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Dehydrogenating properties of supported low-percentage palladium-containing catalysts

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Abstract. The catalytic and certain physicochemical properties of low-percentage palladium and bimetallic (Pd–Re, Pd–Co, and Pd–lanthanide oxides) supported catalysts have been examined in the dehydrogenation reactions of cyclanes, cyclenes, cyclohexadienes, their functional derivatives, and heterocyclic compounds and also in the aromatisation of petrol fractions at elevated temperatures and at hydrogen pressures ranging from atmospheric upwards. The influence of thermodynamic factors on the dehydrogenation reaction is discussed and the mechanism of this reaction is considered. The bibliography includes 160 references.

I. Introduction

During the 1950s–1960s, the catalytic reactions of C_6–C_8 hydrocarbons designed to obtain aromatic hydrocarbons were vigorously investigated both in our country and abroad. In particular, the dehydrogenation reaction of cyclanes served as a model for the selection of active metal oxide catalysts. This reaction is also of practical interest, since the aromatisation of cyclanes makes it possible to increase the octane number of the petrols obtained in the catalytic reforming process.

Mainly platinum is mentioned in the extensive patent literature of those years devoted to catalytic aromatisation in the presence of Group VIII metals. Active studies in this field were performed in the USA.[1,2] Together with the platinum catalysts, certain patents mentioned palladium catalysts on various carriers.[3–9] However, there is no information in these patents about the methods for the preparation of the catalysts, their activation, stability, etc.

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Studies on the selection of effective low-percentage supported metal oxide catalysts, including those containing palladium, for the dehydrogenation of cyclanes and the aromatisation of petrol fractions under reforming conditions at elevated temperatures and hydrogen pressures have been carried out since the 1950s at the Zelinskii Institute of Organic Chemistry under the supervision of N I Shuikin and Kh M Minachev.[10]

The fundamental and applied aspects of the use of palladium-containing catalysts on the sibunit carbon carrier (a highly porous graphite-like material) in the reverse hydrogenation reaction and also in oxidation, carbonylation, etc. reactions have been widely discussed in recent years.[11–15] The palladium–carbon catalysts also exhibit an activity in the dehydrogenation reaction of cyclanes.[16] However, whereas the palladium catalysts are widely used in the hydrogenation reaction, they have not found so far a large-scale use in the dehydrogenation reaction. Nevertheless, the problem of the replacement in supported catalysts of platinum, which is active in the dehydrogenation of cyclanes and in the aromatisation of petrol and other fractions resulting from the processing of petroleum, by the less scarce palladium is of current interest.

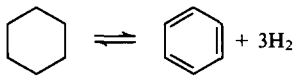
Supported palladium catalysts are also used in fine organic synthesis, which leads to new simpler procedures for the synthesis of valuable products. Heterocyclic rings constitute the structural basis of a large number of medicinal substances both of natural and of synthetic origin. The molecules of these compounds also contain various aliphatic and aromatic substituents. Derivatives of five- and six-membered heterocycles and their condensed systems constitute a class of medicinal heterocyclic compounds of practical importance.[17] Dehydrogenation reactions in the presence of supported palladium catalysts are employed to obtain some of them.

Studies designed to develop effective dehydrogenating supported palladium catalysts (monometallic and bimetallic) for the conversion of cyclanes, cyclenes, cyclohexadienes, and their derivatives and for the aromatisation of petrol fractions and the synthesis of indole, coumarin, papaverine and their derivatives, will be examined in the present review.

II. Thermodynamics of the dehydrogenation reactions of naphthenes

1. The influence of pressure

The dehydrogenation of six-membered naphthene hydrocarbons involve an appreciable increase in volume, so that an increase in pressure hinders their occurrence.



Calculations have shown[18] that the influence of pressure is particularly marked at temperatures below 500 °C. An increase in temperature from 400 to 600 °C at the same pressure shifts the equilibrium towards the formation of aromatic hydrocarbons. An increase in pressure from 14 to 56 atm at 510 °C has a negative effect on the formation of aromatic hydrocarbons, in particular on the conversion into benzene of cyclohexane and methylcyclopentane after the isomerisation of the latter to cyclohexane. The influence of pressure in this reaction is greater than in the conversion of methylcyclohexane into toluene.[19] An increase in pressure from 21 to 42 atm at 444 °C leads to a decrease in the yield of benzene obtained from cyclohexane from 70% to 33%.[20] In the presence of the Pd/Al_2O_3 catalyst at 460 °C, a space velocity (v) of 1.0 h^{-1}, and for the ratio H_2:HC = 5:1 (HC = hydrocarbon), an increase in pressure from 35 to 65 atm reduces the yield of aromatic hydrocarbons derived from ethylcyclohexane from 57.7% to 44.7%.[21]

2. The influence of temperature

In the presence of supported catalysts containing Group VIII metals, an increase in temperature from 440 °C to 510 °C (P_{H_2} = 21 atm, v = 3.0 h^{-1}, H_2:HC = 4:1) increases the yield of aromatic hydrocarbons derived from cyclohexane, methylcyclohexane, and methylcyclopentane from 70% to 93%, from 83% to 92%, and from 56% to 72% respectively.[20] In reactions involving cyclohexane and methylcyclohexane, the content of aromatic hydrocarbons in the catalytic reaction mixture reaches the equilibrium value.[22] An increase in temperature from 426 to 540 °C promotes the dehydrocyclisation of n-heptane; the yield of aromatic hydrocarbons increases from 2% to 25%.[20]

Thus, in conformity with thermodynamic postulates, an increase in hydrogen pressure inhibits the dehydrogenation reactions of six-membered cyclanes but at a higher temperature this influence becomes less marked. For example, at 510 °C the yield of benzene from cyclohexane is almost independent of pressure.[20] An increase in pressure from 10.5 to 35 atm at 496 °C also has an insignificant influence on the dehydrogenation of methylcyclohexane.[19]

Nevertheless, the reforming process is carried out in industry under a hydrogen pressure in order to suppress reactions leading to the formation of a 'carbonaceous film' on the catalysts,[23,24] which reduce their activity.[25-28]

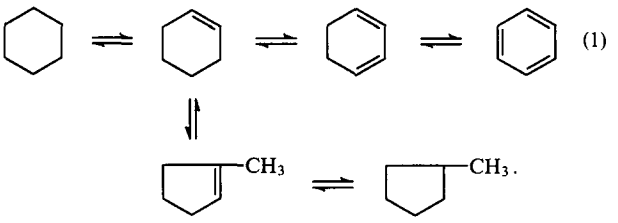
3. The influence of other factors

Apart from temperature and pressure, the aromatisation reaction is also influenced by the space velocity at which the starting material is supplied and by the starting material: hydrogen ratio.[19,29,30] As a rule, an increase in space velocity diminishes the yield of aromatic hydrocarbons. The change in the molar ratio of the circulating hydrogen and the starting material in the range (4-11):1 has little effect on the yield of the aromatisation product.[29] However, under platforming conditions, where the effluent gas consists mainly of hydrogen, the recirculating gas hinders the formation of the 'carbonaceous film' on the catalyst[24] and increases the lifetime of the latter, and thereby eliminates the need for frequent regeneration.

III. The mechanism of the dehydrogenation of cyclanes and cyclenes

At one time the sextet[31-41] and doublet[32,37,42-44] mechanisms of the dehydrogenation reaction as well as the mechanism postulating the initial formation of cyclohexene with subsequent disproportionation to cyclohexane and benzene[45-47] were widely discussed in the literature.

On metal oxide catalysts operating at an elevated pressure, the dehydrogenation of six-membered cyclanes[48,49] is to a large extent accompanied by their isomerisation with formation of five-membered cyclanes. A number of workers[50-52] considered the following scheme [scheme (1)] for the conversion of cyclohexane on metal oxide catalysts:



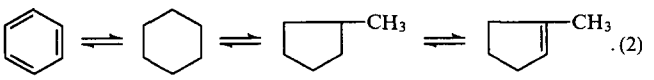
(1)

The isomerisation reaction proceeds via the carbonium ion mechanism.[53,54]

The reactions of radioactive cyclohexane have been investigated on the 1% $Pd-HF-Al_2O_3$ catalyst under reforming conditions (T = 480 °C, P_{H_2} = 21 atm, v = 1-2.5 h^{-1}, H_2:HC = 5:1).[55] In the presence of this catalyst, cyclohexane is converted into benzene (59%-63%) and methylcyclopentane (19%-23%), cyclohexene also undergoing dehydrogenation and isomerisation. However, cyclohexene, which is more reactive than cyclohexane, reacts almost completely. The specific radioactivity of the initial cyclohexene was zero and it might have been expected that it would increase with increasing degree of conversion. However, the results of the analysis of the reaction products showed that cyclohexene is almost nonradioactive, whereas benzene and methylcyclopentane are radioactive. Hence it follows that cyclohexane is not converted into cyclohexene. Thus the result failed to confirm the hypothesis that cyclohexene is an intermediate in the dehydrogenation of cyclohexane to benzene and in its isomerisation to methylcyclopentane. On a bifunctional catalyst, benzene and methylcyclopentane can apparently be obtained from cyclohexane without the intermediate formation of cyclohexene or at least without its desorption from the catalyst surface.[55]

In view of the results presented above, the role of methylcyclopentene in the expansion of the methylcyclopentane ring was investigated under the same conditions (T = 480 °C, P_{H_2} = 20 atm, v = 2.5 h^{-1}, H_2:HC = 5).[56,57] The reactions of a mixture of [6-^{14}C]methylcyclopent-1-ene and methylcyclopentane were investigated on the 1% Pd/Al_2O_3 catalyst. It was shown that the specific radioactivities of cyclohexane and benzene and also methylcyclopentane in the reaction products are similar and are in the range 2.0%-3.6% of the specific radioactivity of the initial [6-^{14}C]methylcyclopent-1-ene, whereas the specific radioactivity of the latter in the catalytic reaction mixture is much higher (12.1%-36.8%). Hence it follows that cyclohexane and benzene are obtained from methylcyclopentane without the intermediate formation of methylcyclopent-1-ene.

Scheme (2) therefore characterises the interconversions of the cyclanes more accurately than scheme (1):



(2)

But at the same time, it is necessary to take into account the possible conversion of methylcyclopent-1-ene into cyclohexane and benzene via scheme (1) as well, since the specific

radioactivities of cyclohexane and benzene exceed somewhat that of methylcyclopentane, which would be impossible for a strictly consecutive mechanism.

Thus cyclohexene is not an essential intermediate in the formation of benzene and methylcyclopentane from cyclohexane[55,57] and methylcyclopentene is likewise not an obligatory intermediate in the formation of benzene from methylcyclopentane.[56,58] This is confirmed by the experimental data for the reactions of cyclohexane and cyclohexene under reforming conditions (T = 450 °C, P_{H_2} = 21 atm, v = 10 h^{-1}, H_2 : HC = 5) where the 0.5% Pt – 0.3% F – Al_2O_3 catalyst was poisoned with thiophene.[59] When mixtures of cyclohexane or cyclohexene with thiophene were passed through the system, a sharp decrease in the dehydrogenating capacity of the catalyst was observed, while the benzene content in the catalytic reaction mixtures diminished respectively from 74.2% and 90% to 15.4% and 46.6%. Thus the addition of thiophene to cyclohexane and cyclohexene diminishes the yield of benzene almost by a factor of 5 and only by a factor of 2 respectively.

The hypothesis[60] that thiophene acts predominantly on the cyclohexene dehydrogenation centres conflicts with the above results, so that the data of Hensel et al.[60] are inconsistent with scheme (1). The ratio of the concentrations of cyclohexane and methylcyclopentane in the catalytic mixtures obtained from cyclohexane is much closer to the equilibrium ratio than in the catalytic reaction mixture obtained from cyclohexene. These data also indicate that cyclohexene cannot be regarded as an essential intermediate in the isomerisation of cyclohexane to methylcyclopentane under reforming conditions.

In order to test scheme (1) and the data of Hensel et. al.,[60] a study was made of the reactions of cyclohexane and cyclohexene on the 1% Pd/AlO_3 and 1% $Pd/Al_2O_3 \cdot HF$ catalysts. The dehydrogenating functions of these catalysts were poisoned by thiophene, after which they were restored by treatment with a hydrocarbon. In contrast to the experimental conditions in the study of Isagulyants and Ryashentseva,[59] a much lower rate of supply of the hydrocarbons (5.5 h^{-1}) at 460 °C, P_{H_2} = 20 atm, and H_2 : HC = 5 was chosen to make sure that the catalytic reaction products contained also methylcyclopentene in addition to benzene and methylcyclopentane. For comparison, a study was also made of the reactions of cyclohexane and cyclohexene under the same conditions on the industrial AP-56 aluminoplatinum catalyst. On the palladium catalysts, the yield of methylcyclopentene was found to be higher by 2% – 5%, whilst that of benzene was lower by 12% – 16%, than on the platinum catalyst. This shows that the palladium catalysts are less active in the dehydrogenation reaction and are more active in the isomerisation process. After a mixture of cyclohexane with 1% of thiophene was passed through the system, the degree of activity of the aluminopalladium catalysts fell sharply (almost by a factor of 12), in contrast to the aluminoplatinum catalyst, while its isomerising activity remained almost unchanged. The dehydrogenating activity of the aluminopalladium catalyst was restored to the extent of 55%, while that of the fluorinated catalyst was restored to the extent of 50% relative to the initial activity after regeneration with cyclohexane for 6.5 and 8 h respectively. On the other hand, the activity of the platinum catalyst was 94% restored after passing cyclohexane for 4 h. Hence it follows that the dehydrogenating centres on the aluminopalladium catalyst are more sensitive to thiophene than the corresponding centres on the aluminoplatinum catalyst. In contrast to the platinum catalysts, the palladium catalysts convert cyclohexene into methylcyclopentenes to the extent of 12% – 27%, which indicates their higher isomerising activity.[61,62] The dehydrogenating activity of the aluminopalladium catalyst fell from 13.7% to 6.9% and that of the similar fluorinated catalyst fell from 21.7% to 13.9% when cyclohexene was passed (T = 460 °C, P_{H_2} = 20 atm, v = 5.5 atm, and H_2 : HC = 5) through the system after the latter had operated for 3 h. At the same time, their isomerising activity increased: the yield of methylcyclopentenes rose from 18% to 44% and from 10% to 17.5% respectively. Up to 0.5% of cyclohexadiene was detected in the catalytic reaction mixtures. Under the same conditions, the isomerising and dehydrogenating activities of the aluminoplatinum catalyst remained unchanged.

After cyclohexene mixed with thiophene was passed over the palladium catalysts, the degree of formation of benzene fell by a factor of 2.3. Their isomerising activity (the yield of methylcyclopentenes) decreased only insignificantly under these conditions, which is inconsistent with the hypothesis[50] that dehydrogenating centres of two types are present on the catalyst surface and that cyclohexane is converted into cyclohexene on sections of the first type, while benzene is formed from cyclohexene on those of the second type. On further passage of cyclohexene, the dehydrogenating functions of the palladium catalyst are not restored, in contrast to the platinum catalysts, and the catalyst is irreversibly poisoned. The yield of benzene obtained from cyclohexene is much lower than that of the benzene obtained from cyclohexane. On the aluminoplatinum catalyst, this difference is difficult to observe owing to the high degrees of conversion. On the aluminopalladium catalysts, the yield of the benzene derived from cyclohexane was 54% – 58%, whilst that of the benzene derived from cyclohexene was 18% – 22%.

According to the results of Ryashentseva et al.,[61] only the centres for the dehydrogenation of cyclohexane to benzene should be poisoned. Consequently, according to scheme (1), the yields of methylcyclopentane derived from cyclohexane and cyclohexene should be similar. The experimental yield of benzene under the conditions of the conversion of cyclohexane mixed with thiophene was 3%, which indicates the inhibition of the benzene formation centres. The yield of methylcyclopentane proved to be 4%, i.e. the hydrogenation centres were also inhibited, which conflicts with the results of Isagulyants and Ryashentseva.[59] When a mixture of cyclohexane with thiophene was allowed to react, the yield of methycyclopentane did not diminish.

It follows from these data that the reactions involving the isomerisation of cyclohexane and cyclohexene proceed independently and probably on different isomerising centres.[62] This has been confirmed by the results obtained on the fluorinated aluminopalladium catalyst. In the presence of the latter, the yield of methylcyclopentane derived from cyclohexane increases, compared with the yield on the aluminopalladium catalyst, from 9.8% to 12.8% after 1 h, whereas the yield of methylcyclopentenes obtained from cyclohexene diminishes from 27.2% to 12.1%.[61] After the passage of the cyclohexene – thiophene mixture over the palladium catalysts, the content of methylcyclopentene was ten times greater than the content of methylcyclopentane. The absence of cyclenes from the products of the catalytic reaction involving cyclohexane and the presence in the latter of methylcyclopentane also cannot be accounted for by scheme (1).

All these findings confirmed the conclusion[55,59] that cyclohexene is not an essential intermediate in the conversion of cyclohexane into methylcyclopentane and benzene. On the aluminopalladium catalyst, the reactions of cyclohexane and cyclohexene proceed by independent paths, probably via different intermediates.[61] However, these is also evidence in support of the conversion of cyclohexane into benzene on metals to a large extent via the intermediate formation of cycloalkenes.[63] The difficulty of detecting the intermediate cycloalkenes is associated with the fact that their reactivity increases greatly in the sequence cyclohexane < cyclohexene < cyclohexadiene and hence cycloalkenes are present in the products in appreciable amounts only for very low degrees of conversion.

Apart from the consecutive path leading to the dehydrogenation of cyclohexane, which includes the desorption of cyclohexene, another path may also exist where cyclohexane is converted directly into benzene via a stage involving the formation of surface cyclohexene or bypassing it. The choice between these paths is apparently determined by the nature of the

chemical bond between the adsorbed hydrocarbon molecule and the catalyst surface.[63] According to the data of Tetenyi et al.,[64] the contribution of the path involving the direct hydrogenation of cyclohexane to benzene increases, while that of the dehydrogenation via the intermediate cyclohexene diminishes in the sequence

Co > Ni > Rh > Ir > Re > Pd > Pt.

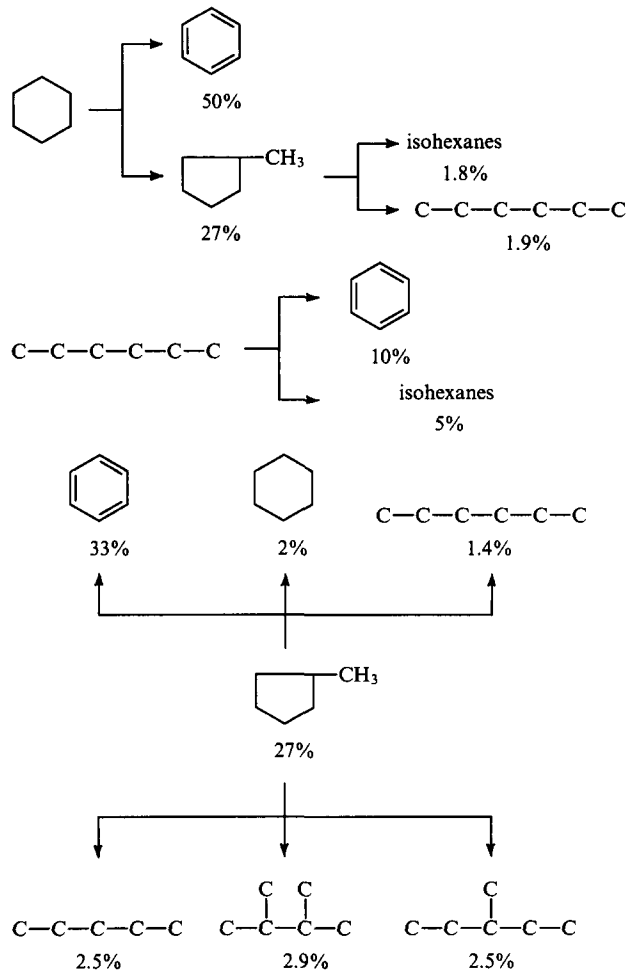
IV. Palladium-containing supported catalysts in the dehydrogenation reactions of cyclanes and their functional derivatives

According to Balandin's multiplet theory,[65] there should be a structural correspondence between the catalyst multiplet and the part of the reactant molecule oriented on it which is altered in the reaction. The hexagonal symmetry of the multiplet necessary for the hydrogenation of benzene and the reverse cyclohexane dehydrogenation reaction is achieved only on cubic face-centred and hexagonal (but not cubic) body-centred crystal lattices. Although platinum and palladium both have type *A* face-centred cubic lattices with constants of 0.27746 and 0.27511 nm respectively, their activities differ appreciably in the reactions considered.

Palladium is used widely in laboratory practice as a dehydrogenation and especially hydrogenation catalyst.[66] In Zelinskii's early studies,[66,67] palladium black without a carrier was used as the catalyst for the reactions of hydrocarbons. In subsequent investigations, palladium black was deposited on various carriers (asbestos, activated charcoal, etc.) in order to obtain catalysts with a maximum surface area. However, the concentration of the active metal was fairly high even in such cases and varied in the range 30%–40%,[68,69] sometimes attaining even 70%.[70] Such catalysts were characterised by a high activity in the hydrogenation of benzene and only a satisfactory activity in the dehydrogenation of cyclohexane. Their low dehydrogenating activity and low stability were explained by the fact that, after deposition on activated charcoal, palladium black exists in the form of a hydride (with a crystal lattice parameter of 4.04 Å instead of the normal parameter of 3.88 Å).[71] It was established that, during prolonged operation of the catalyst, this parameter remains almost unchanged. The X-ray diffraction patterns taken after prolonged operation of the catalyst were found to contain, apart from the lines due to palladium, also secondary lines which did not refer to either palladium or its hydride. The appearance of a new finely dispersed palladium phase was explained by the low stability of the palladium catalysts.[72] A phase of this kind did not appear during the employment of platinum catalysts.

The low-percentage palladium catalysts containing from 2.0% to 0.5% of Pd/C exhibit a high dehydrogenating activity.[73,74] Their X-ray diffraction study before and after use showed that they contain only one crystalline palladium phase and X-ray diffraction patterns did not reveal the appearance of any new lines after the participation of the catalyst in the reaction. The low-percentage catalysts are apparently more active and stable because their palladium lattice has favourable parameters. However, even these palladium catalysts lose their activity comparatively rapidly under the conditions of prolonged operation, especially with petrol fractions containing, in addition to the six-membered cyclanes, also five-membered cyclanes, aromatic hydrocarbons, and alkanes.

Systematic studies led to the development of a 0.5% Pd/Al_2O_3 catalyst treated with hydrofluoric acid and hydrogen sulfide,[10] which is capable of operating at an elevated H_2 pressure and a high temperature. The reactions of cyclohexane, n-hexane, and methylcyclopentane,[48] which constitute the basis of the reforming of petrol fractions, were investigated on this catalyst at $T = 480$ °C, $P_{H_2} = 20$ atm, $v = 1.0\ h^{-1}$, and $H_2 : HC = 5$.



It was shown that, together with the dehydrogenation of cyclohexane, the dehydroisomerisation of methylcyclopentane and the skeletal isomerisation and dehydrogenation of n-hexane take place on this catalyst. When gumbrin (a natural aluminosilicate containing 86.89% of SiO_2 or 4.14% of Al_2O_3 and having a specific surface of 260 $m^2\ g^{-1}$) is used as the carrier, methylcyclopentane is also formed from cyclohexane together with benzene on a 0.5% palladium catalyst under reforming conditions ($T = 475–480$ °C, $P_{H_2} = 20$ atm, $v = 1.0\ h^{-1}$, and $H_2 : HC = 5 : 1$). Under these conditions, the carrier itself (gumbrin) exhibits pronounced isomerising properties — 19.2% of methylcyclopentane is formed on this carrier from cyclohexane, the reaction being accompanied by slight cracking.[75] Treatment of the catalyst with hydrogen sulfide enhances its dehydrogenating and isomerising properties: the benzene content in the catalytic reaction mixture increases from 28.5% to 40.2%, while that of methylcyclopentane increases from 19.2% to 22.7%. This bifunctional catalyst may be useful for refining low-octane petrols.

The 0.5% Pd/Al_2O_3 and 0.5% Pd/SiO_2 catalysts have been investigated in the conversion of methylcyclohexane.[76] The experiments were performed under the following conditions: $T = 460$ °C, $P_{H_2} = 20$ atm, $v = 1.1\ h^{-1}$, and $H_2 : HC = 5 : 1$. The toluene contents in the products when the above catalysts were used amounted to 82% and 93% respectively. Under similar conditions, ethylcyclohexane underwent various reactions on the 0.5% Pd/Al_2O_3 catalyst: dehydrogenation, hydrogenolysis of the side chain, and isomerisation with ring contraction and subsequent opening of the five-membered ring.[77] The increase in pressure from 35 to 65 atm increases the degree of conversion of ethylcyclohexane from 61.4% to 84.8%. The introduction of fluorine into the catalyst lowers its dehydrogenating activity and increases its isomerising activity. It has been suggested that

fluorine in the form of PdF_2 partially shields the catalyst active centres, diminishing thereby its dehydrogenating activity.

The kinetics of the dehydrogenation of cyclohexane have been investigated on palladium-containing supported catalysts treated with hydrofluoric acid or hydrogen sulfide.[78] The apparent activation energies and pre-exponential factors in the Arrhenius equation for the reactions on the 0.5% Pd/Al_2O_3 and 0.5% $Pd/Al_2O_3 \cdot HF$ catalysts, calculated from the initial activity, hardly differed. After the treatment of the 0.5% $Pd/Al_2O_3 \cdot HF$ catalyst with hydrogen sulfide, the activation energy increased appreciably, while the pre-exponential factor changed by several orders of magnitude.

On the most active hydrogen sulfide-treated 0.5% $Pd/Al_2O_3 \cdot \cdot HF$ catalyst at atmospheric pressure, $T = 450$ °C, and $v = 0.3$ h^{-1}, cyclohexane is 94% dehydrogenated to benzene.[79]

New palladium-containing catalysts, obtained by depositing the metal on $AlPO_4$ and $AlPO_4 \cdot SiO_2$ colloidal systems, have been used successfully for the reduction of nitrobenzene.[80] Similar modified catalysts, containing 0.5% of palladium on the SiO_2, $AlPO_4$, and $SiO_2 \cdot AlPO_4$ carriers, have been investigated in the cyclohexane and methylcyclohexane dehydrogenation reactions under pulsed conditions.[81] In terms of dehydrogenating capacity, the platinum-containing catalysts proved to be much more active than the palladium-containing ones. Table 1 presents the results of experiments on the dehydrogenation of cyclohexane on these catalysts.

Table 1. Dehydrogenation of cyclohexane on various metal-containing catalysts[81] (atmospheric pressure, $T = 425$ °C, pulse size 8.34×10^{-5} moles).

Metal	Carrier	Yield of C_6H_6 (%)	Activity[a]
Pd	SiO_2	13.6	9.00
Pt	SiO_2	82.3	3.90
Pd	$AlPO_4$	5.2	2.87
Pt	$AlPO_4$	25.5	1.45
Pd	$SiO_2 \cdot AlPO_4$	13.8	4.01
Pt	$SiO_2 \cdot AlPO_4$	72.0	3.73

[a] The number of moles of cyclohexane converted per m^2 of the metal multiplied by 10^3.

During the last decades, physical methods permitting the study of highly dispersed metal particles distributed on the surface of the carrier have developed vigorously. New approaches to the selection of metal-containing supported catalysts have appeared.[82-87] The state of palladium on aluminium oxide has been investigated by the XPS method and its strong interaction with the carrier has been demonstrated.[88] The interaction of the metal with the carrier is influenced by the ligand environment. For example, impregnation catalysts obtained with the aid of $PdCl_2$ or $Pd(NO_3)_2$ solutions have different properties. The state of palladium also changes during the reduction of the catalyst. The aluminium oxide carrier is capable of retaining chlorine.

The strong interaction of $PdCl_4^{2-}$ with the acceptor centres of γ-Al_2O_3 has been observed.[89] On the other hand, palladium interacts weakly with the carrier of the Pd/SiO_2 catalyst. Zerovalent palladium is formed already at 100 °C, but the metal is not fully reduced, the most dispersed zerovalent palladium particles interacting with the carrier. According to the results obtained by transmission electron microscopy, the average Pd(0) particle size is 4.5 nm in the 1% Pd/Al_2O_3 catalyst at 300 °C and 8.5 nm in the 1% Pd/SiO_2 catalyst.

Current ideas about the interaction of the metal with the carrier were taken into account[90] when the properties of the 0.5% Pd/γ-Al_2O_3 and 0.5% Pd/sibunit catalysts were investigated in the dehydrogenation of cyclohexane. A strong interaction of the carrier with the metal is manifest in the first catalyst, while the sibunit carbon carrier hardly undergoes such interaction.[91] The specific surface of the active alumina was 225 m^2 g^{-1} for an overall pore volume of 0.68 cm^3 g^{-1}, while the specific surface of sibunit (granulated carbon) was 590 m^2 g^{-1} for a particle size of 2–2.5 mm.[91] The data concerning the dehydrogenation of cyclohexane on these catalysts are presented in Table 2.

Table 2. Dehydrogenation of cyclohexane (atmospheric pressure, $t = 1$ h, H_2 stream).[16]

Catalyst	Reaction conditions		Yield[a]	Content of C_6H_6 (%)
	T/°C	v/h^{-1}		
0.5% Pd/γ-Al_2O_3	425	0.75	51.0	87
	450	0.75	89.4	47
	480	0.75	63.7	98
0.5% Pd/γ-Al_2O_3	440	1.5	83.6	81
(treated with	440	0.7	81.2	85
H_2S)	450	1.5	91.8	85
	455	0.6	95.2	90
	460	0.5	56.6	95
	470	0.5	66.7	100
0.5% Pd/sibunit	430	1.2	75.3	83
	440	1.2	80.0	89

[a] Yield of the catalytic reaction mixture.

Cyclohexane is dehydrogenated in the temperature range 430–480 °C. Treatment of the catalyst with hydrogen sulfide increases the benzene content in the catalytic reaction mixture almost by a factor of 2 ($T = 440-450$ °C, $v = 0.75$ h^{-1}). A high yield of benzene is retained also following an increase in the space velocity at which cyclohexane is supplied by a factor of 2. The Pd/sibunit catalyst likewise exhibits a high dehydrogenating activity under similar conditions.

The dehydrogenating activity in this reaction is apparently influenced more by factors such as the porosity of the carrier, the catalyst grain size, the methods used to activate the catalyst, the composition of the reaction mixture, and other factors (which in fact determine the rate of reaction) than by the metal–carrier interaction.

Ethylcyclohexane was dehydrogenated in the liquid phase under a nitrogen atmosphere at 132 °C on suspended Pd/C and Pd/Al_2O_3 catalysts.[92] The activity of the catalyst was determined from the amount of hydrogen evolved. The results are presented in Table 3.

Table 3. Liquid-phase dehydrogenation of ethylcyclohexane (0.02 mmol per 100 ml of the catalyst) in the presence of supported catalysts containing 0.5% of the metal.[92]

Catalyst	H_2/mmol	Yield of ethylbenzene/mmol
Pd/C	9.22	3.18
Pd/Al_2O_3	3.67	1.25
Pt/C	23.93	7.75
Pt/Al_2O_3	13.04	4.15

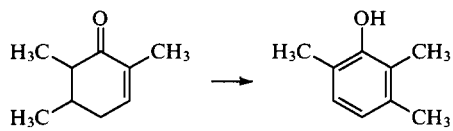
The Pd/C catalyst has a dehydrogenating activity higher by a factor of 3 than Pd/Al_2O_3. However, Table 3 shows that both catalysts are appreciably inferior to the supported platinum catalyst. Under the conditions of liquid-phase dehydrogenation with the recondensation of the ebullition products, the Pd/C and Pd/Al_2O_3 catalysts exhibit a higher activity in the preparation of cyclooctene from cyclooctane than do supported rhodium and ruthenium catalysts.[93] The activity was determined from the degree of desorption of hydrogen.

The use of the Pd/C catalyst leads to new possibilities for the preparation of silicon-containing compounds by the hydrosilylation of cyclohexadiene with subsequent dehydrogenation. Phenylsilicones can be synthesised by this procedure in one stage, in which the liquid silicon hydride and cyclohexadiene react on refluxing in the presence of the Pd/C catalyst and $C_6H_5NO_2$ as the acceptor.[94]

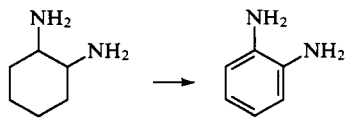
There are data concerning the use of supported palladium catalysts in the dehydrogenation reactions also of other organic compounds.[95-97] The synthesis of 8-hydroxycymene by the dehydrogenation of 8-hydroxymenthene in the presence of a palladium-containing catalyst has been described.[95]

A mixture containing 78% of α-terpineol and 10% of γ-terpineol was passed at 190–200 °C at a rate of 0.4 kg h^{-1} for 588 h over the 0.2% Pd/Al_2O_3 catalyst treated beforehand with a NaOH solution, partly dried, and reduced.[95] This yielded 231.3 kg of product, which contained 154.78 kg of 8-hydroxycymene, 49.40 kg of the dihydroterpineol isomers, 11.98 kg of *p*-cymene and 10.2 kg of the initial terpineol. The degree of conversion was 98.2%. During the tests, the catalyst did not lose its activity.

Phenol and phenol derivatives can be obtained by dehydrogenating a cyclic ketone in the gas phase in the presence of the Pd/Al_2O_3 catalyst.[96] For example, 2,3,6-trimethylphenol has been obtained in 100% yield on passing 2,5,6-trimethylcyclohex-2-en-1-one in a stream of hydrogen at 300 °C at a rate of 0.25 litre per litre of the 0.5% Pd/Al_2O_3 catalyst (the specific surface of the carrier was 4 m^2 g^{-1}). The catalyst was prepared by impregnating the carrier with an aqueous $PdCl_2$ solution and was then dried and reduced with hydrogen at 300 °C. The degree of conversion was 82.6%. The selectivity of the catalyst decreased with increase in the specific surface of Al_2O_3. The selectivity was zero for a specific surface of 170 m^2 g^{-1}.



o-Phenylenediamine has been obtained in a yield of 69% at 200 °C by the dehydrogenation of 1,2-diaminocyclohexane in the gas phase at 175–225 °C, a pressure of 0.1–10 atm, and a supply rate of 0.25 ml min^{-1} over the 5% Pd/Al_2O_3 catalyst containing 0.61% of LiOH under a nitrogen atmosphere.[97]

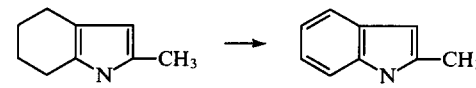


V. Palladium catalysts in the dehydrogenation reactions of heterocyclic compounds

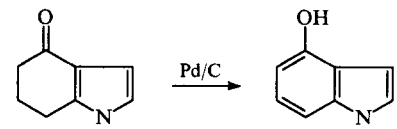
1. Dehydrogenation of tetrahydroindole and its derivatives

The selection of a catalyst for the dehydrogenation of heterocyclic compounds with a pyrrole ring is complicated by the fact that they poison catalysts containing noble metals. Indole and its derivatives were synthesised in the presence of palladium-containing supported catalysts in both liquid and gas phases. Indole and its homologues are important intermediates in fine organic synthesis. They are used as plant growth stimulators, especially β-indolylacetic acid (heteroauxin) and 3-(γ-indolyl)butyric acid.[98] Numerous medicinal preparations used in neurophysiology and psychopharmacology have been obtained from indole derivatives.[99] The principal source of indole is coal tar, which contains 2%–3% of this substance.[100]

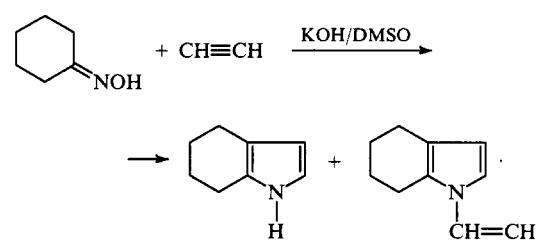
Tetrahydroindole and its derivatives are promising sources for the preparation of pure indole by dehydrogenation. 1-Methylindole has been obtained in 67% yield from 1-methyl-4,5,6,7-tetrahydroindole in the presence of the 10% Pd/C catalyst in the xylene liquid phase under a stream of nitrogen after refluxing for 18 h.[101,102]



4-Hydroxyindole can be obtained in 94% yield by the liquid-phase dehydrogenation of 4-oxo-4,5,6,7-tetrahydroindole in 2-ethylhexyl acetate in the presence of a Pd/C catalyst at 192 °C.[103] The reaction is carried out by refluxing for 7 h.



The possibility of the dehydrogenation of the cyclohexene fragment of 1-vinyl-4,5,6,7-tetrahydroindole (VTHI) and in its mixture with 4,5,6,7-tetrahydroindole (THI) under the conditions of heterogeneous catalysis on low-percentage palladium-containing supported catalysts has been demonstrated.[104] The compounds VTHI and THI became available as a result of the development of a simple method of their synthesis from ketoximes and ethyne by the Trofimov reaction.[105] In the case of cyclohexanone oxime, the process proceeds in accordance with the following mechanism:

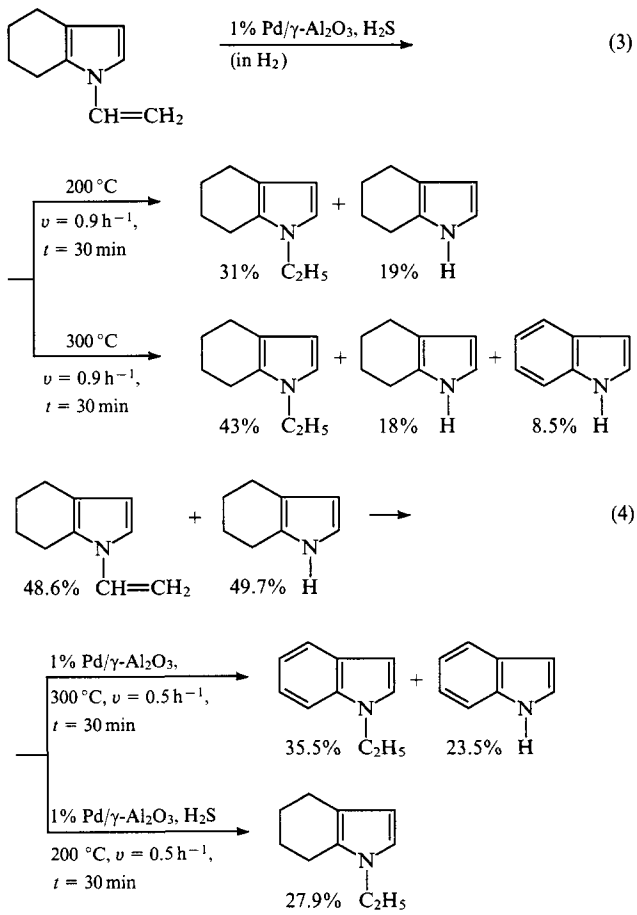


Depending on the medium in which the reaction is carried out, it is possible to obtain high yields (up to 83%–92%) of THI or VTHI.[106] The compounds THI and VTHI are promising indole synthons,[105-108] and are used, in particular, to synthesise α-substituted indoles which are otherwise difficult to obtain.[101,102]

The reactions of VTHI and its mixtures with THI in a solvent were achieved in a flow-type apparatus at atmospheric pressure in the temperature range from 100 to 525 °C, at $v = 0.3-1.2$ h^{-1}, and for a duration of the experiment ranging from 30 min to 3 h. Aluminopalladium catalysts containing 1% and 1.5% of the metal were used. The carriers were industrial γ-Al_2O_3 specimens.

A mixture of 48.6% of VTHI and 49.7% of THI (the remainder comprised cyclohexanone oxime) was obtained in a pilot plant from cyclohexanone oxime and ethyne. It was used without separation into components as the technically most readily available starting material.[109] The results are illustrated in schemes (3) and (4).

On the sulfided 1% Pd/γ-Al_2O_3 catalyst at 200 °C and $v = 1.0$ h^{-1}, 31% of 1-ethyltetrahydroindole (1-ETHI) and 19% of THI (relative to the VTHI passed through the system) are obtained from VTHI in 30 min in a hydrogen stream (3.6 litre h^{-1}), i.e. reactions involving the hydrogenation of the double bond and the cracking of VTHI, accompanied by the hydrogenolysis of the N–C bond, take place. The yield of the remaining cracking products ranges from 5% to 20%. On raising the reaction temperature to 300 °C, the yield of 1-VTHI increases to 42.7%. The six-membered ring is also dehydrogenated with formation of indole (yield 8.5%). The increase in the palladium concentration to 1.5% enhances the hydrogenating properties and weakens the cracking properties of the catalyst. The yield of 1-ETHI reaches 37%.



The principal products of the conversion of the VTHI – THI mixture are 1-ETHI, indole, and 2-ethylindole (2-EI), whose ratios depend on the composition of the catalyst. Indole is formed from VTHI in 47.2% yield on the 1% $Pd/\gamma\text{-}Al_2O_3$ catalyst at 350 °C and $\upsilon = 0.5\ h^{-1}$; the content of 2-ethylindole is 23.7%, while 1-ethylindole is virtually absent. The formation of 2-ethylindole is probably associated with the acid functions of the $\gamma\text{-}Al_2O_3$ carrier, which intensify the migration of the ethyl group to the α-position in the pyrrole ring (the thermal isomerisation of 1-alkylpyrroles to the 2-alkyl derivatives is well known).[110] The principal factor influencing the course of the above reactions on the aluminopalladium catalyst is the temperature, while the space velocity at which the mixture is supplied and the reaction time have little effect on the yield of indole and 2-ethylindole.

The selectivity of the sulfided aluminopalladium catalyst differs appreciably from that of the initial aluminopalladium catalyst. Only 1-ETHI is formed from the 1:1 mixture of VTHI and THI on the sulfided 1% $Pd/\gamma\text{-}Al_2O_3$ catalyst, i.e. the vinyl group is hydrogenated. At 250 °C, $\upsilon = 0.8\ h^{-1}$, and $\tau = 60$ min, the yield of 1-ETHI is 33.8% relative to the mixture passed over the catalyst or 72.9% relative to the reacted VTHI. The increase in temperature to 350 °C does not lead to an appreciable increase in the yield of 1-ETHI, which conflicts with data obtained using pure VTHI. These results indicate that the THI present in the initial mixture influences the reaction. The nature of the solvent (toluene or benzene) and dilution of the mixture have hardly any effect on the catalyst selectivity during the 3 h operation of the latter.[111]

By selecting the catalyst, it is possible to obtain 1-ETHI, indole, or a mixture of indole and 2-ethylindole from VTHI or its mixture with THI. On the sulfided 1.5% $Pd/\gamma\text{-}Al_2O_3$ catalyst, 47.9% of 1-ETHI is formed from VTHI ($T = 250$ °C, $\upsilon = 1.0\ h^{-1}$) and 37.6% of 1-ETHI is formed from the 1:1 mixture of VTHI and THI ($T = 250$ °C, $\upsilon = 0.5\ h^{-1}$). On the 1% Pd/Al_2O_3 catalyst ($T = 350$ °C, $\upsilon = 0.5\ h^{-1}$), 47.2% of indole and 23.7% of 2-ethylindole are formed from the same mixture. The yields of indole from the mixture of VTHI and THI show that the six-membered ring in both VTHI and THI is dehydrogenated.

The reaction of the 1:1 mixture of VTHI and THI on $Pd/\gamma\text{-}Al_2O_3$ involves, together with the reactions indicated above, the dehydrogenation of the six-membered fragment of VTHI with formation of 1-ethylindole, which isomerises to 2-ethylindole. Indole is formed mainly as a result of the dehydrogenation of THI, which reacts more readily than VTHI with the active centres on the catalyst surface. The C=C bond is reduced selectively on the sulfided $Pd/\gamma\text{-}Al_2O_3$ catalyst and 1-ETHI is obtained, while in VTHI the C – N bond undergoes hydrogenation with formation of THI.[104] Hence one may conclude that the hydrogenation and dehydrogenation reactions proceed on different active centres of $Pd/\gamma\text{-}Al_2O_3$ and the sulfided catalyst.

A study has been made of the dehydrogenation of THI on the sulfided aluminopalladium catalysts containing 0.15%, 0.2%, and 0.25% of palladium, on the 0.15% Pb/sibunit and 0.5% Pd/sibunit catalysts, and also on the mixed (0.1% Pd, 0.1% Re)/$\gamma\text{-}Al_2O_3$ catalyst.[111] The results are presented in Table 4.

The hydrogen sulfide-treated 0.5% $Pd/\gamma\text{-}Al_2O_3$ catalyst operated for 30 min at 300 °C and $\upsilon = 1.1\ h^{-1}$, exhibiting an appreciable dehydrogenating activity (the catalytic reaction mixture contained 31% of indole). Other conditions being equal, on raising the temperature to 370 and 400 °C complete conversion of THI into indole takes place. The treatment of this catalyst with hydrogen at a high temperature (650 – 700 °C) enhances its cracking properties, which is indicated by the decrease in the yield of the catalytic reaction mixture from 98% to 87%. Indole is formed already at 300 °C in 100% yield relative to the THI passed over the sulfided 0.25% $Pd/\gamma\text{-}Al_2O_3$ catalyst and the space velocity is reduced by a factor of 2 compared with the value indicated above. During the 48 – 50 min operation of this catalyst, its high activity did not change on varying the temperature from 300 to 400 °C, υ from 0.5 to 0.75 h^{-1}, and the THI content in toluene from 14.5% to 20.8%. The yield of the catalytic reaction mixture was 96% – 100% on the (0.15% – 0.2%) $Pd/\gamma\text{-}Al_2O_3(H_2S)$ catalyst at 350 – 360 °C and $\upsilon = 0.33 - 0.57\ h^{-1}$. When benzene is used as the solvent, the yield diminishes slightly. On the 0.15% $Pd/\gamma\text{-}Al_2O_3(H_2S)$ catalyst, the six-membered fragment of THI is wholly dehydrogenated, but the reaction temperature is somewhat higher compared with the catalyst containing 0.2% of Pd. On the mixed (0.1% Pd, 0.1% Re)/$\gamma\text{-}Al_2O_3(H_2S)$ catalyst, this reaction occurs only when the starting material is supplied at a low space velocity $\upsilon = 0.3 - 0.35\ h^{-1}$. Under these conditions only indole accumulates in the catalytic reaction mixture during the first 40 min, and after 115 – 126 min of operation of the catalyst up to 5% of the unreacted THI remains. The six-membered fragment of THI is fully dehydrogenated after 60 min on the 0.5% Pd/sibunit catalyst at 364 – 370 °C and $\upsilon = 0.7\ h^{-1}$; after this, the activity of the catalyst decreases somewhat. Thus, after the catalyst has been used for 186 min, 6.5% of the unreacted THI remains in the catalytic reaction mixture. Indole has been obtained in a quantitative yield on the 0.5% Pd/sibunit catalyst at 400 °C and $\upsilon = 0.85\ h^{-1}$. The decrease in the palladium concentration in the Pd/sibunit catalyst from 0.5% to 0.15% also made it possible to obtain indole in a quantitative yield during the first 73 min of the operation of the catalyst at 365 °C and $\upsilon = 0.3\ h^{-1}$. However, subsequently its dehydrogenating activity fell. The hydrogen sulfide-treated specimen containing 0.15% of palladium on $\gamma\text{-}Al_2O_3$ has a dehydrogenating activity superior to that of the analogous catalyst on sibunit after being used for 100 min.

Thus the low-percentage catalysts containing 0.15% – 0.2% of palladium, which have been developed, ensure the selective dehydrogenation of the six-membered fragment of THI. Indole is formed quantitatively at 355 – 365 °C and $\upsilon = 0.3 - 0.6\ h^{-1}$.[111]

Table 4. Dehydrogenation of 4,5,6,7-tetrahydroindole on various palladium catalysts (atmospheric pressure, toluene, H_2 flow rate 0.6 litre h^{-1}).[111]

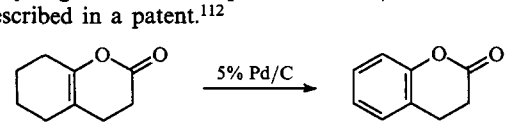
Catalyst	THI content (%)	Experimental conditions			Yield (%)		
		T/°C	v/h^{-1}	t/min	catalytic reaction mixture	THI	indole
0.5% Pd/γ-Al_2O_3	19.5	300	1.1	30	100.0	69.3	30.6
(H_2S)	19.5	340	1.1	25[a]	96.9	25.9	74.1
	20.5	370	1.2	30	96.2	–	100
	20.5	400	1.2	25[a]	97.7	–	100
0.5% Pd/γ-Al_2O_3 (H_2S)[b]	18.1	400	0.98	30	87.0	–	100
0.25% Pd/γ-Al_2O_3	17.7	300	0.6	30	100.0	–	100
(H_2S)	17.7	350	0.6	23	100.0	–	100
	14.5	350	0.5	30	97.5	–	100
	14.5	370	0.5	21	100.0	–	100
	20.8	370	0.75	30	100.0	–	100
	20.8	400	0.75	18	96.2	–	100
0.2% Pd/γ-Al_2O_3	14.3	350	0.42	35	96.2	–	100
(H_2S)	17.1	353	0.48	41	100.0	–	100
	17.3	353	0.6	65[c]	96.0	–	100
0.15% Pd/γ-Al_2O_3	15.6	300	0.52	30	100.0	14.2	85.8
(H_2S)	15.6	355	0.57	19	100.0	1.7	98.3
	19.6	355	0.6	40	99.0	–	100
	13.4	356	0.8	33	100.0	3.1	96.9
	13.3	360	0.47	38	100.0	–	100
	14.8	360	0.48	37	100.0	–	100
	14.9	361	0.48	46[d]	95.7	–	100
(0.1% Pd, 0.1%Re)/	18.0	353	0.49	36	100.0	1.5	98.5
γ-Al_2O_3 (H_2S)	14.8	362	0.44	42	98.8	6.3	93.7
	15.3	355	0.36	48	95.2	–	100
	15.5	355	0.45	36	97.2	3.0	97
	15.5	354	0.44	42	95.4	4.5	95.5
	15.3	355	0.53	66	92.9	11.9	88.1
0.5% Pd/sibunit	18.2	364	0.70	35	95.9	–	100
	18.0	367	0.70	48	93.0	1.9	98.1
	16.8	369	0.57	27[e]	95.0	–	100
0.5% Pd/sibunit[f]	18.0	400	0.85	30	98.0	–	100
0.15% Pd/sibunit	17.0	365	0.32	40	91.5	–	100
	17.3	366	0.34	33	95.0	–	100
	15.4	366	0.31	28	89.5	19.7	80.3

[a] On the same portion of the catalyst.
[b] Treated with hydrogen at 650–700 °C for 15 min.
[c] After the periodic operation of the same portion of the catalyst for 6 h.
[d] After the periodic operation of the same portion of the catalyst for 7 h.
[e] After the periodic operation of the same portion of the catalyst for 3.5 h.
[f] The specimen remaining after the experiments on the dehydrogenation of the cyclohexane for 9 h at 350–450 °C.

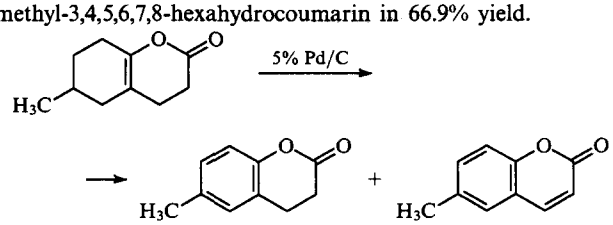
The six-membered fragment of THI is dehydrogenated on the 0.5% Pd/γ-Al_2O_3 catalyst at v = 0.75–1.2 h^{-1} and temperatures lower by 100 °C than in the dehydrogenation of cyclohexane, which makes it possible to employ catalysts with a low palladium content (0.15%–0.2%). The palladium catalyst on sibunit is also promising.

2. Dehydrogenation of dihydrocoumarins

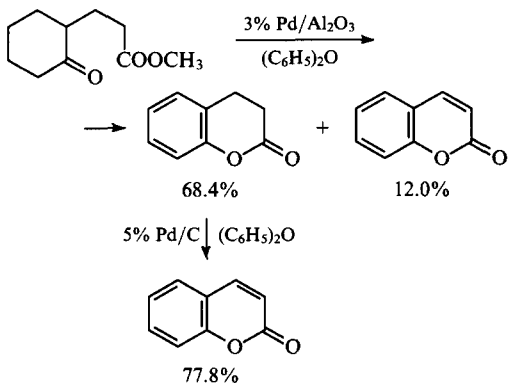
A method of synthesis of coumarin and alkylcoumarins together with the corresponding dihydrocoumarins by liquid-phase dehydrogenation in the presence of Pd/C at 260 °C has been described in a patent.[112]



For the 100% degree of conversion of 3,4,5,6,7,8-hexahydrocoumarin, the yield of 3,4-dihydrocoumarin was 70%. For a degree of conversion of 98.5%, a mixture of 6-methylcoumarin and 6-methyl-3,4-dihydrocoumarin was obtained from 6-methyl-3,4,5,6,7,8-hexahydrocoumarin in 66.9% yield.



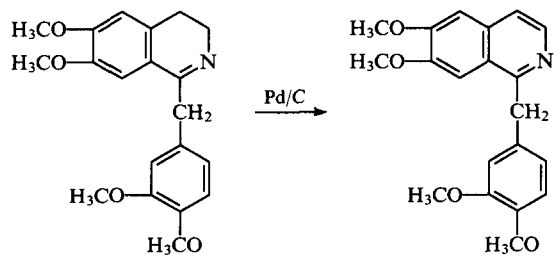
Coumarin has been obtained by the dehydrogenation of oxocyclohexanepropionic acid (OCPA) over Pd/Al_2O_3 in the liquid phase.[113]



For this purpose, OCPA in $(C_6H_5)_2O$ was heated at 250–260 °C in the presence of 3% Pd/Al_2O_3. A mixture of dihydrocoumarin (yield 68.4 mol%) and coumarin (yield 12 mol%) was obtained. Dihydrocoumarin in $(C_6H_5)_2O$ was dehydrogenated in the presence of 5% Pd/C for 14 h, which gave a mixture of 77.8% of coumarin and 22.1% of the unreacted dihydrocoumarin. After the carrier had been changed (5% Pd/Al_2O_3), the courmarin content fell to 50.8%, while that of the unreacted dihydrocoumarin rose to 49.1%.

3. Dehydrogenation of dihydropapaverine

Synthetic 1-benzyl-6,7,3',4'-tetramethoxyquinoline is identical with the natural alkaloid papaverine, which belongs to the class of opiate alkaloids and is widely used as a medicinal preparation. One of the last stages in the preparation of the synthetic papaverine is the dehydrogenation of dihydropapaverine at 200–250 °C in solution in tetralin in the presence of Pd/C under an inert gas (N_2, CO_2) stream.[17]



Dihydropapaverine was dehydrogenated on a catalyst containing 5% of palladium and deposited on an unwoven graphite material (UGM) with a volume concentration of 9.11 g cm^{-3} and a filtration coefficient of 5.3 × 10^{-2} cm s^{-1}.[114] The activity of the catalyst, determined from the evolution of hydrogen, increased after the introduction of CH_2O (to give a 1:1 mixture). The 5% Pd/UGM catalyst had the same activity as the industrial $Pd/BaSO_4$ (volume concentration 1.21 g cm^{-3}, filtration coefficient 3.5 × 10^{-5} cm s^{-1}), but a disadvantage of the latter is high hydrodynamic resistance. Papaverine can be obtained on the 5% Pd/UGM catalyst under both periodic and continuous conditions.[114]

VI. Palladium catalysts for the aromatisation of petrol fractions

The aromatisation of petrol fractions, carried out in catalytic reforming, ensures an increase in the octane number, such increase including the effect due to the dehydrogenation of naphthalenes. Aromatisation under platforming conditions is promoted by a high temperature and a low hydrogen pressure. However, when the pressure is too low, the catalyst activity falls rapidly owing to the deposition of carbon residues on its surface. The selectivity of the reaction on supported metallic catalysts is a complex function of the catalyst composition, pressure, temperature, the composition of the gas phase, etc.

The reforming catalysts possess a bifunctional activity because, together with the main reaction involving the dehydrogenation of six-membered cyclanes, reactions also occur in which five-membered cyclanes isomerise to six-membered ones with subsequent dehydrogenation, dehydrocyclisation reactions, alkane isomerisation reactions, and cracking. The presence on the catalyst surface of both the metal and of acid centres is therefore required. The platforming processes were carried out on platinum deposited on alumina, which possesses acid properties.[115–117]

Palladium, the crystal lattice of which has the same structure as that of platinum, is appreciably inferior to the latter as regards activity in reactions of both individual hydrocarbons and their mixtures.

The 0.5% $Pd/\gamma\text{-}Al_2O_3 \cdot HF$ catalyst treated with hydrogen sulfide exhibited an appreciable activity in the dehydrogenation of cyclohexane to aromatic hydrocarbons and retained its stability during operation of 262 h under the conditions of the reforming of the petrol fraction, with a boiling point of 96–114 °C, from the Il'sko-Khadyzhensk deposit (n_D^{20} = 1.4155, d_4^{20} = 0.7493, content of aromatic hydrocarbons 7.5%, sulfur content 0.0025%) at 450–460 °C, P_{H_2} = 20 atm, v = 1 h^{-1}, and H_2:HC = 5:1.[74,79] As a result of the dehydrogenation, the content of aromatic hydrocarbons rose to 36%–40%. Despite the high reaction temperature, the catalyst hardly induced any cleavage of the hydrocarbons to C_1–C_4 compounds and the effluent gas consisted of 98%–99% of hydrogen.[79]

The influence of hydrofluoric acid and of the treatment with hydrogen sulfide on the 0.5% $Pd/\gamma\text{-}Al_2O_3$ catalyst has been investigated under conditions of the reforming of the 89.5–125 °C petrol fraction containing 0.017% of sulfur compounds (calculated relative to sulfur).[118,119] The data on the composition of the fraction before and after reforming are presented in Table 5.

In the presence of the hydrofluoric acid-treated 0.5% $Pd/\gamma\text{-}Al_2O_3$ catalyst and in contrast to the initial 0.5% $Pd/\gamma\text{-}Al_2O_3$ catalyst, aromatic hydrocarbons are formed not only from six-membered cyclanes but also from five-membered cyclanes and alkenes. All the specimens also exhibit a desulfurising activity — the sulfur content decreases from 0.017% to 0.001%. The sulfided specimen is more resistant under these conditions to the action of sulfur compounds. However, when petrols containing sulfur compounds are used, the stability of the catalyst decreases with time and its aromatising capacity diminishes after 60 h of continuous operation.[119] The yield of

Table 5. Group composition of the petrol fraction with b.p. 89.5–126 °C (reforming conditions: T = 470–480 °C, P_{H_2} = 20 atm, v = 1.0 h^{-1}, H_2:HC = 12.5).[118,119]

Hydrocarbons	Content (mass %)			
	before reforming	after reforming on catalysts containing 0.5% Pd on		
		$\gamma\text{-}Al_2O_3$	$\gamma\text{-}Al_2O_3 \cdot HF$	$\gamma\text{-}Al_2O_3 \cdot HF$ (H_2S)
Alkanes:	52.7	60.2	62.3	61.8
normal	29.3	29.7	25.7	26.9
with a tertiary carbon atom	22.5	28.1	34.6	29.3
with a quaternary carbon atom	0.9	2.4	2.0	5.6
Cyclopentanes	14.6	10.8	4.4	5.4
Cyclohexanes	18.5	1.0	0.8	1.0
Aromatic hydrocarbons	5.6	20.3	26.4	24.8

aromatic hydrocarbons decreases to 12%–12.5% after 27 h on the 0.5% $Pd/\gamma\text{-}Al_2O_3$ catalyst, after 46 h on the 0.5% $Pd/\gamma\text{-}Al_2O_3 \cdot HF$ catalyst, and after 13 h of reforming the petrol fraction on the sulfided 0.5% $Pd/\gamma\text{-}Al_2O_3 \cdot HF$ specimen. It is appropriate to mention that the sulfur content in the reformates proved to be identical in all cases. It is extremely likely that the decrease in the aromatising capacity of the most active 0.5% $Pd/\gamma\text{-}Al_2O_3 \cdot HF(H_2S)$ catalyst is associated with the removal from the latter of part of the chemisorbed sulfur, i.e. with the decomposition of PdS at a high temperature and a hydrogen pressure of 20 atm. The specific surface of the sulfided palladium catalyst is smaller by a factor of 1.5, whilst the temperature coefficient of the rate of dehydrogenation of cyclohexane to benzene is much higher than on the other two catalysts.[78] It may be that this explains why the sulfided specimen has the highest activity under the conditions of the reforming of the petrol fraction.

Thus the introduction of hydrofluoric acid into the aluminopalladium catalyst increases its isomerising capacity, whilst treatment with hydrogen sulfide increases its resistance to the sulfur compounds present in the petrol fraction.

The reforming of the petrol fraction with a boiling point of 89.5–126 °C and containing 0.017% of sulfur has also been investigated on palladium/aluminosilicate catalysts (containing 85.35% of SiO_2 and 11.91% of Al_2O_3) with different specific surfaces (S = 263, 240, 204, 180, and 93 $m^2 g^{-1}$).[120] The aluminosilicate catalysts, which are used extensively in the petroleum processing industry for cracking, are known to possess acid properties and hence to exhibit not only a cracking activity but also an extremely high isomerising activity. The deposition on the aluminosilicate of finely disperse palladium, which possesses dehydrogenating and hydrogenating properties, made it possible to create active aromatisation catalysts. An appreciably greater increment in the content of aromatic hydrocarbons (24%–33% instead of 17%–22%) is observed on these catalysts than on the 0.5% $Pd/\gamma\text{-}Al_2O_3$ catalyst. Aluminosilicate catalysts containing 0.5% of palladium also ensure the desulfurisation of the fraction: the sulfur content falls from 0.017% to 0.001%.[121] During the first hours of the operation, these catalysts exhibit an appreciable cracking activity and therefore it is more convenient to employ them in the reforming of higher-boiling petroleum fractions. In contrast to the catalyst deposited on alumina, on the palladium/aluminosilicate catalyst five-membered cyclanes and n-alkanes are involved in the aromatisation process in addition to the six-membered cyclanes.

VII. Bimetallic supported catalysts for the dehydrogenation of cyclanes and the aromatisation of petrol fractions

Low-percentage bimetallic supported catalysts, containing palladium and rhenium, were first developed at the Institute of Organic Chemistry of the USSR Academy of Sciences in the 1960s — several years earlier than the Pt–Re reforming catalyst (see below). The behaviour of the Pd–Re catalysts in the reactions of C_6 hydrocarbons, including the dehydrogenation of cyclohexane and methylcyclohexane at elevated temperatures and hydrogen pressures, has been widely investigated.[121–123]

Table 6 presents data on the reactions of cyclohexane and methylcyclohexane on catalysts containing 1% of Pd and 1% of Re and deposited on $\gamma\text{-}Al_2O_3$ and $Al_2O_3 \cdot SiO_2$.[122,123]

Together with benzene, methylcyclopentane is also formed. Table 6 shows that the (Pd, Re)$/Al_2O_3 \cdot HF$ catalyst treated with hydrogen sulfide exhibits the highest dehydrogenating activity. When it is employed, the benzene content in the catalytic reaction mixture increases from 67% to 87% and toluene is formed from methylcyclohexane in 90% yield. The use of aluminosilicate as the carrier instead of the hydrogen fluoride-treated alumina decreases the dehydrogenating activity of the catalyst.[123] The decrease in the specific surface of the aluminosilicate from 350 to 108 $m^2 g^{-1}$ also weakens the dehydrogenating activity of the catalyst. The introduction of hydrofluoric acid (0.5% or 1.5%) enhances the acid properties of the catalyst and increases the contribution of the reactions involving the hydrocracking of n-hexane and the hydrogenolysis and dehydroisomerisation of methylcyclopentane. When the aluminosilicate carrier was used, the highest dehydrogenating activity was shown by the (1% Pd, 1% Re)$/Al_2O_3 \cdot SiO_2$ 0.5%HF catalyst treated with hydrogen sulfide. The use of active bimetallic catalysts for the reforming of petrol fractions has also been studied (see below).

The dehydrogenation of cyclohexane has been investigated on the (1% Pd, 1% Re)$/Al_2O_3$ catalyst containing 0.3% of fluorine and treated with hydrogen sulfide in the temperature range from 370 to 420 °C, for the molar ratio hydrogen : cyclohexane = 3 : 1, at rates of supply of cyclohexane from 0.012 to 0.04 mol $g^{-1} h^{-1}$, and at a hydrogen pressure of 10 atm.[124] At 370, 400, and 425 °C, the equilibrium yields of the benzene obtained by the dehydrogenation of cyclohexane are respectively 65%, 83.3%, and 95.2%. The kinetics of the dehydrogenation reaction were investigated in a flow type apparatus. The quantities calculated by the kinetic equation

Table 6. Reactions of cyclohexane on palladium supported catalysts (T = 480 °C, P_{H_2} = 10 atm, v = 1.0 h^{-1}, H_2 : HC = 5).[122,123]

Composition of catalyst	(1% Pd, 1% Re)$/Al_2O_3 \cdot HF$	(1% Pd, 1% Re)$/Al_2O_3 \cdot HF(H_2S)$	(1% Pd, 1% Re)$/Al_2O_3 \cdot SiO_2 \cdot HF(H_2S)$		
			A	B	C[a]
Propane–pentanes	1.3	traces (1.1)	1.7	0.2	1.5
2,2-Dimethylbutane	traces	– (–)	1.2	0.8	–
2-Methylpentane	1.3	0.5 (–)	0.6	0.2	0.4
3-Methylpentane and cyclopentane	1.2	0.4 (–)	0.4	0.1	–
n-Hexane	1.2	0.5 (–)	0.6	0.4	0.4
Methylcyclopentane	12.0	5.3 (–)	17.3	14.6	14.2
Cyclohexane	16.0	2.2 (–)	19.1	48.2	61.3
Methylcyclohexane	–	– (3.5)	–	–	–
Benzene	67.0	87.0 (5.4)	59.1	35.5	22.6
Toluene	–	4.0 (90.0)	–	–	–
Overall yield of catalyst (%)	95	95 (93)	92	96	99

Note. The numerals in brackets indicate the degree of conversion of methylcyclohexane.
[a] The specific surfaces of the catalysts were 350 $m^2 g^{-1}$ (A), 160 $m^2 g^{-1}$ (B), and 108 $m^2 g^{-1}$ (C).

agreed with experimental data. The apparent activation energy for the dehydrogenation of cyclohexane was found to be 74.5 kJ mol^{-1}. The apparent activation energies for the isomerisation of cyclohexane and for the reverse reaction (the isomerisation of methylcyclopentane) in the temperature range 370–390 °C amounted to 72.0 and 48.5 kJ mol^{-1} respectively.

The properties of the sulfided 0.5% palladium catalysts deposited on alumina and of bimetallic catalysts containing 0.5% of palladium and 0.5% of rhenium were compared in the dehydrogenation of cyclohexane at atmospheric pressure (450 °C, v = 1.4–1.5 h^{-1}).[16]

The introduction of rhenium increased the yield of the catalytic reaction mixture from 91.8% to 94.2% and the benzene content from 85% to 91% and also made it possible to reduce the reaction temperature to 400 °C. At this temperature, the benzene content was 81% for a 92.4% yield of the liquid catalytic reaction mixture. Hence it follows that the palladium–rhenium bimetallic catalyst is more active than the pure palladium catalyst.

The nature of the promoting activity of rhenium both in aluminopalladium and aluminoplatinum catalysts[125–128] is not totally clear. It has been shown[129] that, in the absence of the second metal, rhenium deposited on Al_2O_3 is reduced to the metallic state almost completely at a concentration of 4%–5% and with greater difficulty at a concentration of 0.5%. This can be explained by the fact that, on low-percentage catalysts, rhenium and its oxides are in a highly disperse state and interact strongly with the acceptor sections of the carrier surface, which hinders reduction. The addition of rhenium does not affect the mechanism of the action of the bifunctional catalyst but reduces appreciably the rate of its deactivation.[121] It may be that, in contrast to palladium, rhenium promotes the removal of the coke-formation products from the catalyst surface.

The well known ability of rhenium to increase the stability of the catalyst can be explained by the fact that rhenium oxides hydrogenate the products preceding the formation of coke during catalytic reforming.[116,117]

An attempt has been made to discover a relation between the adsorption of hydrogen on promoted palladium-containing catalysts, on the one hand, and the state of the metals and their activity in the dehydrogenation of cyclohexane, on the other.[130] For this purpose, a detailed study was made of the overall content of hydrogen on the catalyst surface, the number of forms of chemisorption, and the temperature at which the maximum rate of desorption is attained and the activation energy for desorption and its kinetic order were calculated. The state of the active phase in both one-component and modified palladium catalysts was investigated by means of a series of physicochemical methods (thermoprogrammed desorption, diffuse reflection spectroscopy, X-ray phase analysis). The palladium catalysts deposited on alumina contained 0.02 mass%–0.35 mass% of the metal and were promoted with 0.1 mass%–6.3 mass% Co, Ce, or In. It was shown that the catalysts for the dehydrogenation of cyclohexane to benzene must be capable of activating hydrogen in both weakly and strongly bound forms. Since the centres for the chemisorption of hydrogen in the weakly bound forms are unoccupied during the reaction, they can serve as the sites for the formation of the intermediate adsorption complex in the dehydrogenation of cyclohexane. The adsorption of hydrogen in the weakly bound form is characteristic of palladium catalysts modified by non-noble metals, which contain the most reduced forms of both palladium and of the promoting Ce and Co additives and also incorporate mixed centres formed as a result of their interaction.

The introduction of neodymium oxide into the aluminopalladium catalyst increases appreciably its dehydrogenating activity.[131] The dehydrogenating activity of such catalysts was investigated at atmospheric and elevated hydrogen pressures. The results are presented in Table 7.

It follows from the data presented that the 1% Pd/Al_2O_3 catalyst containing 10% of Nd_2O_3 has the maximum dehydrogenating activity. An increase in pressure increases the yield of the product on the aluminopalladium catalysts containing 4.5% and 10% of Nd_2O_3. The stability of all the specimens was tested. After 18 h operation of the first catalyst, the benzene content fell from 91.8% to 48%. The same decrease in activity on the (1% Pd, 10% Nd_2O_3)/Al_2O_3 catalyst was reached after 40 h.

Table 8 presents data concerning the influence of other cerium- and yttrium-subgroup lanthanide oxides on the dehydrogenating activity of aluminopalladium catalysts.[132]

Evidently the lanthanide oxides increase appreciably the dehydrogenating activity of the aluminopalladium catalysts. The introduction of 10% of the lanthanide oxide lowers the specific surface of the alumina slightly (in the range 15–25 m^2 g^{-1}). The catalysts prepared were characterised by similar pH values with the sole exception of the catalysts containing neodymium oxide. The introduction of the lanthanide oxide diminished slightly the acidity of the aluminopalladium catalysts virtually regardless of the nature of the lanthanide oxide. Since all nine lanthanide oxides exert almost the same influence on the activity of the catalyst, in the preparation of such catalytic systems one can employ the most readily available and cheapest lanthanides and their mixtures.

Bimetallic catalysts containing palladium and rhenium on alumina were first developed in our country.[121] The use of these catalysts in the reforming of petrol fractions was investigated in 1962.[122] Later the properties of the platinum-rhenium supported catalysts designed for reforming began to be studied in Germany and the USA.[133,134] Platinum-rhenium/carbon catalysts were described in 1965[133] and the (Pt, Re)/Al_2O_3 catalyst

Table 7. Reactions of cyclohexane on the (1% Pd, Nd_2O_3)/Al_2O_3 catalysts (atmospheric pressure, T = 480 °C, v = 1.0 h^{-1}).[131]

Catalyst	s/m^2 g^{-1}	pH[a] of catalyst	Composition of catalytic reaction mixture (mass%)			
			cyclo-hexane	benzene	methylcyclo-pentane	C_4–C_6 alkanes
Pd/Al_2O_3	112	4.7	92.1	6.0	0.9	–
Pd/Al_2O_3[b]	112	4.7	74.7	22.3	–	3.0
Pd/Al_2O_3[c]	112	4.7	51.7	34.8	12.7	0.8
(Pd, 4.5% Nd_2O_3)/Al_2O_3	157	4.0	44.4	52.7	0.5	2.4
(Pd, 4.5% Nd_2O_3)/Al_2O_3[b]	157	4.0	6.9	91.8	1.0	0.3
(Pd, 10% Nd_2O_3)/Al_2O_3	127	4.3	39.1	60.9	–	–
(Pd, 10% Nd_2O_3)/Al_2O_3[c]	127	4.3	5.6	93.3	1.1	traces
(Pd, 15% Nd_2O_3)/Al_2O_3	125	4.3	45.3	54.7	–	–
(Pd, 20% Nd_2O_3)/Al_2O_3	134	4.3	59.7	40.3	–	–

[a] The pH of the aqueous extract from the catalyst under standard conditions.
[b] v = 0.4 h^{-1}.
[c] P_{H_2} = 10 atm.

Table 8. Reactions of cyclohexane on catalysts containing 1% of Pd, 10% of a lanthanide oxide, and 89% of Al_2O_3 (T = 480 °C, v = 1.0 h^{-1}, P_{H_2} = 10 atm).[132]

Catalyst	$s/m^2\ g^{-1}$	pH[a] of catalyst	Composition of catalytic reaction mixture (mass %)				Yield of benzene at P_{H_2} = 1 atm[a]
			C_3-C_5	methylcyclo-pentane	cyclo-hexane	benzene	
Pd	147	5.3	3.5	2.7	71.4		22.4[b]
			0.8		51.7	38.4	2.8
Pd, Y_2O_3	129	6.8	4.2	2.1	11.0	82.7	50.0
Pd, Pr_2O_3	122	6.1	1.1	2.0	4.4	92.5	65.9
Pd, Nd_2O_3	151	4.3	traces	1.1	5.6	93.3	60.9
Pd, Sm_2O_3	146	6.8	1.1	1.8	8.6	88.5	55.2
Pd, Tb_2O_3	122	6.0	–	1.6	4.2	94.2	51.2
Pd, Dy_2O_3	120	6.6	1.4	4.4	10.1	84.5	49.8
Pd, Ho_2O_3	126	6.2	traces	1.6	8.0	90.4	59.9
Pd, Er_2O_3	141	6.3	1.3	1.7	10.5	86.5	73.2
Pd, Yb_2O_3	144	6.6	1.3	1.4	9.9	84.7	53.0

[a] v = 0.4 h^{-1}.
[b] residual cyclohexane.

was described in 1968.[134] The latter catalyst was prepared by the method described previously.[121] The 'rheniforming' process for improving the quality of petrol fractions was introduced in the USA in 1970.

The introduction of bimetallic catalysts is regarded as the greatest achievement in petroleum processing after the development in 1949 of the aluminoplatinum platforming catalyst. The advantage of the process on the bimetallic catalysts has been examined in detail in a monograph.[135] We shall note some of them. Rheniforming in the presence of the $(Pt, Re)/Al_2O_3$ bimetallic catalyst yields a reformed product with a higher octane number than that obtained in platforming on Pt/Al_2O_3. As a consequence of the high volume flow rates of the starting material, the productivity increases. The yield of the reforming product, hydrogen, and aromatic hydrocarbons rises, the useful lifetime of the catalyst increases, and the cracking of alkanes and naphthenes is reduced to a minimum. The employment of a lower pressure becomes possible, which promotes the occurrence of dehydrocyclisation and makes it possible to reduce the molar ratio of the circulating hydrogen and the starting material (H_2 : HC).[135] Preliminary purification of the petrol fractions to remove sulfur compounds is essential in rheniforming processes. The introduction of rhenium into the aluminoplatinum catalyst increases the lifetime of the latter, according to American workers, by a factor of 2–4 compared with that of the aluminoplatinum catalyst; the regeneration of the catalyst after three months' use ensures the complete restoration of its high initial activity.[135]

The influence of rhenium on the activity and stability of the aluminopalladium catalyst has been investigated under the conditions of the reforming of petrol fractions containing sulfur compounds (0.0123% of sulfur).[122] In the products obtained by reforming the Baku petrol B-70, the content of aromatic hydrocarbons increased from 5.5% to 57% after treatment for 25 h, while the concentration of sulfur compounds diminished from 0.0123% to 0.009%, i.e. by a factor of 1.4. During the initial period of the operation of the catalyst, the content of aromatic hydrocarbons reached 80%. The introduction of 1% of Re into the 1% $Pd/Al_2O_3 \cdot HF(H_2S)$ catalyst increased its stability almost by a factor of 4. However, after 111 h of continuous operation, the content of aromatic hydrocarbons fell to 14%.

The reforming of the 71–102 °C fraction of the Karadag petrol was investigated on the most active catalyst (1% Pd, 1% Re)$/Al_2O_3 \cdot HF(H_2S)$ in stationary and fluidised beds.[136] The results are presented in Table 9.

Table 9. Characteristics of the initial fraction with b.p. 71–102 °C of the Karadag petrol and the reforming products obtained with the process carried out in stationary and fluidised catalyst beds (T = 480 °C, v = 0.8–3.5 h^{-1}, P_{H_2} = 10 atm, H_2 : HC = 5–20).[136]

Component	Composition of fraction (mass %)	Composition of reforming products (mass %)		
		after treatment in a stationary bed for 25 h	after treatment in a fluidised bed for	
			25 h	100 h
Isopentane	1.4	1.2	1.1	0.9
n-Pentane	2.7	2.1	2.5	1.9
2,2-Dimethyl-butane	0.3	0.4	0.7	0.5
2-Methylpentane and 2,3-dimethyl-butane	5.9	6.3	6.1	5.8
3-Methyl-pentane	4.8	3.9	4.6	4.5
n-Hexane	12.4	10.9	11.6	10.3
n-Isoheptanes + dimethylcyclo-pentanes + cyclohexane + methylcyclo-pentane	48.9	36.7	30.7	37.4
Methylcyclo-hexane	15.4	1.1	0.8	2.8
Benzene	3.7	15.1	18.7	12.9
Toluene	4.5	21.3	23.2	23.0

It follows from Table 9 that, after 25 h of the operation of the catalyst, the content of aromatic hydrocarbons in the reforming products in the stationary and fluidised beds is 36%–42%. The content of benzene has then been increased by a factor of almost 4, whilst that of toluene increased by a factor of 5. The contents of the C_5 and C_6 alkanes remained almost unchanged. The fraction of isomeric hexanes (total hexanes) is ~50% in the initial petrol fraction. Approximately the same fraction of hexanes was attained earlier[121] on the same catalyst in the isomerisation of n-hexane in a stationary bed. Thus aromatic hydrocarbons are mainly formed as a result of the dehydrogenation of

six-membered cyclanes and to a slight extent as a result of the dehydroisomerisation of alkylcyclopentanes. The activity of the stationary catalyst bed gradually diminishes and, after it has worked for 40 h, the content of aromatic hydrocarbons in the reforming products falls to 29%, whilst in the fluidised bed their content after the catalyst has worked for 100 h diminishes only to ~36%. Hence it follows that the stability of the catalyst in the fluidised bed is 4 times greater than in the stationary bed. This can apparently be accounted for by the fact that in the fluidised bed the catalyst has a much larger macrosurface than in the stationary bed.

After 100 h of operation, the catalyst was regenerated with air in the fluidised bed at atmospheric pressure and 400 °C, was treated with hydrogen, and the experiment was again carried out at a pressure of 10 atm, a space velocity of 1.5–2.0 h^{-1}, and H_2 : HC = 10. The content of aromatic hydrocarbons in the reformate increased by a factor of 5, as before. Consequently, the hydrogen sulfide-treated rhenium–aluminopalladium catalyst fully recovers its activity as a result of regeneration.

VIII. Certain characteristic features of the catalytic and physical properties of palladium-containing supported catalysts

The available information about the physicochemical properties of supported palladium and palladium-rhenium catalysts for the dehydrogenation of cyclanes in the reforming of petrol fractions is extremely limited.[137–139] X-Ray diffraction analysis of the 0.5% Pd/Al_2O_3 catalyst, the same catalyst containing 0.5% of fluorine, and the fluorinated specimen subjected to an additional treatment with hydrogen sulfide showed that the palladium in all the specimens and the aluminium oxide in the first two specimens are in a crystalline state. The lattice constant of the aluminium oxide in these two cases is virtually the same, amounting to 7.91 and 7.90 Å respectively. The crystal dimensions are in the range 50–100 Å. The absence of Al_2O_3 reflections not coinciding with the palladium reflections (d = 2.349 and 1.384) is characteristic of the X-ray diffraction patterns of the sulfided specimen. It is therefore impossible to regard it as strictly demonstrated that the aluminium oxide in this specimen is in the crystalline state (lattice constant 7.86 Å).[78] The chemical treatment with hydrofluoric acid and hydrogen sulfide probably alters markedly the size and shape of the crystals and leads to the dispersion of the aluminium oxide. The palladium in the sulfided specimen is less saturated by hydrogen than in the first specimen. The rate of conversion of cyclohexane into benzene increases most markedly (by a factor of 4) with increase in temperature from 300 to 350 °C at atmospheric pressure in a flow system on the sulfided palladium-containing catalyst. The results obtained in tests of the activities and stabilities of these specimens under the conditions of the reforming of petrol fractions (see above) are related to the temperature coefficients of the rate of reaction.

Since the specific surfaces of the test specimens hardly changed during the dehydrogenation of cyclohexane, it follows that the differences between the activities and stabilities are induced by the chemical composition of the catalyst and not by structural features. It follows from data on the phase composition[78] that the impurities which are bound to be present in the specimens by virtue of the characteristics of the method of preparation can exist only in the form of surface compounds (AlF_3 or $HAlF_4$ and also PdS) or, which is less probable, in the form of an amorphous phase. Even at low concentrations, these compounds can influence significantly the activities and stabilities of the catalyst. It may be that the high activity and stability of the sulfided palladium specimen is due to the presence of PdS on the latter. The partial or complete sulfiding of the palladium surface apparently increases the temperature coefficient of the rate of dehydrogenation. This appears entirely probable, because sulfides are known to be active at higher temperatures than the metals forming part of their composition. For example, nickel sulfide hydrogenates the carbon–carbon bond at temperatures above 150 °C, whereas metallic nickel in the active form hydrogenates it already at room temperature.

Table 10. The contents of sulfur and carbon in the catalysts after prolonged operation under the conditions of the reforming of the petrol fraction with b.p. 89.5–124 °C (sulfur content in the fraction 0.017%).[78]

Catalyst	Duration of operation of catalyst/h	Content (%)	
		S	C
0.5% Pd/Al_2O_3	27	0.040	0.25
0.5% $Pd/Al_2O_3 \cdot HF$	46	0.035	0.28
0.5% $Pd/Al_2O_3 \cdot HF$ (H_2S)	73	0.039[a]	0.27

[a] The initial reduced catalyst contained 0.125% of sulfur.

Data on the contents of sulfur and carbon in palladium-containing catalysts are noteworthy (Table 10).[78]

Regardless of the duration of the operation under the conditions of the reforming of petrol, the contents of sulfur and carbon remain almost unchanged in all the catalysts. If the accumulation of carbon had been limited by the coke saturation of the cracking surface centres, it would have been difficult to expect identical amounts of it on catalysts to have different properties. Therefore the data in Table 10 concerning the content of carbon are more likely to indicate that, after the formation of the 'carbonaceous film', the rate of hydrogenation of the film becomes equal to the rate of its formation on the catalyst surface, i.e. a certain equilibrium is established. Since the sulfur content in the catalyst does not increase with increase in the productivity in the operation of the latter, one may reach the unambiguous conclusion that the rupture of the sulfur compounds in petrol with formation of elemental sulfur on the catalyst does not occur and that sulfur is evolved in the form of hydrogen sulfide. The sulfur content in the initial sulfided catalyst was 0.125%. After the transition of the catalyst to the deactivated state as a result of performing the petrol reforming process on the latter, the sulfur content fell to 0.04%. Under these conditions, the sulfur content could have decreased only as a result of the formation and removal of H_2S.

It is appropriate to note that, when the activity fell to the same value, the sulfur contents in all the catalysts were also identical. It is extremely likely that the decrease in the activity of the sulfided catalyst is associated with the removal from the latter of part of the chemisorbed sulfur (the decomposition of PdS at a high temperature and hydrogen pressure).

The catalytic properties of metal oxide supported catalysts are known to be greatly influenced by the recrystallisation of the active phase. The specific surface of the metal in the alumino-palladium and aluminopalladium-rhenium catalysts has been estimated by a modified method involving the gas titration of the chemisorbed hydrogen by ethene[140,141] and also by the oxygen chemisorption method. Heat treatment of the Pd/Al_2O_3 catalyst at 640 °C increases the specific surface of palladium from 106 to 446 $m^2\ g^{-1}$.[137] The high H : Pd = 0.95 ratio shows that palladium is present on the carrier in a virtually atomic state. Oxygen titration yields lower specific surfaces (S increases on heat treament from 91 to 360 m^2 per gramme of palladium).

The specific surface of the metal (52 $m^2\ g^{-1}$) on the (Pd, Re)/Al_2O_3 catalyst is smaller than on Pd/Al_2O_3. Heat treatment of the catalyst increases the overall specific surface of palladium and rhenium. The specific surface of palladium in the bimetallic specimen is four times greater than in the palladium specimen. Thus in air rhenium does not inhibit the recrystallisation of palladium on the carrier but increases the thermal stability of the catalyst.

The effect of coke on the crystallisation of palladium and rhenium on different carriers has been examined.[138] X-Ray

diffraction study of palladium-rhenium catalysts on silica before and after saturation with coke (4%–5% of coke) under the conditions of the aromatisation of hydrocarbons at atmospheric pressure and 500 °C led to the identification only of lines corresponding to palladium. The introduction of rhenium into the Pd/SiO_2 catalyst retards the crystallisation of palladium on saturation with coke.

The relation between the activity of the $(Pd, Co)/Al_2O_3$ bimetallic catalyst in the dehydrogenation of cyclohexane and its adsorption capacity with respect to hydrogen has been investigated.[139] The dehydrogenation was carried out at 300–480 °C and atmospheric pressure under pulsed conditions. The specimen was subjected to a preliminary treatment in a stream of hydrogen at 520 °C for 15 min. The adsorption properties of the catalyst in relation to hydrogen (adsorption capacity, number of chemisorbed forms of hydrogen, the strength of the bond between hydrogen and the metallic catalyst surface) were determined by the thermoprogrammed desorption method. The conversion of cyclohexane on the 0.1% Pd/Al_2O_3 catalyst began at 340 °C and the maximum yield of benzene, equal to 38%, was attained at 480 °C. The Co/Al_2O_3 systems containing 1.66%, 3.0%, and 4.28% of the metal proved to be inactive. The activity of the $(Pd, Co)/Al_2O_3$ bimetallic catalyst is determined to a large extent by the concentration of the non-noble metal in the latter. The dehydrogenating activity of the palladium catalyst increases sharply after the introduction of 1% and 1.66% of cobalt: the yield of benzene at 480 °C reaches 83.4% and 68.4% respectively. At lower (0.1% and 0.5%) and higher (3.0% and 4.28%) cobalt concentrations, the degrees of conversion of cyclohexane into benzene are appreciably lower. C_1-C_6 hydrocarbons—cyclohexane cracking products—are formed on the bimetallic catalyst, in contrast to Pd/Al_2O_3.

The spectrum of the desorption of hydrogen from the Pd/Al_2O_3 catalyst contains one temperature range (600 to 700 °C) with a temperature of the maximum rate of adsorption of 660 °C. Kinetic calculations showed that hydrogen is desorbed in accordance with a second-order equation ($n = 2$) and that the activation energy for desorption is $E_{des} = 480$ kJ mol^{-1}. This indicates the atomic nature of the chemisorbed hydrogen and a high strength of the hydrogen–metal bond. The adsorption capacity of palladium in Pd/Al_2O_3 is low (0.1 ml per gramme of the catalyst), which corresponds to the ratio H:M = 0.54. Data have been obtained also for the Co/Al_2O_3 catalyst. On thermal desorption of hydrogen from the (0.1% Pd, 1.66% Co)$/Al_2O_3$ catalyst (the most effective in the dehydrogenation of cyclohexane), two forms of chemisorbed hydrogen (I and II) were detected. Hydrogen begins to be evolved at a lower temperature (300 °C) and the evolution takes place over a much wider temperature range (300 to 700 °C) than on the one-component palladium and cobalt catalysts. These results indicate a greater energy nonuniformity of atomic hydrogen and a weaker hydrogen–metal bond in the $(Pd, Co)/Al_2O_3$ catalyst. The strongly bound hydrogen (form II) is desorbed with $E_{des} = 280.5$ kJ ml^{-1}, whilst the weakly bound hydrogen (form I) is desorbed with $E_{des} = 118.5$ kJ mol^{-1}. The centres which bind hydrogen more strongly ($T_{des} > T_{reaction}$) are coated by adsorbed hydrogen on the catalysts showing a lower activity in the dehydrogenation of cyclohexane, whilst the centres for the weak chemisorption of hydrogen are virtually absent and their surface is coated only by the strongly bound forms.

The modifying effect of rhenium in the platinum-rhenium supported catalyst can be accounted for by the formation of bimetallic (alloyed) Re–Pt particles on the catalyst surface[125,126] or by the localisation of the platinum clusters on the low-valence rhenium ions bound to the carrier surface.[127] It is also possible to create catalysts containing transition metal complexes fixed on the carrier surface.

Bimetallic catalysts containing discrete surface structures of predominantly one composition can be obtained by the thermal decomposition of fixed surface complexes incorporating the atoms of the active metal and of the modifying element. Organic ligands are easily removed on reduction of the catalyst, which makes it possible to investigate the influence of the modifying element under conditions which rule out the uncontrollable modification of the deposited metal and of the carrier surface by the decomposition products. In the case of platinum-containing catalysts, the low-valence Group IV–VIII elements bound to the SiO_2 surface can serve as centres for the stabilisation of the reduced platinum atom or clusters.[128] By virtue of the formation of a chemical bond with the element of the additive, the deposited platinum is not sintered over a wide range of reduction temperatures.

The formation of zerovalent compositions[142] on the surface of the (0.5% Pd, 1.2% Si, 1.2% Cr)$/Al_2O_3$ specimen obtained by the method of Ermakov and coworkers[127,128] has been demonstrated by laser micromass spectrometry. Peaks corresponding to Cr_2O^+, $Cr_2O_3^+$, and SiO^+ are absent from the mass spectrum, which indicates the absence of chromium and silicon oxides. The presence of zerovalent silicon has been confirmed by XPS data. The presence of zerovalent chromium and silicon under the conditions of the preparation of the specimens favoured the formation on the surface of intermetallic compounds of the type of Pd_3Cr and Pd_2Si, which should promote an increase in the selectivity and stability of the catalyst in the dehydrogenation and aromatisation reactions as a result of the suppression of side processes involving the cleavage of the C–C bonds and saturation by coke.[142] On the Pd/Al_2O_3 catalyst modified by chromium and silicon compounds, it is possible to aromatise unsaturated cracking petrols containing alkenes and alkadienes without the preliminary hydropurification of the starting material.[142]

The formation of the alloy may improve the properties the platinum–rhenium catalyst compared with the platinum reforming catalyst usually employed.[143] The palladium–rhenium alloy was first investigated in the 1950s.[144] The limit of the solubility of rhenium in palladium corresponds to a ~20% rhenium content. The alloys remain single-phase up to a rhenium concentration of 7.4 mass% (12.8 at.%). When small amounts of rhenium (0.35 mass% and 2.24 mass%) are introduced into palladium, the electrical resistance of the specimen increases. Palladium and rhenium are transition metals with incomplete *d* shells. The valence of palladium is higher than that of rhenium, since the number of electrons in the $d+s$ levels in it is greater. The phase diagram for the palladium–rhenium system, like that for the platinum–rhenium system, belong to the peritectic type and reveals the presence of two limited solid solutions and no chemical compounds. The principal factors determining the nature of the interaction of the elements according to Tylkina et al.[145] are their position in the Periodic System, the isomorphous nature of the crystal structures, and the difference between the atomic dimensions and electronegativities. According to the Hume–Rothery rule, the formation of a continuous series of solid solutions requires that the difference between the atomic radii does not exceed 7%–8%, while the appearance of limited miscibility requires that the difference should not be greater than 15%. The platinum group metals and rhenium have virtually identical atomic radii. The size factor does not exceed 3%.

Another condition for miscibility is the similarity of the crystal lattices. This is why palladium, which has a face-centred cubic lattice, forms only limited solid solutions with rhenium, which has a hexagonal close-packed lattice. A significant characteristic of the elements is their electronegativity[146] because it is a function of the atomic radius and valence and may serve as a measure of the electron binding energy in the atom. It is known that, for a difference between the electronegativities of 0.2 e.u., one should expect continuous miscibility, while for a difference of 0.4 e.u. limited miscibility is to be expected. The electronegativities of rhenium and palladium are identical and equal to 2.08 e.u.

In the interaction of metals, the difference between their melting points plays a significant role. When the difference between the melting points is small (up to ~20 °C), there is a continuous miscibility, whereas in the case where it is considerable (up to ~50 °C) limited miscibility obtains. The difference between the melting points and the peritectic transformation temperature are also related. The greater the difference between the melting points of the two metals, the lower the peritectic transformation temperature, and the greater the extent of the two-phase region. The difference between the melting points of rhenium and palladium is 51 °C and that between the melting points of rhenium and platinum is 44 °C. For other platinum group metals, this difference is much smaller.

The above considerations suggest that the high effectiveness of the palladium–rhenium catalyst is associated with the formation on its surface of a palladium–rhenium alloy.

The formation of the surfaces of bimetallic catalysts is complex and takes place in several stages. It depends both on the carrier and on the conditions in the preparation of the catalyst. Furthermore, as a consequence of the specificity of the interaction of the components in small clusters, the composition of the catalyst surface may differ from that of the bulk-phase of the alloys.

The reasons for the promoting effect of the second metal in bimetallic supported catalysts have not been ultimately elucidated. There is a possibility of the interaction of the carrier with rhenium, the stabilisation of some kind of intermediate oxidation states by alumina, fusion, or the formation of metal clusters. However, one must assume that, since the coke deposition process is very slow, it is a consequence of side reactions. The second metal may more effectively catalyse the removal of the corresponding intermediates than palladium.

The prediction of the catalytic effect and selection of catalysts with specified properties is still one of the current problems in hetereogeneous catalysis.[147–153] Studies carried out by Boreskov's school[149–151] and other investigators have shown that, for a constant chemical composition of the catalyst, the specific catalytic activity depends slightly on the dispersity of the active component, the degree of its crystallinity, and the method of preparation. A stationary composition of the catalyst is established under the influence of the reaction mixture and its catalytic activity is independent of its initial state. For the majority of reactions, the postulate of the approximate constancy of the specific activity of the catalyst holds. These reactions belong to the class of the so called structure-insensitive reactions. On the other hand, the reactions for which appreciable deviations are observed are structure-sensitive.[154,155]

Together with nickel, palladium is one of the most active hydrogenation catalysts. The advantage of palladium over nickel consists in the fact that it readily dissolves hydrogen, which diffuses through the metal.[148] The hydrogenation reaction is structure-insensitive.

Analysis of the data presented in the review suggests that dehydrogenation on palladium-containing supported catalysts belongs to the class of structure-sensitive reactions, the rate of which depends on the accessibility and structure of the active centres. For such a reaction, the method of preparation of the catalyst is much more important than for the structure-insensitive reverse hydrogenation reaction. In particular, much attention must be devoted to the selection of the carrier, the regulation of its porosity, the preliminary treatment, the determination of the depth of impregnation, and other similar factors.[153]

Sulfur- and nitrogen-containing heterocyclic compounds are known to be catalytic poisons for platinum group metals. The catalyst is poisoned as a result of the stable chemisorption of such compounds on the surface of the deposited metal. Apparently, more strongly chemisorbed sulfur- and nitrogen-containing intermediates are formed on palladium catalysts than on sulfided palladium-containing catalysts and the higher activity and stability of the latter in the aromatisation reactions of petrol fractions containing sulfur compounds and in the dehydrogenation of heterocyclic molcules are associated with this factor. The greater stability of the hydrogen sulfide-treated palladium-containing catalysts compared with the untreated catalysts may also be associated with the formation on the surface of palladium sulfide, which, like other metal sulfides, is more resistant to the poisoning effect of sulfur and nitrogen compounds. Furthermore, metal sulfides are much less subject to saturation by coke than the metals themselves, as a result of which, nickel sulfide may prove to be more active, for example in the hydrocarbon hydrogenation reaction, than metallic nickel. Sulfide catalysts are bifunctional in their nature. They exhibit both hydrogenating-dehydrogenating and acid properties.[149] The great interest in sulfide catalysts is associated with their wide-scale application in hydropurification processes. The nature of the active component in metal sulfide supported catalysts and the mechanism of the activation of the C–S bond and of the hydrogen molecule in the hydropurification process still remain obscure.[156] A certain amount of attention has also been devoted to problems of the catalytic elimination of nitrogen-containing compounds, but their content, for example, in petroleums, is much lower than the content of sulfur compounds and the number of obscure and unsolved problems in that field remains even greater.

The modification of palladium supported catalysts with rhenium may induce an increase in the activity of palladium as regards reduction and promotes the attainment of a higher dispersity of the metal particles than in the Pd/Al_2O_3 catalyst.[135] Rhenium ensures a high thermal stability of alumino-palladium–rhenium catalysts, diminishes coke deposition, and can be more effective than palladium in removing the sulfur- and nitrogen-containing intermediates from the catalyst surface.[137,157]

Sulfided palladium and palladium-containing bimetallic supported systems are active catalysts for the dehydrogenation of cyclanes, cyclenes, cyclohexadienes, and their functional derivatives and may be used both for the synthesis of aromatic hydrocarbons and for the refinement of petrol fractions. Severe requirements as regards the content of aromatic hydrocarbons in the fuel have now begun to be imposed in certain developed countries.[158,159] One of the methods for the reduction of the concentration of such hydrocarbons may involve the use of sulfided palladium — rhenium supported catalysts for the hydrogenation of petroleum fractions.[160] Palladium-containing supported catalysts exhibit a high activity and selectivity in the dehydrogenation reactions of nitrogen- and oxygen-containing compounds in processes involving the preparation of valuable products of fine organic synthesis, such as indole, coumarin, their derivatives, and papaverine. The heterocyclic nuclei of the above compounds are known to serve as the structural basis for a large number of medicinal compounds, perfumes, dyes, etc.

The search for new ways of preparing supported catalysts containing a metal in a highly disperse state, modification, the synthesis of new carriers, the discovery of a relation beween the catalytic activity and the adsorption properties of the deposited metal and its valence state on the carrier, and other similar studies will promote the development of the scientific foundations for the selection of catalysts with specified properties in particular reactions. Further continuation of these researches by application of the latest physicochemical methods is one of the most important problems in heterogeneous catalysis.

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