the influence of the poisons on the properties of the metal and carrier.

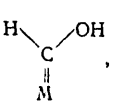
Sulphur compounds are poisons for all the catalysts investigated in the reactions occurring preferentially on metallic centres (hydrogenation and dehydrogenation). Nitrogen compounds do not have such a pronounced effect on the dehydrogenating activity at comparable concentrations but they do poison selectively the acid centres of the carrier, which is indicated by the change in the activity of the catalysts in the isomerisation reactions.[55]

The poisoning action of hydrogen sulphide is due to its interaction with platinum involving the formation of fairly stable sulphides. The toxicity of sulphide sulphur is determined by the presence of an unshared electron pair.[56] The comparatively weak influence of nitrogen is associated with the conversion of ammonia in the presence of water into the ammonium ion, which has a "non-toxic" fully shielded structure (Ref.31, page 307, Ref.56). The influence of sulphur and nitrogen compounds on the isomerising properties of platinum and palladium catalysts depends on the nature of the carrier. Thus sulphur compounds suppress the isomerisation of n-hexane on the Pd–CaY catalyst but do not influence the isomerising properties of the fluorine-promoted aluminoplatinum catalyst.[55] The latter indicates the absence of influence by sulphur on the slow stage in the isomerisation of paraffinic hydrocarbons—the structural isomerisation of olefins.

The poisoning of the aluminofluoroplatinum catalyst by sulphur (at concentrations in excess of 0.01 wt.%) is due to its effect on the rate of the paraffin dehydrogenation stage, which determines in the given instance the rate of isomerisation. Another possible cause is the action of sulphur on the acid centres of the alumina (Ref.3, page 88). There are data indicating the influence of carriers on the sensitivity of the deposited platinum to poisoning by sulphur. In the case of a stable (irreversible) adsorption of sulphur on platinum without a carrier, the ratio of the surface S and Pt atoms is 0.5.[57–59] Such adsorption fully deactivates the metal (and leads to the absence of adsorption of CO, H_2, O_2, acetylene, ethylene, and benzene at temperatures below 400 °C).[59] For the same or even a higher degree of surface coverage by sulphur, the platinum on alumina is capable of adsorbing CO, H_2, and O_2[60–64] and retains its activity in the reactions involving the hydrogenation of aromatic hydrocarbons[60] and the isomerisation of n-pentane.[64] In the adsorption of CO on platinum converted into a sulphide, there is a possibility of the formation of groups of the type CO–Pt–S.[61] Presumably bridged sulphide Pt_2S is also formed on massive platinum, while on more isolated deposited platinum centres the linear PtS structure predominates.[65] As the degree of surface coverage of platinum by sulphur is 0.5, isolated adsorption centres should be retained in this case on the surface of the aluminoplatinum catalyst, which agrees with the absence from the IR spectra of "sulphided" catalysts of the band due to the bridge-type form of adsorption of CO[63] and with the independence of the position of the maximum due to the linear CO–Pt form of adsorption from the degree of surface coverage of the Pt–Al_2O_3–F (Ref.3, pages 49,57; Ref.64) and Pt–Al_2O_3[66] catalysts.

The mechanism of the poisoning effect of sulphur on the Pt–Al_2O_3–Cl catalyst for low-temperature isomerisation should differ fundamentally from that examined above. In this case, the toxicity of sulphur is due to the dissociative adsorption of H_2S on the donor–acceptor centres of chlorinated alumina (Ref.3, page 88; Ref.67, pages 50–55).

The effect of carbon oxides on the different functions of platinum and palladium catalysts on alumina and of zeolitic catalysts has also been studied.[68] The dehydrogenating activity of all the catalysts fell in the presence of carbon monoxide regardless of the nature of the carrier, which indicates a direct interaction of CO with the metal of the catalyst. The toxicity of carbon monoxide is due to the formation of adsorption complexes with platinum. In the presence of carbon monoxide, the degree of chemisorption of hydrogen on the metal surface increases, which can be attributed to the formation of the complexes



the toxicity of CO in relation to platinum decreasing as a consequence of its hydrogenation to methane. However, for a

constant supply of the poison, the detoxification phenomenon may not be observed. Presumably, the poisoning of the platinum catalyst by carbon oxides is associated with their simultaneous action on the metal and the carrier–alumina or zeolite. The poisoning effect of CO and CO_2 on alumina is due to the formation and adsorption of water on its acid centres. The effect of carbon monoxide on platinum or palladium has been explained by the competitive adsorption of hydrocarbons and carbon oxides on the metal surface. Since carbon monoxide is adsorbed more strongly, its presence in hydrogen even in small amounts suppresses the dehydrogenation of cyclohexane and the isomerisation of n-pentane (Ref.3, page 90).

The study of the poisoning of platinum and palladium catalysts by water has shown that in this case the properties of the carriers are of decisive importance in the isomerisation of paraffinic hydrocarbons (Ref.3, page 91). The poisoning by water is thus caused by its interaction with the acid centres of the carrier. The rehydration of the catalysts based on alumina results in the formation of new hydroxy-groups which reduce the concentration of the active centres of the Al_2O_3 surface. In zeolite-containing systems, this phenomenon is observed at much higher water concentrations and the palladium-zeolite isomerisation catalyst is therefore relatively resistant to poisoning by water.[68] The metallozeolitic isomerisation catalysts (Pt–CaY, Pd–CaY) are relatively insensitive even to poisoning by nitrogen compounds[55] and carbon dioxide.[68]

The characteristic features observed in the study of the influence of poisons on the rates and selectivities of the reactions occurring on platinum and palladium catalysts established the permissible content of the poisoning impurities in the raw material and hydrogen and have led to the recommendation of measures for the protection of catalysts against the action of these impurities.[3]

3. Industrial application

Depending on the catalyst employed, the isomerisation of paraffinic hydrocarbons takes place with high yields at temperatures in the range 20–370 °C, hydrogen pressures in the range 0.5 to 3.5 MPa, space velocities at which the raw material is supplied in the range 2.0–3.0 h^{-1}, and a hydrogen: hydrocarbon molar ratio of 2–3 (Table 2).

Isomerisation reactions of paraffinic hydrocarbons of several types are used nowadays in industry, the differences between them being determined by the properties of the catalyst employed (Table 2).

In the high-temperature isomerisation reactions of pentane–hexane fractions, metal–fluorine-promoted alumina and metal–alumino-silicate systems are used as catalysts. The attainable degree of isomerisation of n-pentane in one pass at temperatures in the range 360–400 °C amounts to 50–55% and the octane number of the isomerisation reaction mixture resulting from the pentane–hexane fraction reaches 75 measured purely by the research method (RM) (Ref.3, page 76).

The application of high-silica zeolites of the type of mordenite[3,4,13] has served as the basis of a moderate-temperature isomerisation process for the pentane–hexane fraction, which is carried out at 230–260 °C; the isomerisation reaction mixture obtained after a single pass of the raw material has an octane number of 80–82 (RM).

The isomerisation reactions of n-butane, n-pentane, and of the pentane–hexane fraction at temperatures in the range 140–180 °C on aluminoplatinum catalysts modified by organochlorine compounds or aluminium chloride have been developed to the greatest extent. The vast majority of industrial plants use the technology of the low-temperature isomerisation of the pentane–hexane fraction via the "one pass" scheme with formation of an isomerisation reaction mixture having an octane number of 83–84 (RM).

If it is necessary to obtain individual isoparaffins, the part of the paraffinic hydrocarbons which have not reacted must be returned to the process. When n-butane and n-pentane are isomerised, recirculation is economically useful and is generally used. In the isomerisation of pentane–hexane fractions, which contain a large number of hexane isomers having similar boiling points but different octane characteristics, the usefulness of the recirculation of n-hexane

Table 2. Conditions in the isomerisation of n-pentane (P) and n-hexane (H) in the presence of different catalysts.[3,69]

Catalyst	$Pt–Al_2O_3–F$		Pd–Ca–H–Y		Pt–H–M		$Pt–Al_2O_3–Cl$		$HSbF_6$	$HTaF_6$
	P	H	P	H	P	H	P	H	P	H
Temperature, °C	370	360	330	320	260	260	140	140	50	20
Pressure, MPa	3.5	3.5	3.0	3.0	2,0	2,0	3.0	3.0	0.5	0,5
Rate of supply of raw material (space velocity), h^{-1}	2—3	2—3	2.0	2.0	2.0	2.0	2.0	3	2.5	2,5
H_2 : hydrocarbon molar ratio	2	2	3	3	2	3	2	2	0	0
Degree of conversion per pass, wt.%	52—55	70	57	75	57	73	75	87	84	94
Yield of C_1–C_4 (P) or C_1–C_6 (H), wt.%	1.5—2	2.5	1.8	2 9	1 2	3.4	0.5	1	0,5	0.5–2.5
2,2-Dimethylbutane content in C_6, wt.%	—	9.1	—	12 8	—	14.6	—	25.2	—	46.1
Octane number of product (according to RM) formed per pass*	75		76		80		83		89	

*In the experiment using the pentane–hexane fraction with the ratio C_5: C_6 = 1 : 1.

and of its low-octane monosubstituted isomers is determined by the required octane number of the isomerisation reaction mixture. The energy expenditure on the recirculation increases with increase in the octane number of the isomerisation reaction mixture. There is a corresponding increase in the intrinsic cost of the isomerisation reaction mixture as well, which depends also on the method of isolation of the paraffinic hydrocarbons—fractionation or extraction on molecular sieves; the latter method is much more economical.[3]

One of the ways of increasing the antiknocking capacity of the isomerisation reaction mixtures obtained from the hexane fraction involves their processing by selective hydrocracking on metallo-zeolitic catalysts. The selective hydrocracking of normal paraffinic hydrocarbons takes place in this process; the selectivity of the action of the catalyst, determined by the molecular sieve effect of zeolites of the type of erionite and ZSM, can be explained by the difference between the critical diameters of molecules of different structure (Ref.3, pages 145, 174).

The isomerisation of C_7 and higher paraffins (combined with partial hydrocracking) is used to improve the characteristics of diesel fuels and oils. A number of corresponding Soviet and foreign technological processes are known in which 98% conversion of the raw material is attained in one pass.[3,4]

More than 80 plants for the isomerisation of n-butane, n-pentane, and pentane–hexane fractions are functioning at the present time throughout the world. The tendency towards a decrease in the content of tetraethyl-lead and of aromatic hydrocarbons in automobile petrols has promoted an increase in the number of isomerisation plants being built and in the planning stage[70] and an expansion of the manufacture of the corresponding catalysts.[71]

III. Disproportionation of paraffinic hydrocarbons

The disproportionation of paraffinic hydrocarbons, which takes place in the simplest case in accordance with the equation

$$2C_nH_{2n+2} \leftrightarrows C_{n-x}H_{2n+2-2x} + C_{n+x}H_{2n+2+2x}, \quad (1)$$

was first observed[72] as a side reaction in the isomerisation of paraffinic hydrocarbons in the presence of aluminium chloride. Later this reaction was studied by Moldavskii and co-workers.[73–75]

The conversion of n-pentane at 50–90 °C resulted in the formation of 25–40% of products heavier than C_5 compounds and of up to 30–50% of light hydrocarbons (mainly butanes).[74] The products for the interaction of copper and lead sulphates with hydrogen chloride, which were regarded as HCl donors, were used as activating additives. It was shown later that the promoting effect of metal sulphates and chlorides is manifested also in the absence of HCl under anhydrous conditions and is evidently caused by the formation of molecular complexes between aluminium chloride and the promoting salts.[76,77] The study of the disproportionation of C_5–C_7 paraffins on aluminium chloride at temperatures up to 100 °C established that, together with copper salts, those of zinc, cadmium, gallium and a series of Group VI–VIII elements exhibit the properties of promoting agents.[78]

The disproportionation in the presence of aluminium chloride is accompanied by the extensive isomerisation of the products obtained and by polymerisation side reactions leading to the deactivation of the catalyst, which restricts the applicability of the catalytic system in question.

The deficit of C_4 and C_5 hydrocarbons which arose in the 1970's, combined with the availability of superfluous C_6–C_8 paraffins, stimulated the interest of investigators in this reaction. It was established that extensive (more than 50%) disproportionation of paraffinic hydrocarbons can be achieved at a pressure above 1 MPa in the presence of high-silica zeolites (mordenite and type ZSM zeolites),[7,79–81] as well as bifunctional catalysts containing Group VI and VIII metals and a non-acid carrier.[82,83] In the latter case, the process proceeds without the isomerisation of the products of the kind which occurs on aluminium chloride and zeolites.

On zeolitic catalysts, the paraffin disproportionation products are undoubtedly formed via repeated intermediate reactions, as a result of which the composition of the products does not correspond to the equivalent contents of paraffins which are lighter and heavier than the initial hydrocarbon.

This type of process makes it possible to obtain the light homologues closest to the initial paraffinic hydrocarbons virtually without the formation of low-molecular-weight C_1 and C_2 products, the appearance of such products being inevitable in the usual hydrogenolysis. Thus the conversion of n-butane into propane with a selectivity of about 90% has been achieved on H-mordenite:[80]

$$3C_4H_{10} + H_2 = 4C_3H_8.$$

Table 3. Proportions of the products of the disproportionation of C_5–C_7 paraffins on the H-mordenite catalyst[9] [T = 320–340 °C, p = 5 MPa, rate of supply of raw material (space velocity) 1 h^{-1}, molar ratio hydrogen : raw material = 0.5].

Products*	n-Pentane	n-Hexane	n-Heptane	Products*	n-Pentane	n-Hexane	n-Heptane
C_1	4.8	1.2	1.5	C_5	—	26.8	14.7
C_2	9.3	2.5	1.9	C_6	15.7	—	6.6
C_3	21.0	30.6	36.8	C_7	—	1.1	—
C_4*	49.2	37.8	38.0	C_8	—	—	0.5

*iso : n ≃ 2 : 1.

According to the results of Bursian et al.,[9] the predominance of light paraffins in the disproportionation products on the metallo-mordenite catalyst becomes more pronounced on passing from n-pentane to n-hexane, which can be explained by the vigorous hydrocracking of heptanes (Table 3). Indeed, n-heptane undergoes hydrocracking under the conditions investigated with formation of equimolecular amounts of propane and butanes. Thus the reaction of n-hexane can be described by the overall equation

$$2C_6H_{14} + H_2 = C_3H_8 + C_4H_{10} + C_5H_{12}. \quad (2)$$

In this sense, this process can be regarded as bimolecular hydrocracking.[9] The significant role of disproportionation in the hydrocracking of paraffins on metallozeolitic catalysts had been pointed out previously.[84] Approximately 70% of paraffinic C_4 and C_5 hydrocarbons have a branched structure. Together with the main reaction, side reactions involving the unimolecular hydrocracking of the raw material and the C_4 and C_5 products take place

to a slight extent: the yield of the C_1 and C_2 products does not exceed 5 mol % relative to the hexane which has reacted, while the yield of propane is close to the stoichiometric value corresponding to Eqn. (2).

There exist different points of view concerning the mechanism of the disproportionation of paraffinic hydrocarbons. Some workers[7,77,81] believe that it takes place via a condensation fragmentation mechanism, i.e. without the formation of low-molecular-weight alkylating agents. According to other workers,[75,85] the reaction takes place via a transmethylation mechanism.

According to the results of Kogan et al.[86] and Zhdanov et al.,[87] considerable amounts of C_7–C_{10} alkylbenzenes are formed in the reaction of C_5 and C_6 paraffins on H-mordenite and H-ZSM-5 zeolite in the presence of benzene at 300–380 °C and a pressure of 3.5 MPa (the degree of alkylation of benzene exceeds 50%), which is regarded as confirmation, in principle, of the transalkylation mechanism.[75,85] However, from the same data[86,87] one can conclude that the intermolecular transfer of the C_2, C_3 fragments plays the most significant role because the main primary alkylation products are ethylbenzene (on H-mordenite) and propylbenzene (on H-ZSM-5).

Analysis of the few data available[7,79–83] shows that metal-containing high-silica zeolites are the most promising catalysts of the disproportionation of C_6 and C_7 paraffins with formation of isoparaffinic C_4 and C_5 hydrocarbons. The reaction is carried out at a hydrogen pressure of 3–10 MPa, temperatures in the range 300–450 °C, and with the raw materials supplied at a space velocity of 0.5–2 h^{-1}. For the vigorous occurrence of the disproportionation reaction, it is essential to maintain a higher partial pressure of the hydrocarbon than in hydrocracking.

In a study of the disproportionation of mixtures of isobutane and n-hexane on a metallozeolitic catalyst with formation of isopentane [the reverse of reaction (1)], it was shown that, with increase in the isobutane : n-hexane molar ratio from 0.5 to 2.7, the yield of isopentane increases from 14.3 to 49.3 wt.%.[7] The data on the hydrocracking of n-hexane presented in the above study[7] for comparison show that the disproportionation ensures a more favourable composition of the reaction products (an increased content of isopentane and isohexanes).

The industrial application of paraffinic hydrocarbon disproportionation processes will make it possible to increase the manufacture of the acutely deficient C_4 and C_5 paraffins by processing their nearest homologues without the formation of the C_1 and C_2 light products, which are of little value, and, as can be seen from Eqn. (2), will significantly restrict the consumption of hydrogen compared with hydrocracking.

IV. Dehydrogenation of paraffinic hydrocarbons on aluminoplatinum catalysts

The dehydrogenation of C_4 and C_5 paraffinic hydrocarbons was first achieved on oxide catalysts. This led to the creation of large-scale industrial processes involving the dehydrogenation of butanes and isopentane on chromium oxide catalysts promoted by the addition of alkali metals (Ref.11, pages 147, 157; Ref.17). The dehydrogenation of higher n-paraffins to the corresponding mono-olefins was also initially investigated on aluminochromium catalysts.[18] Subsequently, in order to increase the selectivity and stability of aluminochromium catalysts, the reaction was carried out in hydrogen on catalysts promoted by lithium or potassium.[88,89]

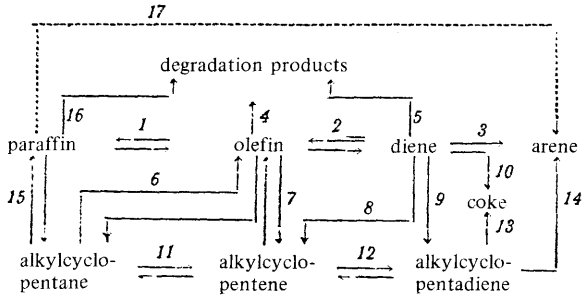
In connection with the development of the industrial manufacture of polymetallic reforming catalysts and the growth of the requirement for higher linear mono-olefins in order to obtain surfactants and detergents, at the end of the 1960's the dehydrogenation of C_8–C_{18} n-paraffins on an industrial scale began to be carried out on platinum polymetallic catalysts.[10,90] The number of patents for the dehydrogenation of lower paraffins, starting with propane, as well as ethylbenzene on platinum increased.[15] Data concerning the development of similar processes for the dehydrogenation of C_3–C_5 paraffins to mono-olefins appeared in the 1980's.[5,6,8,90] The main advantages of the platinum catalysts, namely their ability to effect the reaction at a high rate and with a high selectivity (90–95%), make them especially valuable in the light of modern requirements for the intensification of technology and the economic use of raw materials.[91,92] Nevertheless, it follows from reviews and monographs,[17,18,93–96] that the characteristic features of the dehydrogenation of paraffinic hydrocarbons to olefins or metallic catalysts have been little described in the literature compared with the dehydrogenation on oxides.

1. Thermodynamics, kinetics, and mechanisms

According to data for equilibrium in the reaction involving the dehydrogenation of paraffins to mono-olefins, a degree of hydrogenation which is acceptable in practice (30–40% for light paraffins and 10–15% for higher paraffins) in hydrogen is attained at a pressure not exceeding 0.2–0.4 MPa (Table 4).

According to Kazanskii et al.[101] and Isagulyants et al.,[102] the set of the possible reactions of paraffinic hydrocarbons heavier than C_5 on platinum catalysts can be represented by the following Scheme:

Scheme 1



The main mono-olefin formation reaction (*1*) is catalysed by metallic centres and is the primary process relative to most of the side reactions (*2–14*), which occur both on the metal and on the carrier. This is the reason for the need to modify both components of the catalyst and for the significant restriction of the contact time.

Studies on the kinetics of the dehydrogenation of paraffins with formation of olefins on platinum were begun comparatively recently. The kinetic data for the dehydrogenation of C_{10}–C_{14} n-paraffins on catalysts promoted by the addition of lithium and tungsten,[103] tin,[104] and lead[105] agree with the consecutive parametrisation scheme (reactions *1–3* in Scheme 1).

The rate of formation of mono-olefins from higher n-paraffins (C_{10}–C_{12}) on an aluminoplatinum–tin catalyst at 430–470 °C and atmospheric pressure can be expressed by the equation[104]

$$r = (k_1 p_1 - k_2 p_2 p_{H_2})/(p_{H_2}^{1.5} + n_2 p_2 + n_3 p_3),$$

where p_1, p_2, and p_3 are the partial pressures of the paraffin, the mono-olefins, and the diolefins respectively and k_1, k_2, n_2, and n_3 are constants ($n_3 \gg n_2$).

Table 4. Equilibrium degrees of dehydrogenation of paraffins to mono-olefins*.

p, MPa	Initial H_2:RH molar ratio	Equilibrium degree of dehydrogenation (mol%) at different temperatures, °C			
Propane (Ref.22)**		477	527	577	627
0.1	0	14	25	41	59
0.1	1	4	11.5	26	47
0.2	0	9.5	17 5	30	46
0.2	1	2	6	16	32
Isobutane (Ref.97)**		427	527	627	727
0.1	0	14	42	78	95
0.1	1	3.5	29	71	93
0.2	0	9	32	66	91
0 2	1	1.5	17	56	87
n-Butane (Ref.98, 99)**		427	527	627	727
0.1	0	10	37	75	93
0.1	1	2 5	21	66	91
0.2	0	7.5	27	61	87
0.2	1	1	13	50	83
Isopentane (Ref.98)**		427	527	627	727
0.1	0	19	57	88	97
0.1	1	7	45	84	96
0.2	0	4.5	44	80	94
0.2	1	3.5	30	73	92
n-Dodecane (Ref.100)		440	460	480	500
0.2	1	12	19	28	38
0.2	8	8	12	19	28
0.4	1	7	11	17	24
0.4	8	4	7	11	16
n-Octadecane (Ref.100)		440	460	480	500
0.2	1	18	27	38	49
0.2	8	12	19	28	39
0.4	1	10	16	24	34
0.4	8	6	10	16	24

* The reaction products are equilibrium mixtures of mono-olefins with different positions of the double bond in the molecule.
** The equilibrium degrees of dehydrogenation are quoted in the literature source only for a pressure of 0.1 MPa in the absence of hydrogen; the remaining values have been calculated.

Aromatic hydrocarbons do not influence the rate of formation of olefins under the conditions investigated.

The kinetics of the dehydrogenation of isobutane on bimetallic aluminoplatinum catalysts (promoting agents—copper, cadmium, indium, tin, and selenium; 500–600 °C; 0.1 MPa) correspond to the equation[106]

$$r = k_1 p_1 \gamma/(p_2 + k_2 p_{H_2}^{0.5}),$$

where γ is the coefficient which allows for the reversibility of the reaction; for the significance of the other notation, see above.

The mechanism of the dehydrogenation reaction includes the following stages:[104,106,107]

(1) the adsorption of the paraffinic hydrocarbons with elimination of one hydrogen atom; (2) the elimination of a second hydrogen atom with formation of an adsorbed olefin; (3) desorption of the olefin; (4) desorption of hydrogen.

In the case of consecutive dehydrogenation to the diolefin and an aromatic hydrocarbon, additional stages involving the readsorption of the mono- and di-olefin and the desorption of the diolefin and the aromatic product appear. Appreciable differences as well as common features (first order with respect to the initial hydrocarbon, inhibition by the reaction products) are characteristic of the kinetics of the dehydrogenation of paraffins with different molecular weights. Thus, according to isotopic data, the slow stage in the dehydrogenation of isobutane is dissociative adsorption of the paraffin,[106] while in the dehydrogenation of higher paraffins the slow stage is the desorption of the products.[104]

The presence of promoting agents can induce significant differences in the kinetics and chemistry of the dehydrogenation reaction on platinum. On bimetallic catalysts (in contrast to the unpromoted catalyst), the aromatisation via pathways related kinetically to olefins (reactions *2*, *6*, and *7* in the Scheme) is inhibited with a corresponding increase in the contribution of the "latent" aromatisation pathway *17* without the desorption of the intermediate products.[108]

A kinetic equation has been obtained[109] for the rate of dehydrogenation of isopentane to isopentenes in the presence of water vapour on a platinotin catalyst deposited on a zinc–aluminium oxide spinel (546–589 °C, 0.1 MPa) with allowance for the deactivation of the catalyst by coke:

$$r = \frac{k_1 p_1}{(1 + b p_1)^2}\left(1 - \frac{p_2 p_{H_2}}{p_1 K_e}\right)\exp(-\alpha c_c),$$

where K_e is the dehydrogenation equilibrium constant, k_1 and b are constants, c_c is the concentration of coke in the catalyst, and α is a parameter; for the significance of other notation, see above.

2. Catalysts

Platinum paraffin dehydrogenation catalysts are highly dispersed multi-component systems deposited on a thermostable oxide carrier with a high surface area. The concentration of platinum and the promoting agents does not usually exceed 1 wt.%. The most widely used carrier is γ-alumina.[10,15] Previously such platinum catalysts were widely used in the low-pressure reforming process.[31,32]

When the dehydrogenation process is carried out in the presence of steam at a temperature of about 600 °C, extremely stable spinels based on alumina and containing magnesium[110] or zinc[111] are used as the carrier.

In order to suppress the acidity, alkali or alkaline earth metals are introduced into the catalyst and also the halogen (chlorine) is removed. Group IB–VIB elements are added mainly with the aim of modifying the platinum.

Lithium or potassium as well as germanium subgroup elements are most often used as the promoting agents.[15] The nature of the surface of the highly dispersed deposited platinum catalyst is usually considered in terms of clusters—non-crystalline species whose size is as a rule less than 1 nm.[112]

The state of the atoms and the character of their interaction in clusters and crystals differ significantly, which is due to the coordinative unsaturation of the majority of atoms in the former case. Complex clusters, incorporating either only metal atoms (clusters of the alloy type[112]) or the atoms of an active metal together with the low-valence cations of the promoting agent stabilised by interaction with the carrier,[95,113] are formed on the surfaces of polymetallic deposited catalysts. Depending on the particle size and the nature of the interaction of the active metal with the carrier and the promoting agents, a significant change in the specific activity and selectivity of the active metal can occur[95,114,115] owing to both the geometrical effect (dilution of the active metal by the inert component, decrease in the size of the clusters) and the electronic effect (modification of the active metal as a result of the electronic interaction with the promoting agents[116,117]). The main cause of the deactivation of platinum dehydrogenation catalysts under the reaction conditions is coke deposition. Apart from the blocking of the surface of the metal and of the carrier pores by coke,[118] contact between platinum and the hydrocarbon medium diminishes the surface area of the metal as a result of its crystallisation[119] or the formation of a spinel with aluminium oxide.[120]

These effects evidently represent special forms of a general process involving the formation of the catalyst surface under the influence of the reaction mixture, which has been considered by Balandin,[121] Roginskii,[122] and Boreskov.[123]

Saturation by carbon alters the activity and selectivity of platinum in the hydrogenolysis, isomerisation, and dehydrocyclisation reactions of n-hexane[124] and in the dehydrogenation of cyclohexene (Ref.125, page 487). The degree of the poisoning of the catalyst by coke is not determined exclusively by its concentration and may differ significantly depending on the coke formation conditions and the nature of the catalytic reaction. The causes of the variation in the toxicity of coke may be (a) a difference in the structure of the coke deposits[125,126] (in particular the influence of the ordered and disordered layers of coke may be significantly different[125]), (b) a change in the quantitative distribution of coke between the metal and the carrier when the coke formation conditions are altered,[127] and (c) selective poisoning of the metallic centres catalysing the given reaction (deuterium exchange, dehydrogenation, and hydrogenolysis[128,129]).

The most important feature of modern polymetallic catalysts is their increased stability under coke formation conditions. The causes of the resistance to coke of catalysts of this kind is believed to be a decrease in the intensity of coke deposition as a result of the poisoning of the strong acid centres by the promoting agents (when tin is introduced[130,131]), saturation of the intermediates—precursors of coke (rhenium[132,133]), or hydrogenation of the carbon deposits (iridium[134]). At the same time, data have been obtained in recent years which indicate a sharp limit to the saturation of platinum by carbon in deposited dehydrogenation catalysts promoted by the zinc, gallium, and germanium subgroup elements, without the reduction in the overall coke concentration.[15,65,66,135–142] A similar effect involving protection against coke is caused, according to IR spectroscopic data for CO[135,136,138] and data for the chemisorption of benzene,[66] by the weakening of the adsorption of the reactants on platinum associated with the migration of the precoke intermediates onto the carrier, i.e. with the accumulation of coke outside the surface of the active metal.

The rhenium–sulphur system affords analogous protecting properties in relation to coke,[15,65] which has been explained by the high stability of rhenium sulphides.[65] A dependence of the promoting effect of rhenium on the presence of sulphur in platinum catalysts has been observed.[143,144]

The ideas examined here make it possible to explain the retention of the high effectiveness of bimetallic aluminoplatinum dehydrogenation catalysts even for a coke content exceeding 10% of the mass of the catalyst (Ref.31, pages 355, 358; Ref. 32, page 101; Refs.145–148).

3. Technological processes involving the dehydrogenation of paraffinic hydrocarbons

The dehydrogenation of higher n-paraffins is carried out in a stationary bed of a non-acid polymetallic aluminoplatinum catalyst with the raw material supplied at high space velocities (20–40 h^{-1}), in the presence of a small excess hydrogen pressure (0.3–0.4 MPa), and at a temperature 450–500 °C. The degree of conversion per pass is ~10 wt.%, which necessitates the repeated recirculation of the unreacted paraffins.[10,15,149,150] The low degree of dehydrogenation makes it possible to carry out the process in a single adiabatic reactor.

The "Pacol" process developed by the UOP Corporation (USA), characterised by the above features, has found application in industry.[149,150] The synthesis of mono-olefins by this method is promising because of the exclusively high (not less than 90%) selectivity and economy of the process. An additional valuable product is also the hydrogen-containing gas with a purity of 96 vol.%, whose yield relative to the initial raw material is 2–2.7 wt.%. The catalytic dehydrogenation reaction mixture can be used directly for the alkylation of benzene with isolation of the unreacted paraffins in the stage involving the fractionation of the alkylation products. When olefins are used to synthesise higher alcohols using the oxo synthesis, the catalytic reaction mixture is directed from the dehydrogenation plant to the stage in which olefins are isolated by adsorption (the "Oleflex" proces), where a concentrate containing 90–95% of the linear mono-olefins is obtained. By 1983, 22 "Pacol" plants were in operation or were being built[150] with an output of 25 000–100 000 tonnes of olefins per year. The development of a forced version of the process with a conversion of 13–14.5% per pass has been reported.[150]

It follows from Table 5 that Soviet technological processes have analogous basic parameters. An increase in the degree of conversion from 10–11% to 16–17% makes it possible to reduce the number of circulations of the unreacted raw material by a factor of 1.5 and to diminish the energy expenditure, in agreement with the conclusions reached by Vora et al.[150] In industrial practice, the catalyst is replaced by a fresh portion after a single raw material cycle, the old one being directed to the platinum extraction stage.

The possibility of the selective dehydrogenation of C_3–C_5 paraffinic hydrocarbons to mono-olefins on promoted aluminoplatinum catalysts with an up to 15 day reaction cycle was demonstrated at the beginning of the 1980's.[90,97,151] In an isothermal reactor with a fixed catalyst bed, where the raw materials were supplied at a rate of 1000 h^{-1} (with respect to the gas), a 30–40 wt.% conversion of C_4 and C_5 paraffins was achieved with a selectivity up to 91–92.5 wt.% with respect to mono-olefins. These parameters are significantly better than in the fluidised chromium

oxide catalyst bed (Table 6). The coke content in the catalyst at the end of the cycle reaches 12–15 wt.% (0.007–0.012 wt.% relative to the raw material passed through the system).

Table 5. Characteristics of the dehydrogenation reactions of C_{11}–C_{14} paraffinic hydrocarbons on a polymetallic aluminoplatinum catalyst.[15]

Parameters	Regime	
	normal	severe
Pressure, MPa abs.	0.4—0.5	0.3
Conversion, wt.%	11.2	17.8
Selectivity in formation of n-monoolefins, wt.%	90	85*
Duration of reaction cycle, days	30	20

Note. Temperature 460–500 °C, rate of supply of liquid raw material (space velocity) 20–30 h^{-1}, molar ratio hydrogen : raw material = 8 : 1.
** Without the hydrogenation of dienes.

The considerable interest in the synthesis of C_3–C_5 olefins by the paraffin dehydrogenation method is due to their wide application in petrochemistry, mainly for the preparation of synthetic rubber monomers and polyolefins[15–17] and to the considerable growth of the extraction of the raw material—liquefied petroleum gases.[152] Three new processes have been developed for this purpose during a short period.[153]

In the "Oleflex" process of the UOP Corporation (USA), a unit of three adiabatic reactors, analogous to the reactor for the "Pacol" process, is used with intermediate heating of the stream to compensate for the endothermicity of the reaction (~130 kJ mol^{-1}). The process is carried out in a fluidised bed of a polymetallic platinum catalyst (of the type of the catalyst for the "Pacol" process) with continuous regeneration. Coke formation does not exceed 0.02 wt.% relative to the raw material.[97] The working cycle of the catalyst, withstanding more than 250 regenerations,[97] is 3–14 days.[153] For a 45% conversion of isobutane, the selectivity for the formation of isobutene was 87.5% and that for the dehydrogenation of isopentane, taking into account the formation of isoprene, was 77.5 wt.%.[97]

In the "Star" process of the Philips Company, carried out in an isothermal tubular reactor with a fixed catalyst bed in the presence of steam,[153] a promoted platinum catalyst based on a thermostable spinel is also used judging from the patents of this Company.[17,111]

According to Choudhury's communication,[153] for an 8 h working catalyst cycle the selectivity in the dehydrogenation of isobutane reaches 95 mol % with ~50% conversion, which agrees with patent and research data for the dehydrogenation of paraffins on catalysts of this kind under similar conditions.[111,154] The "Oleflex" and "Star" processes are being tested on a semi-industrial scale.[153]

Thus, among the three new C_3 and C_4 paraffin dehydrogenation processes, two are based on the use of polymetallic platinum catalysts, which indicates the maintenance of the tendency towards the expansion of their applications noted previously.[15]

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Table 6. Parameters of the dehydrogenation reactions of butanes and isopentane on different catalysts.[16,151]

Parameter	n-Butane		Isobutane		Isopentane	
	a	b	a	b	a	b
Temperature, °C	545—560	570—600	540—570	580—620	530—560	550—610
Pressure, MPa	0.2	0.1—0.2	0.25	0.1—0.2	0.2	0.1—0.2
Hydrogen : raw material molar ratio	0.75:1	—	1:1	—	2:1	—
Rate of supply of raw material (space velocity) (with respect to gas), h^{-1}	1000	100—300	1000	100—300	700	100—300
Degree of conversion per pass, wt.%	31	41—43	40	44—48	30	43—45
Yield of olefins relative to raw material which has reacted, wt.%	92.5	72—76	91.1	77—82	92.0	68—74
Selectivity, % of theoretical	96.0	75—79	94.5	80—85	94.5	70—76

Note. Catalysts: a) aluminoplatinum; b) K-5 aluminochromium.

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