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Rhenium-containing catalysts in reactions of organic compounds

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Abstract. The problems in the use of rhenium compounds and supported mono-, bi-, and poly-metallic rhenium-containing catalysts for carrying out reactions involving the metathesis of alkenes and unsaturated functional compounds, the hydrogenation and dehydrogenation of hydrocarbons, the conversion of hydrocarbons and their industrial mixtures, and the hydrogenation of fractions comprising carboxylic acids and the products of the hydroformylation of synthetic aliphatic acid esters are examined. The characteristic features of the behaviour of platinum – rhenium/alumina catalysts under reforming conditions are described. The specificity of the action of rhenium heptasulfide in the hydrogenation reactions of condensed N-containing aro matic compounds and in the reductive C-alkylation of indoloisoquinoline by alcohols is noted. The bibliography includes 251 references.

I. Introduction

Rhenium, discovered in 1925,[1,2] occupies a special place in the family of rare elements. In its various compounds, rhenium can exhibit oxidation states ranging from -1 to $+7$. The commonest oxidation state of $+7$ is characteristic of compounds such as rhenic acid and its salts or rhenium heptoxide.

Supported metallic and metal oxide catalysts are of great importance in heterogeneous catalysis. One of the requirements which must be met by a supported metal is its resistance to recrystallisation during the catalytic process. It is therefore useful to introduce into a catalyst a metal with a high melting point, which promotes an increase in the resistance of the catalyst to ageing. Such a metal may be rhenium, the melting point of which is 3170 °C. It is also noteworthy that the high solubility of ammonium perrhenate, rhenium heptoxide, and rhenium pentacarbonyl in water facilitates the preparation of rhenium catalysts by the impregnation method.

A series of patents, the authors of which described the ability of rhenium to catalyse a wide variety of chemical reactions, appeared soon after the discovery of rhenium.[3] The relevant data, published up to 1984, have been presented in a monograph.[4]

Reactions involving the hydrogenation of ethene to ethane and the preparation of methane from CO and hydrogen on rhenium-containing copper catalysts were investigated at the beginning of the 1930s.[5,6] The introduction of rhenium greatly increased their activity.

It was shown in 1935 that rhenium catalysts exhibit a higher activity in the dehydrogenation of alcohols than platinum, nickel, zinc, and copper.[7] An extensive investigation of the catalytic properties of rhenium and of its compounds with oxygen, sulfur, and selenium under the conditions of the liquid-phase hydrogenation of more than 100 organic compounds at an elevated pressure in a static system was carried out in the 1950s.[8,9] In contrast to the usual catalysts, rhenium oxides are capable of reducing carboxylic acids to the corresponding alcohols (ranging from ethyl to undecyl alcohol) and carboxylic acid amides to amines. Rhenium sulfides have a superior activity to that of the familiar catalysts for the dehydrogenation of alcohols to aldehydes and ketones, such as platinum, nickel, zinc, or copper.

The hydrogenation of hydrocarbons on supported rhenium – carbon catalysts was achieved in 1958.[10,11] The Re/Al_2O_3 catalysts showed a high activity in the conversion of C_5-C_7 hydrocarbons in the reforming process at elevated temperatures and hydrogen pressures.[12] At the same time, at atmospheric pressure the Re/Al_2O_3 and $Re/Al_2O_3 \cdot SiO_2$ catalysts proved to be appreciably less active than platinum/alumina catalysts.[13]

The promoting effect of rhenium introduced into a palladium/alumina catalyst was observed in 1962.[14] Bimetallic (1% Re, 1% Pd) catalyst supported on Al_2O_3 and $Al_2O_3 \cdot SiO_2$ exhibited a high activity in the reactions of C_6 hydrocarbons and in the reforming of petrol fractions,[14,15] ensuring an increase in their octane number as a result of the increase in the content of aromatic and paraffinic isohydrocarbons.

The disproportionation reaction of alkenes (metathesis), which makes it possible to convert an individual alkene into two others, one of which has a higher and the other a smaller molecular mass than the initial hydrocarbon, was discovered in 1964.[16] Thus ethene and butenes were obtained from propene on Re_2O_7/Al_2O_3 at 25 – 100 °C. Rhenium behaves in this reaction similarly to transition metals such as tungsten and molybdenum. Since 1966, the disproportionation reaction has begun to be used in industry (the 'triolefin' process). Information about the development of this process has been reported.[17]

A catalyst containing 0.01% – 3.0% of Pt and 0.01% – 5.0% of Re on alumina, which is active in the dehydrogenation of

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cyclohexane to benzene and in the reforming of the petrol fraction, was patented in the USA in 1968.[18] The first factory in which an effective and stable bimetallic catalyst R-16, containing platinum and rhenium supported on an oxide, began to operate in May, 1968.[19] The R-16, R-19, R-22, E-500, and E-501 bimetallic catalysts were introduced into industry by the American Companies Universal Oil Products, Chevron Research Co., and Engelhard Minerals and Chemicals Co., while the process itself came to be called 'rheniforming'.

In our country, the Lenneftekhim Scientific-Industrial Conglomerate (SIC) developed polymetallic rhenium-catalysts of the KR series for the reforming process.[20, 21] The first industrial batch of the KR-104 catalyst (containing 0.36% of Pt and 0.20% of Re) was prepared in 1976. The properties of improved compositions of the KR-108 and KR-110 catalysts were not inferior to the best world-class specimens.

About 75% – 80% of the mined rhenium has been used for the production of various alloys, which are widely employed in electrical engineering and in electronics, aviation, rocket, and space technology. Petroleum-processing undertakings became major consumers of rhenium in 1969. They began to use it in combination with platinum as the catalyst for the reforming process.[4] As early as 1978, 92% of rhenium was consumed in the USA for the production of bimetallic Pt – Re catalysts for the conversion of petrol fractions into high-octane petrols. The importance of the employment of rhenium as the reforming catalyst has been noted at the plenary session of the International Symposium on Rhenium and Rhenium Alloys in Orlando (USA),[22] which was devoted to the 70th anniversary of the discovery of this element.

The development of studies on rhenium-containing catalysts used in petroleum processing and in basic and fine chemical synthesis during recent years is analysed in the present review.

II. Catalytic properties of rhenium oxide/alumina systems

The metathesis of alkenes reduces to the exchange of alkylidene fragments between alkene molecules:

$$R^1R^2C{=}CR^3R^4 + R^5R^6C{=}CR^7R^8 \rightleftharpoons$$
$$\rightleftharpoons R^1R^2C{=}CR^5R^6 + R^3R^4C{=}CR^7R^8 .$$

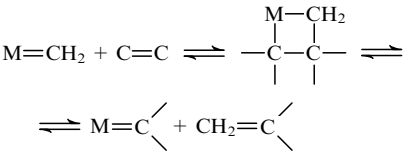
Valuable compounds, which may be used in perfumery, agriculture, and other fields, are formed in the metathesis of alkenes with functional groups.[23 – 26]

Catalysts containing rhenium, molybdenum, and tungsten (Re_2O_7/Al_2O_3, MoO_3/Al_2O_3, and WO_3/Al_2O_3) are the most active in the metathesis of alkenes. The rhenium/alumina catalyst merits special attention because it exhibits a high activity and selectivity even at room temperature and atmospheric pressure. The metathesis of propene in the presence of Re_2O_7/Al_2O_3 occurs at 50 °C, whereas on MoO_3/Al_2O_3 and WO_3/Al_2O_3 the corresponding temperatures are 207 and 402 °C respectively.[27] Catalysts containing rhenium with a lower valence, for example $Re_2(CO)_{10}/Al_2O_3$, are also active in this reaction.

Nowadays investigators have concentrated attention on the improvement of rhenium/alumina catalysts. Their activity in the metathesis of functional alkenes can be increased by introducing small amounts of promoting additives, for example allyltin,[25, 26, 28] which is known as the cocatalyst in homogeneous catalytic systems. Such additives increase the effectiveness also of heterogeneous systems, initiating the formation of a metallocarbene in accordance with the scheme

$$Re(CH_3)_2 \longrightarrow Re{=}CH_2 + CH_4 .$$

One of the stages of the widely known carbene chain mechanism of metathesis [29] involves the formation of a metallocyclobutane:



Rhenium/alumina catalysts containing < 5% of Re_2O_7 exhibit a slight activity in the metathesis of alkenes.[30, 31] A necessary reaction stage on these catalysts is the reduction of the carbene formed. Propene and higher alkenes are capable of reducing Re_2O_7 on aluminium oxide even at room temperature.[32]

1. The metathesis of olefins and unsaturated functional compounds

The properties of the $Re_2O_7/Al_2O_3 \cdot SiO_2$ catalyst containing 3 mass % of Re_2O_7 have been investigated at room temperature in relation to the model reaction involving the disproportionation of propene to ethene and but-2-ene in a microcatalytic flow system.[33] Its activity, exceeding that of Re_2O_7/Al_2O_3, was further increased on introduction of tetramethyl- and tetraethyl-tin as a result of the participation of the Brønsted acid centres of the support in the process. The removal of surface OH groups reduced the activity of the catalyst. SnR_4 probably stabilises the active complex, which is especially important in the metathesis of functional alkenes.[34] SnR_4-promoted Re_2O_7/Al_2O_3, which is more active than the catalyst containing the oxides of other metals, for example MoO_3, WO_3, or V_2O_5, is used as the catalyst in this process.[35]

The new catalytic system $Re_2O_7/Al_2O_3 \cdot B_2O_3$ has been tested in relation to the model reaction involving the metathesis of methyl oleate — a typical functional alkene:[36]

$$2Me(CH_2)_7CH{=}CH(CH_2)_7COOMe \rightleftharpoons$$
$$\rightleftharpoons Me(CH_2)_7CH{=}CH(CH_2)_7Me +$$
$$+ MeOOC(CH_2)_7CH{=}CH(CH_2)_7COOMe .$$

The catalysts were prepared by impregnation and partial drying at 110 °C. The amount of B_2O_3 introduced was 5%, 10%, 15%, and 20%. The catalyst containing 3 mass % of Re_2O_7 deposited on Al_2O_3 to which 15 mass % of B_2O_3 had been added exhibited the highest activity. The optimum catalyst activation temperature was 477 °C. For a reaction time longer than 1.5 h, a higher degree of conversion was achieved on this catalyst than on 18% Re_2O_7/Al_2O_3. The added B_2O_3 interacts with the acid centres of Al_2O_3 and weakens the linkages between rhenium particles and aluminium oxide. When the content of deposited B_2O_3 is in excess of the optimum value, the amount of rhenium reduced on the surface diminishes, which lowers the activity of the catalyst. The high activity and selectivity of the low-percentage $Re_2O_7/Al_2O_3 \cdot B_2O_3$ catalyst at room temperature has been explained by the presence on the surface of strong Brønsted acid centres.

The catalytic activity may be altered by employing various cocatalysts. The promoting effect diminishes in the series [36]

$$SnEt_4 \geqslant SnBu_4 > PbBu_4 > PbEt_4 > SnMe_4 .$$

The most active metathesis catalysts — Re_2O_7/Al_2O_3, $Re_2O_7/SiO_2 \cdot Al_2O_3$, $Re_2O_7/Al_2O_3 \cdot B_2O_3$, and $M_xO_yRe_2O_7/Al_2O_3$ (M_xO_y = MoO_3, WO_3, or V_2O_5) — were investigated by the temperature-programmed reduction method and thermal analysis.[37] The rhenium particles in the $Re_2O_7/SiO_2 \cdot Al_2O_3$ and $M_xO_yRe_2O_7/Al_2O_3$ specimens exhibit redox properties. The presence of V_2O_5, WO_3, or MoO_3 diminishes the thermal stability of the rhenium particles in the Re_2O_7/Al_2O_3 catalysts in the following sequence:

$$Re_2O_7/Al_2O_3 > Re_2O_7/SiO_2 \cdot Al_2O_3 > Re_2O_7/Al_2O_3 \cdot B_2O_3 .$$

The unequal activities of these catalysts in the metathesis of alkenes and functional alkenes cannot be accounted for either by the different capacities of the rhenium particles for reduction, or

by possible steric hindrance in the formation of the rhenium–cyclobutane complex, or by a change in the thermal stability of the rhenium particles.[36]

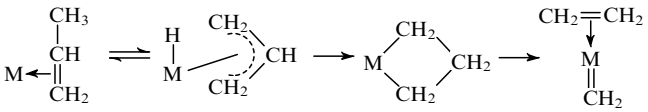
The activity of the Re_2O_7/Al_2O_3 catalysts of the metathesis of propene increases on raising the heat treatment temperature during their preparation.[38] The optimum heat treatment temperature depends on the Re_2O_7 content and is in the range 827–927 °C. For a low Re_2O_7 content, the maximum heat treatment temperature is required. The much higher activity of the catalyst containing 3 mass % of Re_2O_7 has been attributed to the redistribution of the ReO_4 groups on the Al_2O_3 surface, which has been confirmed by spectroscopic data. The catalyst heat-treated at a high temperature can be regenerated after deactivation by heat treatment at the usual temperature of 550 °C without appreciable loss of the initial activity.

The strength of the Brønsted and Lewis acid centres increases with increase in the amount of Re_2O_7 supported on Al_2O_3.[39] The impregnation of a catalyst having a low rhenium content (6 mass % of Re_2O_7) with hydrochloric acid promotes the manifestation of Brønsted acidity. With increase in the Re_2O_7 content, the Brønsted acidity of the aluminosilicate gradually increases, while the Lewis acidity passes through a maximum. The activity of the Re_2O_7/Al_2O_3, $M_xO_yRe_2O_7/Al_2O_3$ ($M_xO_y = V_2O_5$, MoO_3, or WO_3), and $Re_2O_7/SiO_2 \cdot Al_2O_3$ catalysts of the metathesis of alkenes is directly correlated with their Brønsted acidity, in contrast to the Lewis acidity. Thus, in order to increase the activity of low-percentage rhenium catalysts in the metathesis of alkenes, it is necessary to increase their Brønsted acidity by introducing various modifying agents.[39]

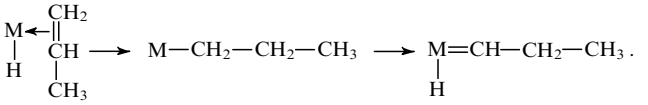
After heat treatment, a monolayer containing Re^{7+} ions is formed on the surfaces of the Re_2O_7/Al_2O_3 catalysts.[40] For a low content of rhenium, the latter enters mainly into monomeric tetrahedrally coordinated ReO_4^+ ions, while in the presence of a high rhenium content Re–O–Re linkages are formed. After interaction with the reactants, the rhenium is reduced and carbene complexes active in the metathesis are formed. The fraction of active rhenium ions is less than 1%. In the absence of cocatalysts, Re_2O_7/Al_2O_3 altogether fails to exhibit an activity in the metathesis of alkenes with polar functional groups. The modification of the support, for example the introduction of SiO_2 into Al_2O_3, increases the activity of the catalyst. The addition of a third metal oxide, for example MoO_3, WO_3, or V_2O_5, increases the turnover number of the reaction for a low content of deposited rhenium. The addition of a tetraalkyltin not only increases the activity of the catalyst in the metathesis of alkenes but also makes it possible to achieve the metathesis of alkenes containing functional groups. The increase in the activity of low-percentage catalysts after their preliminary treatment with hydrogen at 500 °C and subsequent chemisorption of oxygen at 77 °C has been investigated by the temperature-programmed reduction, XPES, laser Raman spectroscopic, and EPR methods.[40] After such treatment, the signal due to adsorbed O_2^- ions was observed in the spectra. The active centres are formed in accordance with the scheme

$$Re^{4+}-O-Al^{3+} \xrightarrow{O_2} Re^{5+}-O-Al^{3+}(O_2^-)$$

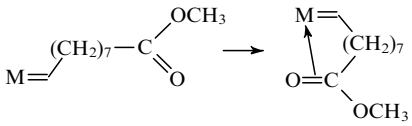
It has been suggested that the carbene complex is formed during metathesis as a result of the generation of acid vacancies, which is followed by reactions of the type



or



Catalysts such as Re_2O_7/Al_2O_3 are highly polar and therefore react with polar compounds, for example with alkenes, as well as water, which may be present in the reactants and is a catalytic poison. Molecules with polar groups are capable of blocking the free centres necessary for metathesis, for example



Other possible causes of deactivation have also been discussed.[40]

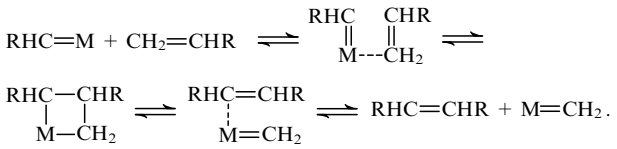
The possibility of regenerating the 12% Re_2O_7/Al_2O_3 catalysts, promoted by tetrabutyltin with the ratios Sn : Re = 1 : 4, 2 : 4, and 3 : 4, and also of 3% $Re_2O_7/SiO_2 \cdot Al_2O_3$ promoted by tetraethyltin has been investigated. The metathesis of propene was carried out on these catalysts in a microcatalytic flow reactor at 20 and 80 °C and a pressure of 1.5 atm.[41] The activity of the deactivated catalyst could be partially restored by increasing the content of the promoting agent and also by carrying out regeneration in a stream of oxygen with subsequent repeated addition of the promoting agent. Nevertheless, there was a partial loss of activity after each regeneration cycle. A study of the catalyst surface by scanning electron microscopy and X-ray diffraction after the temperature-programmed reduction showed that the loss of activity is associated with the formation on the surface of the oxide SnO_2, which interacts with Re_2O_7.

The study of the reactivity of alk-1-enes in metathesis under industrial conditions over the 12% Re_2O_7/Al_2O_3 catalyst in the liquid phase[42] showed that the rate of reaction diminishes with increase in the length of the hydrocarbon chain (from hex-1-ene to dec-1-ene). It has been suggested that this is associated with the fact that the rate of reaction is determined by the desorption of the product. Alkenes with a long chain and a symmetrical disposition of the inner double bond are formed in the metathesis of higher alkenes (oct-1-ene, dec-1-ene):

$$2CH_2{=}CH(CH_2)_nCH_3 \rightleftharpoons$$

$$\rightleftharpoons CH_2{=}CH_2 + CH_3(CH_2)_nCH{=}CH(CH_2)_nCH_3 .$$

The reaction proceeds in accordance with the mechanism



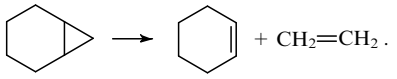
Four products — ethene, tetradec-7-ene, hexadec-7-ene, and octadec-9-ene — are formed in the joint metathesis of oct-1-ene and dec-1-ene.[42]

The kinetic description of the metathesis of oct-1-ene on $Re_2O_7/\gamma\text{-}Al_2O_3$ in the liquid phase was based on the metallocarbene mechanism.[43] The rate-limiting stage is either the internal conversion of the carbene complex or the desorption of the product. It was not possible to make a final choice on the basis of the experimental data. The proposed mathematical model makes it possible to describe the deactivation of the catalyst as a function of the duration and temperature of the reaction. The apparent activation energy for metathesis is 22.5 kJ mol^{-1} and that for the deactivation of the catalyst is 12.0 kJ mol^{-1} The constancy of the degree of conversion under the conditions of the deactivation of the catalyst can be maintained by gradually increasing the reaction temperature. Calculation within the framework of the mathematical model showed [43] that the temperature-programmed regime makes it possible to convert a much larger amount of oct-1-ene in each catalytic cycle.

The Re_2O_7/Al_2O_3 catalyst modified by the introduction of B_2O_3 into the support has been used for the metathesis of methyl oleate.[44] The concentration of Lewis and Brønsted acid centres

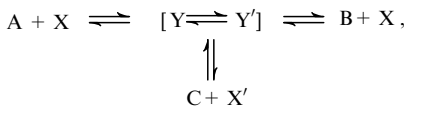
was determined spectroscopically during the reaction and also during the heat treatment of the support and the catalyst. When $\leqslant 5\%$ of B_2O_3 is introduced, the Al_2O_3 and B_2O_3 phases are present simultaneously in the specimen, each containing surface hydroxy-groups. For a higher B_2O_3 content, the hydroxy-groups of aluminium oxide are fully coated by boron oxide. The number of hydroxy-groups linked to boron diminishes with increase in the B_2O_3 content as a result of the formation of boron-containing linear polymers. When Re_2O_7 is supported on B_2O_3-free Al_2O_3, the ReO_4 groups react in the first place with the Lewis acid centres. If the B_2O_3 content exceeds 3%, then the surface hydroxy-groups are also substituted by the ReO_4 groups, which increases the catalytic activity. The ReO_4 groups which have reacted with the Lewis acid centres of the boronated support substitute the hydroxy-groups of the aluminium oxide during heat treatment. The hydroxy-groups of boron oxide are substituted only after heat treatment during $\geqslant 2$ h at 550 °C. For a B_2O_3 content greater than 10%, the reaction of the hydroxy-groups of boron with ReO_4 competes with the condensation reaction of two neighbouring hydroxy-groups. If it is supposed that the ReO_4 group substituted for the OH group of the support is a precursor of the active centre, then the increase in the activity of Re_2O_7 as a result of the introduction of B_2O_3 into Al_2O_3 can be explained either by the restoration of the linkages between the strong Lewis acid centres and ReO_4 or the formation of new surface hydroxy-groups, which serve as the acid centres.[44]

The metathesis of cyclopropane hydrocarbons with different structures, namely n-butylcyclopropane, bicyclo[4.1.0]heptane (norcarane), and 1-methyl-1-phenylcyclopropane, at 20 °C has been investigated on a 20% Re_2O_7/γ-Al_2O_3 catalyst prepared by impregnating the support with a saturated NH_4ReO_4 solution containing tetrabutyltin.[45] The reactions were carried out under an argon atmosphere, using hexane or octane as the solvent. Ethene was present in the gas phase in all cases. The liquid phase contained $\sim 1\%$ of cyclohexene — the product of the elimination of carbene in the metathesis of norcarane:



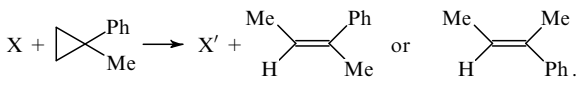
When the reaction involved bicyclo[3.1.0]hexane, ethene was also present among the gaseous products, but the liquid product did not contain cyclopentene. This has been explained by the greater tendency of cyclopentene to polymerise. C_6-C_{12} monoalkenes, including undec-5-ene (55 mass %), dodec-6-ene (35 mass %), dec-5-ene (5 mass %), nonene, octene, heptene, and hexene ($\sim$ 1 mass % each), were formed from n-butylcyclopropane. The degree of conversion of 1-methyl-1-phenylcyclopropane into ethene was 40%.

The scheme proposed for this process [46] combines the carbene chain mechanism of metathesis and the mechanism involving the formation of cyclopropane compounds:



where A and B are alkenes, C are cyclopropane compounds, X and X′ are catalytic centres, and Y and Y′ are intermediate complexes.

In the reaction involving 1-methyl-1-phenylcyclopropane, X probably represents a catalytic centre for metathesis, arising in the activation of the rhenium/alumina catalyst by tetrabutyltin.[45] The interaction with a substrate molecule, accompanied by the isomerisation of the initial hydrocarbon, is necessary for the transformation of X into the X′ centre:



The isomerisation products may be *cis*- and *trans*-2-phenylbut-2-enes, which apparently polymerise. Carbene may also be eliminated from the initial molecule on the centre produced, while the elimination product (α-methylstyrene) also isomerises. Thus the cyclopropane hydrocarbons isomerise on the rhenium/alumina catalyst and eliminate carbene with evolution of ethene, while the compounds formed polymerise or undergo metathesis.[45]

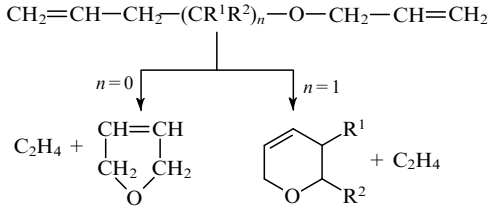
It has been established by the XPES method that the activity of the Re_2O_7/Al_2O_3 catalysts is determined by the reduction of Re^{7+} to give an intermediate oxidation state, which begins at 200–300 °C. The reduction of rhenium in Re_2O_7/Al_2O_3 is known to be more difficult than in Re_2O_7/SiO_2.[47, 48] The state of rhenium in a fresh unpromoted 15% Re_2O_7/Al_2O_3 metathesis catalyst and in a specimen promoted with phenylcyclopropane has also been investigated by the XPES method.[49] The rhenium in the unpromoted catalyst exists in the form of ReO_4 tetrahedra linked to the support *via* one oxygen atom. The promotion of the catalyst with phenylcyclopropane has been explained [49] by the appearance on the surface of fragments with a rhenium–carbon bond in which the atomic ratio Re : C = 1 : 1. Such fragments may be carbene complexes containing the Re=C double bond. The composition includes > 90% of the total number of rhenium atoms in the catalyst. The high concentration of these complexes on the surface of the specimen ensures its high catalytic activity in the metathesis of hex-1-ene, which has been confirmed experimentally.

2. Metathesis of functional alkenes

The metathesis of alkenes containing functional groups has been achieved on promoted and unpromoted rhenium/alumina catalysts.[50–57] The experiments were performed at atmospheric pressure in a liquid-phase static system with stirring, ensuring that the reaction occurred in the kinetic region. The metathesis of allyl chloride, the allyl ether of allylcarbinol, allylbenzene, and diallyl ether [50] was achieved on catalysts supported on alumina and containing 0.5%–1.5% of Re with 5% or 10% of Mo or 1.5% of Re with 5% or 10% of V,[50] in which the molar ratios of the initial substances and Re_2O_7 were 560–3000 at temperatures of 22 and 55 °C. Tetrabutyltin was used to promote the catalyst. The conversion of the initial substances into the corresponding bifunctional or cyclic unsaturated compounds (2,5-dihydrofuran and 2,3-dihydro-α-pyran) was 15%–20% (after 30 min) for a selectivity of 93%–95%. The catalyst containing 0.5 mass %–1.5 mass % of Re_2O_7 and 5 mass %–10 mass % of MoO_3 or V_2O_5 proved to be optimal.

The structure of the alkenyl fragment in an alkenyl allyl ether influences the selectivity and rate of its metathesis.[51] The reactions of allyl-, methylallyl-, and phenylallyl-carbinols and the allyl ethers of allyl-, methyl-, dimethyl-, and phenyl-carbinols have been investigated on a rhenium/alumina catalyst promoted with tetrabutyltin (15 mass % of Re_2O_7, 5 mass % of SnR_4, and 80 mass % of -γ-Al_2O_3) at temperatures ranging from 0 to 80 °C and for molar ratios of the initial substance and Re_2O_7 between 60 and 460. The reactivity of the ethers investigated depends on the structure of the alkenyl fragment. The presence of substituents at the carbon atom directly adjoining the oxygen atom retards the intramolecular metathesis. In the temperature range 20–80 °C, the metathesis was characterised by a low activation energy (of the order of 10–13 kJ mol^{-1}).

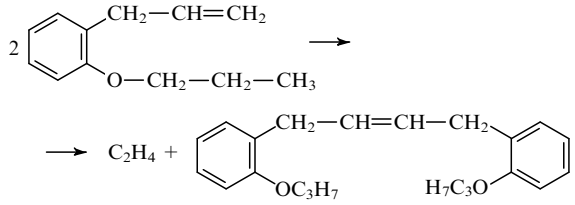
The unsaturated cyclic ethers are formed in accordance with the scheme



R^1, R^2 = H, CH_3, C_6H_5.

The intramolecular reaction predominates in the metathesis of ethers with two double bonds.[51]

If the hydroxy-group of *o*-allylphenol is converted beforehand into an ether group, it is possible to achieve a high rate of metathesis of the corresponding compound. The metathesis of *o*-(allyl)propoxybenzene with formation of 1,4-bis(*o*-propoxyphenyl)but-2-ene has been carried out on a rhenium/alumina catalyst promoted with tetrabutyltin at 22 °C in solvents (hexane or benzene).[52] The selectivity reached 94% – 96%. It is suggested that the metathesis proceeds *via* the intermolecular mechanism.



Aromatic alkenyl compounds can be arranged in the following sequence in terms of their reactivity in the above reaction: allylbenzene > *o*-(allyl)propoxybenzene > styrene.

The influence of the preliminary treatment of the support on the activity of a catalyst containing Re_2O_7 (15 mass %), $(C_4H_9)_4Sn$ (5 mass %), and γ-Al_2O_3 (80 mass %) has been investigated in relation to the metathesis of n-hex-1-ene, allyl chloride, and diallyl ether.[53] Treatment with water and a 0.1 N aqueous solution of hydrochloric acid increased the rate of metathesis of n-hex-1-ene and allyl chloride. This can be explained by the increase in the number of active centres of the catalyst and the increase in the acidity of the support, since an increase in acidity, especially Brønsted acidity, promotes the metathesis of unsaturated compounds with a functional group.[35] On the other hand, treatment of the support with ammonium hydroxide diminished the rate of metathesis.

When the support of the Re_2O_7/γ-Al_2O_3 catalyst was treated with trialkyl borate, which decomposes to boron trioxide, the rate of metathesis of n-hex-1-ene and diallyl ether decreased by a factor of 2.5 – 3 compared with the initial untreated specimen.[54] Thus the Re_2O_7 content can be increased from 10 mass % – 15 mass % to 1 mass % – 2.5 mass % without diminishing the activity of the catalyst. The maximum activity is attained for 2 mass % – 4 mass % of Re_2O_7 and 1 mass % – 5.0 mass % of triethyl borate. The structure of the substituent in the trialkyl borate does not affect the rate of metathesis. The degree of conversion of n-hex-1-ene on the catalyst containing 10% of $(C_2H_5O)_3B$, 5% of Re_2O_7, 1.5% of $(C_4H_9)_4Sn$, and 83.5% of Al_2O_3 reached 86.9% after 5 min, whereas the degree of conversion on the catalyst untreated with tetrabutyltin was 32.0% after 20 min. The rhenium/alumina – boron oxide catalyst can operate in the temperature range 0 – 48 °C.

The metathesis of allyl chloride and allylacetone on a similar rhenium/alumina – boron oxide catalyst, prepared using the ratio $Re_2O_7 : Sn(C_4H_9)_4 = 3$ proceeds *via* an intermolecular mechanism in accordance with the equation [55]

$$2CH_2{=}CHCH_2CH_2COCH_3 \longrightarrow C_2H_4 + \underset{\|}{CH(CH_2)_2COCH_3}\,,\ \underset{CH(CH_2)_2COCH_3}{}$$

$$2CH_2Cl{-}CH{=}CH_2 \longrightarrow C_2H_4 + ClCH_2CH{=}CHCH_2Cl\,.$$

The metathesis products are dec-5-ene-2,9-dione and 1,4-dichlorobut-2-ene. As in the metathesis of n-hex-1-ene and diallyl ether, the Re_2O_7 content in the catalyst can be reduced from 15 mass % to 2.5 mass % – 7.5 mass % as a result of the treatment without diminishing the activity and selectivity. However, these active and selective catalysts of the metathesis of unsaturated compounds with functional groups are not sufficiently stable.[54, 55] One of the causes of instability is the ability of the functional group to compete with the C = C bond for the active centres of the catalyst, *i.e.* the deactivation of the catalyst by the reactant.[40] The introduction of variable-valence metals (Mo or V) into the rhenium/alumina catalyst makes it possible to activate it and reduce the rhenium oxide content.[56] In a modification of a rhenium/alumina catalyst, both untreated and treated with $SnBu_4$, with constant-valence metals (Na^+, K^+, Mg^{2+}), its activity in the metathesis of n-hex-1-ene falls and the degree of conversion diminishes from 10.9% to 2.6%. The addition of Pd increases the activity of the catalyst containing 5 mass % of Re_2O_7, but its selectivity decreases from 93% – 98% to 68% – 76%. Preliminary treatment of the rhenium/alumina catalyst with triethyl borate [54, 55] increases its activity.

The stabilising effect of aluminium oxide on rhenium apparently weakens with increase in the degree of its coverage by boron, which agrees with the data of another publication.[36] Treatment of the support with hydrogen chloride and triethyl borate increases the activity of rhenium/alumina catalysts in the joint metathesis of 1,4-dichlorobut-2-ene and 2,3-dimethylbut-2-ene,[56] so that the Re_2O_7 content could be reduced by a factor of two — from 15% to 7.5%. The reaction, the product of which is 4-chloro-2-methylbut-2-ene, proceeds in accordance with the equation

$$ClCH_2CH{=}CHCH_2Cl + CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}{=}C{-}CH_3 \longrightarrow 2CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_2Cl\,.$$

The activity of rhenium/alumina metathesis catalysts depend on the conditions of their activation (duration and temperature of the heat treatment, the medium, *etc.*).[57]

The highest activity of the catalyst containing 5 mass % of Re_2O_7 is reached after its treatment at 620 – 640 °C. The productivity of the catalyst in the metathesis of allyl chloride increases by a factor of 3. After the activation of the rhenium/alumina catalyst containing 15 mass % of Re_2O_7, the degree of conversion of both n-hex-1-ene and allyl chloride at 580 °C increases. The activity and productivity of the catalyst can also be increased by increasing the activation time to 13 h. The rate of metathesis of n-hex-1-ene then increases by a factor of $\sim$ 1.5, while the productivity of the catalyst in the metathesis of allyl chloride increases by a factor of 2 – 3. A further increase in the activation time to 20 h does not alter the activity appreciably. Yet another way of increasing the activity is the deposition of ammonium perrhenate on aluminium oxide with an intermediate heat treatment at elevated temperatures.[57]

III. Catalytic properties of other rhenium compounds

Metallic rhenium is known to be in most cases inferior in its hydrogenating activity to group VIII metals,[4] but some of its compounds exhibit a high hydrogenating capacity.

1. Hydrogenation of organic compounds

Rhenocene hydride $(\eta^5\text{-}C_5H_5)_2ReH$ manifested a high activity in the hydrogenation reactions of cyclohexene, benzene, ethyl acetate, and 36% acetic acid.[58, 59]

At a temperature of 150 °C and a hydrogen pressure P_{H_2} = 100 atm, the degree of conversion of cyclohexene on a catalyst containing 0.8% of Re relative to the mass of the hydrocarbon attained 73% after 1 h in an autoclave. An increase in temperature to 180 °C made it possible to lower the amount of catalyst and the reaction time by a factor of 2 and to obtain cyclohexane in a quantitative yield. Rhenocene hydride was much more active than Re_2S_7 and even ReO_3.[59] When rhenium trioxide was used, the amount of rhenium had to be increased by a factor of 3, the reaction time had to be prolonged by a factor of 8, and the pressure had to be raised by a factor of 2 in order to attain the same activity.

Benzene was hydrogenated fully on rhenocene hydride at 180 °C and P_{H_2} = 100 atm for a reaction time τ = 30 min and for a rhenium content of 1.0% relative to the mass of benzene. In this reaction too, the catalyst was much more active than ReO_3.

The degree of conversion of ethyl acetate (EA) in the hydrogenation reaction at 200 °C, P_{H_2} = 100 atm, and τ = 3 h reached 60%. Under these conditions, ~ 49% of EtOH accumulated in the catalytic reaction mixture. Under comparable conditions, the overall degree of conversion of ethyl acetate into EtOH on Re_2O_7 was lower by a factor of 2. It is noteworthy that platinum and palladium sulfides did not exhibit a hydrogenating activity. A high activity of Re_2O_7 in the ethyl acetate reduction reaction has been observed:[60] the yield of EtOH reached 82% at 175 °C, P_{H_2} = 210 atm, and τ = 5 h. However, up to 6% of AcOH was formed under these conditions. The reaction proceeds in accordance with the equation

$$CH_3COOC_2H_5 + 2H_2 \longrightarrow 2C_2H_5OH\,.$$

The appreciable activity of rhenocene hydride and a fairly high selectivity of the reaction have been noted in the hydrogenation of 36% acetic acid.[59] At 230 °C, P_{H_2} = 120 atm and τ = 3 h for a Re content of 1% and for an overall degree of conversion of ~ 86%, the yield of EtOH was ~ 52%. Ethyl acetate was formed together with EtOH. Rhenocene hydride decomposed under the conditions indicated. The metallic phase formed exhibited an increased activity, since it was more highly disperse than bulk rhenium. The following activity series has been established for the rhenocene hydride-based heterometallic catalysts in the hydrogenation of acetic acid:

$$(C_5H_5)_2ReH > (C_5H_5)_2ReH\cdot AlCl_3 > (C_5H_5)_2ReH\cdot AlHCl_2 \geqslant (C_5H_5)_2ReH\cdot AlBr_3\,.$$

Rhenium pentacarbonyl $Re_2(CO)_{10}$ also exhibits a high hydrogenating activity.[61–63] Cyclohexene was fully hydrogenated on this catalyst after 15 min at 230 °C and P_{H_2} = 50 atm and for a Re content of 1% relative to the mass of the substrate. The hydrogenation of benzene required a higher hydrogen pressure (100 atm). In terms of its activity in the cyclohexene and benzene hydrogenation reactions $Re_2(CO)_{10}$ is superior to rhenium oxides [60] and is slightly inferior to rhenocene hydride.[59] However, it decomposes under the conditions indicated above with formation of a metallic phase exhibiting a higher activity than bulk rhenium. The lower activity of rhenium pentacarbonyl compared with rhenacene hydride can be explained by the fact that part of the metal remains bound in the form of the carbonyl. IR spectroscopic study showed that, under the conditions of the hydrogenation of both cyclohexene and benzene, rhenium carbonyl reacts with the components of the reaction mixture. One cannot apparently rule out the possibility that not rhenium carbonyl itself but its unstable complex is catalytically active. The complex differs from the four known rhenium carbonyl hydrides — the monomeric $HRe(CO)_5$ and the cluster compounds $H_3Re_3(CO)_{12}$, $H_4Re_4(CO)_{12}$ and $HRe_3(CO)_{14}$. It also follows from the analysis of the IR spectra that hydrogenation of benzene entails the formation of a metal carbonyl complex different from that in the hydrogenation of cyclohexene.[62]

Rhenium oxides with the perovskite structure and having the general formula $Ba_2Bi^{III}_{1/3}\square_{2/3}Re^{VII}O_6$, where B^{III} = Y or Sm, or $Ba_3LaZnRe^{VII}\square O_{12}$ (the symbol $\square$ denotes a vacancy in the cationic lattice) also possess hydrogenating properties.[64] The catalysts were synthesised under solid-phase reaction conditions using a known method [65,66] and were identified by X-ray phase analysis. The hydrogenation of ethyl acetate on these catalysts was carried out in a static system (in an autoclave) at 280 °C and P_{H_2} = 100 atm and for τ = 3 h. The $Ba_2Y_{1/3}\square_{2/3}ReO_6$ catalysts showed the highest activity: the overall degree of conversion of ethyl acetate was 35% for a selectivity in the formation of ethanol of 83.4%. After the catalyst worked for 3 h, the reaction products were removed and a fresh portion of ethyl acetate was introduced. After this, the degree of conversion of ethyl acetate into ethanol in the course of 3 h of the reaction increased from 29.2% to 43.2%. Yet another repetition of the same procedure led to a further increase in the degree of conversion from 43.2% to 47.9% (selectivity 86%). The increase in activity may be associated with the activation of the specimen in the course of the experiment by virtue of the reduction of Re(VII). The transition of rhenium to lower oxidation states in the course of the reaction was indicated by a change in the colour of the specimen from yellow or yellow-green to black. Ethyl acetate is reduced on Re_2O_7 even at 230 °C, whereas on the oxides described this requires 280 °C, other conditions being equal. It may be that the hydrogenating activity is determined by the presence in the catalyst not only of rhenium but also of other cations. One may postulate that the hydrogenating activity can be partly accounted for also by the formation of reduced rhenium in a highly disperse state under the experimental conditions.

The hydrogenation of benzene and ethyl acetate has also been achieved on rhenium oxides with the perovskite structure having

Table 1. Hydrogenation of benzene [a] and ethyl acetate [b] on rhenium oxides with the perovskite structure [67] and certain other rhenium catalysts.

Catalyst	Yield of C_6H_{12} obtained from benzene (%) [a]	Hydrogenation of ethyl acetate [b]					
		composition of catalytic reaction mixture (%)			conversion (%)		selectivity (%)
		H_2O	EtOH	ethyl acetate	in EtOH	overall	
$Ba_{3.6}Sr_{0.4}CoRe_2\square O_{12}$	18						
$Ba_{3.2}Sr_{0.8}CoRe_2\square O_{12}$	20						
$Ba_{2.8}Sr_{1.2}CoRe_2\square O_{12}$	20						
$Ba_{2.0}Sr_{2.0}CoRe_2\square O_{12}$	22	3.9	6.9	89.1	6.6	10.6	60.6
$Ba_{1.6}Sr_{2.4}CoRe_2\square O_{12}$	50						
$Ba_{1.2}Sr_{2.8}CoRe_2\square O_{12}$	52	5.7	13.3	81.0	12.7	19.0	67.0
$Ba_{0.4}Sr_{3.6}CoRe_2\square O_{12}$	78						
$Sr_{4.0}NiRe_2\square O_{12}$	90	8.2	10.6	81.2	10.2	18.8	54.0
$Sr_{4.0}CoRe_2\square O_{12}$	90						
$Sr_{4.0}CaRe_2\square O_{12}$	0						
Re_2S_7	3	4.0	20.9	75.1	20.0	24.9	80.3
ReO_3	100 [c]						
$Ba(ReO_4)_2$	0						
$Ba_2Y_{1/3}\square_{2/3}ReO_6$ [d]		4.5	30.5	65.0	29.2	35.0	83.4

Reaction conditions: [a] T = 200 °C, P_{H_2} = 100 atm, τ = 2 h, 1% of Re; [b] T = 280 °C, P_{H_2} = 100 atm, τ = 3 h, 2% of Re; [c] T = 240 °C, P_{H_2} = 100 atm, τ = 4 h, 3% of Re (data of Broadbent and Bartley [60]); [d] data of Ryashentseva *et al.*[64]

the general formula $A_4BRe_2\square O_{12}$, where A = Ba or Sr and B = Co or Ni.[67] The results obtained are presented in Table 1.

For a rhenium content of 1% relative to benzene, the yield of cyclohexane increases from 18% to 78% as the barium content falls.[64] Evidently the presence of the large barium ions (ionic radius 1.36 Å) in the catalyst structure hinders the hydrogenation of benzene. Among barium-containing catalysts, the $Ba_{0.4}Sr_{3.6}CoRe_2\square O_{12}$ specimen had the highest activity under the reaction conditions (200 °C, P_{H_2} = 90–100 atm, Re content 1%) and the yield of cyclohexane, amounting to 78%, remained unchanged for 6 h. In the succeeding 16 h, the yield of cyclohexane fell to 35%. The $Sr_{4.0}CoRe_2\square O_{12}$ and $Sr_{4.0}NiRe_2\square O_{12}$ catalysts proved to be the most active in the hydrogenation of benzene. Benzene was virtually fully hydrogenated on these catalysts, containing 1% of rhenium, at T = 200–300 °C and P_{H_2} = 100–120 atm and for τ = 2–3 h. The catalytic activity increased with increase in the ionisation potential of the cations A(Ba < Sr) and B(Ca < Ni < Co).

The state of the surfaces of the $Sr_4CoRe_2\square O_{12}$ and $Ba_4CaRe_2\square O_{12}$ specimens before and after catalysis has been investigated by the method of thermovacuum electrical conductivity curves (TVE). The specimens exhibited semiconducting properties. After the experiment on a strontium specimen, exhibiting a high hydrogenating activity, changes were observed in the surface possibly due to its reduction. However, the specimen remained a semiconductor, *i.e.* there was no reduction to the metallic or pseudometallic state. The low specific surface of the specimen (1.5 $m^2\ g^{-1}$) and the presence on the surface of ~ 12% of reduced rhenium, relative to its overall content, after catalysis (according to XPES data) made it possible to suggest that metallic rhenium is largely located not on the surface but in the bulk of the catalyst and in a highly disperse form. In order to create active hydrogenation catalysts with the perovskite structure, it is apparently necessary to reduce the rhenium on the surface. It has been demonstrated by the XPES method that Re^{4+} and Re^{6+} ions are present in the $Sr_4CoRe_2\square O_{12}$ and $Sr_4NiRe_2\square O_{12}$ catalysts and may enter into the composition of the active centres.

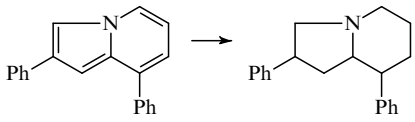
The perovskites $Ba_2Sr_2CoRe_2\square O_{12}$, $Ba_{1.2}Sr_{2.8}CoRe_2\square O_{12}$, containing 2% of Re, and $Sr_4NiRe_2\square O_{12}$ proved to be less active and selective than Re_2S_7 and $Ba_2Y_{1/3}\square_{2/3}ReO_6$ in the hydrogenation of ethyl acetate (T = 280 °C, P_{H_2} = 100 atm, τ = 3 h) (Table 1). Consequently, rhenium oxides with the perovskite structure exhibit different activities in the reactions involving the hydrogenation of the benzene ring and the carbonyl group. The hydrogenation of the latter requires more severe conditions and is more sensitive to the cationic environment of the rhenium oxides.[64]

2. Selective hydrogenation of N-containing condensed aromatic compounds

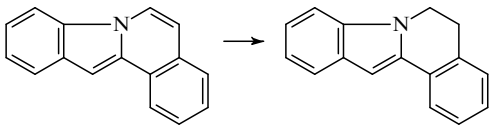
Rhenium heptasulfide exhibits a specific activity in the hydrogenation and reductive *N*-alkylation by C_1–C_4 alcohols of pyridine, picoline, and lutidines.[68–71] It is an effective catalyst of the selective hydrogenation of aryl-substituted pyridines, isoquinolines, indeno[2,1*a*]pyridines, benzo- and dibenzo-indolizines (the reaction does not involve the benzene ring), and dihydroxyanthracenes. In the presence of alcohols, *N*-alkylation takes place on Re_2S_7 simultaneously with hydrogenation. The results have been surveyed in a review.[72]

New compounds, which are of interest from the standpoint of their biological activity, have been obtained by the hydrogenation of compounds of the indolizine series[73] on Re_2S_7 (T = 250 °C, P_{H_2} = 140 atm, τ = 4 h). The following compounds were obtained: 2,8-diphenylperhydroindolizine from 2,8-diphenylindolizine, 1,2,3,4-tetrahydrobenzoindolizine and 1,2,3,4,4a,5-hexahydrobenzo[2,3]indolizine from benzo[2,3]indolizine, 5,6-dihydrobenzo[2,3;5,6]indolizine and 5,6,6a,7-tetrahydrodibenzo[2,3;5,6]indolizine from dibenzo[2,3;5,6]indolizine, 5,6-dihydrodibenzo[2,3;7,8]indolizine and 1-benzylidene-1,2-dihydroisoquinoline from dibenzo[2,3;7,8]indolizine, 4-(4-aminophenyl)-6-ethyl-2,3-dimethylpyridine and 4-(4-aminophenyl)-6-ethyl-2,3-dimethylpiperidine from 6-ethyl-2,3-dimethyl-4-(4-nitrophenyl)pyridine, and 1,2-dihydro-, 1,4-dihydro-, and 1,2,3,4-tetrahydroisoquinolines from 1-benzylisoquinoline.

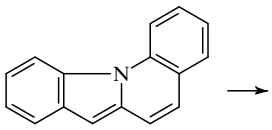
The following reactions merit special attention:



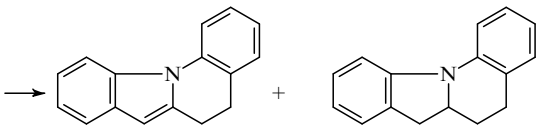
2,8-diphenylindolizine — 2,8-diphenylperhydroindolizine (yield 71%)



dibenzo[2,3;7,8]indolizine — 5,6-dihydrodibenzo[2,3;7,8]-indolizine (yield 90%)



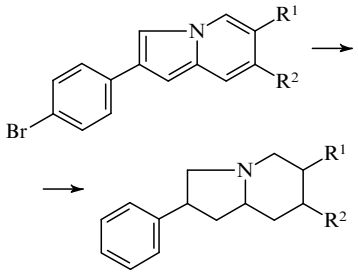
dibenzo[2,3;5,6]indolizine



5,6-dihydrodibenzo-[2,3;7,8]indolizine (yield 40%) — 5,6,6a,7-tetrahydro-dibenzo[2,3;5,6]-indolizine (yield 16%)

The pyridine ring in benzoindolizines is hydrogenated more readily than the pyrrole ring. The presence of phenyl substituents in the indolizine does not prevent its complete reduction, while alkyl substituents hinder the hydrogenation reaction. The annelation of the pyrrole and pyridine rings of indolizine diminishes the degree of its hydrogenation. The nitro-group is reduced to the amino-group.

The hydrogenation of bromo-substituted 6- and 7-alkyl-2-(4′-bromophenyl)indolizines in the presence of Re_2S_7 has also been investigated.[74]

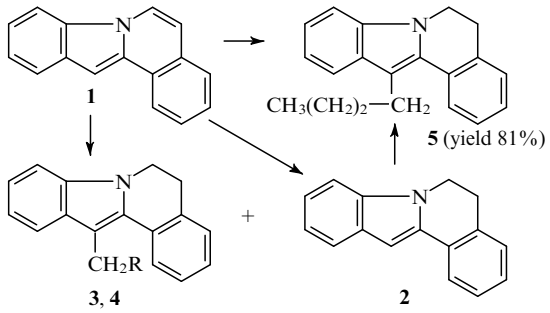


R^1 = Et, R^2 = H; R^1 = H, R^2 = Me; R^1 = H, R^2 = Et; R^1 = H, R^2 = Pr; R^1 = H, R^2 = C_5H_{11}.

Under the conditions selected (T = 260 °C, P_{H_2} = 140 atm, τ = 4 h), a mixture of *trans*- and *cis*-isomers, with respect to the fusion between the pyrrolidine and piperidine rings, of bromine-free 6- and 7-alkyl-2-phenylindolizines is formed. The 6- and 7-alkyl-2-phenylindolizines isolated are characterised by a *trans*-fusion involving the pyridine ring in the 'chair' conformation and

the pyrrolidine ring in the 'envelope' conformation. The nitrogen atom is located outside the plane passing through the four carbon atoms of the pyrrolidine ring. The ratio of the *cis*- and *trans*-isomers of the compounds obtained is 1 : 1.4.

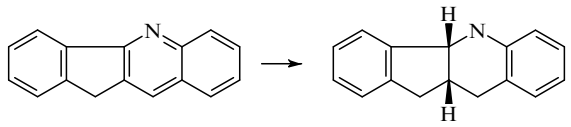
The hydrogenation of indolo[2,1-*a*]isoquinoline **1** in protic solvents (alcohols) has been achieved in the presence of Re_2S_7 (T = 250 °C, P_{H_2} = 140 atm, τ = 4 h).[75] The *N*-alkylation of the initial compound observed previously [72] is ruled out owing to the presence in the molecule of a bridgehead nitrogen atom. Alkylation at the C_{11} atom takes place instead:[75]



R = H (**3**), CH_3 (**4**).

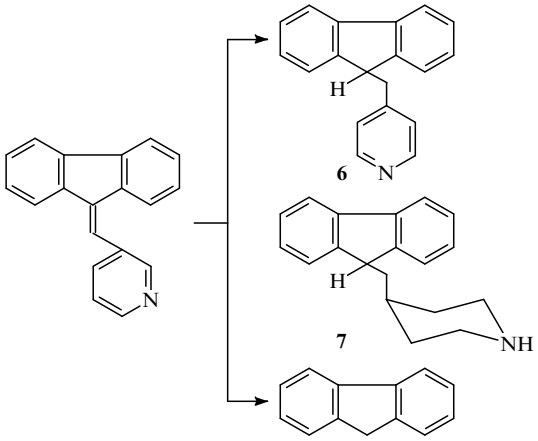
Methanol, ethanol, 1-butanol, and isopropyl alcohol were used as the alkylating agents. A mixture of compounds **2**, **3**, and **4** is formed in the first two instances in a high overall yield. The hydrogenation in 1-butanol leads to the formation of only the 11-butyl derivative **5** in 81% yield. If the dihydro-derivative **2** is subjected to reductive alkylation by 1-butanol, it is converted into 11-n-butyl-5,6-dihydroindoloisoquinoline **5** in a high yield. In the presence of Re_2S_7, the isoquinoline **1** is initially hydrogenated under the conditions indicated above to dihydroisoquinoline **2**, which is subsequently alkylated with formation of the 11-alkyl derivatives of compound **5**. The alkylation proceeds *via* an electronic substitution mechanism, the yield of products increasing with decrease in the acidity of the alcohol.

5,5a,10a,11-Tetrahydro-10*H*-indeno[1,2-*b*]quinoline has been obtained by the hydrogenation of 10*H*-indeno[1,2-*b*]quinoline (T = 250 °C, P_{H_2} = 140 atm, τ = 4 h) in benzene in the presence of Re_2S_7. Its structure was confirmed by mass-spectrometric and IR spectroscopic data, electronic absorption spectra, and ^{13}C and ^1H NMR spectra:[76]



The *cis*-fusion between the indane and tetrahydroquinoline fragments as well as the axial orientation of the proton at the C(5a) atom and the equatorial orientation of the proton at the C(10a) atom have been confirmed by molecular mechanical methods using the PC MODEL program.

The possibility of hydrogenating an exocyclic double bond of the fulvene type on Re_2S_7 has been investigated in relation to 9-(4-pyridylmethylene)fluorene, 9-(4-pyridylmethylene)-4-azafluorene, and 9-benzylidene-4-azafluorene.[77] The hydrogenation of 1-fulvene (T = 250 °C, P_{H_2} = 130 atm, τ = 4 h) proceeds to the extent of 90%. Three compounds — 9-(4-pyridylmethyl)fluorene **6**, 9-(4-piperidinylmethyl)fluorene **7**, and fluorene (the hydrogenolysis product) — were isolated from the products in 33%, 16%, and 10% yields respectively. The hydrogenation involves preferentially the exocyclic double bond of the fulvene fragment with formation of 9-azafluorenyl(pyridyl)methanes.



IV. Catalytic properties of rhenium and its compounds on supports

1. Hydrogenation of benzene and ethyl acetate

The dependence of the properties of supported rhenium-containing catalysts on the nature of the support (α-, θ-, and γ-Al_2O_3, SiO_2, $Al_2O_3 \cdot SiO_2$, MgO), the concentration of the metal (0.3 mass %, 0.4 mass %, 2.0 mass %, and 3.7 mass %) and the nature of the initial rhenium compounds [$HReO_4$, NH_4ReO_4, $KReO_4$, and $Ba(ReO_4)_2$] has been investigated.[78] The degree of dispersion of rhenium, measured by the hydrogen thermal desorption method, was compared with the activities of the supported catalyst in the hydrogenation of benzene (flow system, T = 200 °C, P_{H_2} = 27.3 atm, $P_{C_6H_6}$ = 2.7 atm). Before the start of the experiments, the catalysts were reduced in a stream of purified hydrogen (500 °C, space velocity v_{vol} = 15 000 h^{-1}, τ = 4 h). High-temperature reversible chemisorption of H_2 was observed on the fresh samples. Its overall extent depended on the nature of the support and the concentration and nature of the initial rhenium compounds taken for the preparation of the catalysts. The reversible chemisorption occurred only after the attainment of high degrees of reduction of rhenium. On the other hand, if rhenium was not fully converted into the metallic state, hydrogen was absorbed at temperatures corresponding to the additional reduction temperature. The degree of chemisorption was independent of the specific surface of the support: the maximum chemisorption was observed on Re/MgO (S = 94 $m^2\ g^{-1}$) and the minimum chemisorption was noted on $Re/Al_2O_3 \cdot SiO_2$ (S = 370 $m^2\ g^{-1}$). When the support was impregnated with perrhenic acid, the maximum chemisorption of H_2 was observed on silica gel and the minimum occurred on γ-Al_2O_3. On γ-Al_2O_3, the maximum chemisorption of hydrogen was attained when NH_4ReO_4 was employed, whereas on SiO_2 the minimum chemisorption was observed on the sample impregnated with $KReO_4$. The chemisorption on the catalyst obtained by impregnating aluminium oxide with a solution of the salt NH_4ReO_4 appreciably increased with increase in the concentration of rhenium from 0.3 mass % – 0.4 mass % to 2.0 mass % – 3.7 mass %, while its further increase to 7% was accompanied by a less significant rise in chemisorption. The activity of the reduced rhenium depended on the strength of bonding of the chemisorbed hydrogen and was not correlated with the specific surface of the metal. Two regions of the thermal desorption of hydrogen were observed: at 70 – 400 °C (form I) and at 500 – 800 °C (form II). In order to estimate the degree of dispersion of rhenium, it is useful to employ the quantities characterising the desorption of form I.

The activities of the $Re/\gamma\text{-}Al_2O_3$ catalysts containing 10.4 mass % and 1.04 mass % of rhenium, subjected to a preliminary treatment with hydrogen at 550–800 °C (hydrogenation of benzene) or at 80–300 °C (hydrogenolysis of benzene) did not change or decrease with decrease in temperature.[79] A low concentration and high degree of dispersion of rhenium are unfavourable for both reactions, particularly for the hydrogenation of benzene. The activity of the low-percentage catalyst with an average rhenium particle size $l = 1.7–2.6$ nm was several times lower in both reactions than the activity of the high-percentage catalyst with $l = 3.4–4.4$ nm and rhenium powder with $l = 166$ nm.[80] The activity of the high-percentage catalysts in the hydrogenation reaction did not change when the average particle size was increased from 3.4 to 4.4 nm. The results obtained indicate a low activity of very small metallic particles and the presence of highly specific active centres for the hydrogenolysis of benzene. The negative influence of the decrease in the particle size of the metal on its activity in the hydrogenation of benzene has also been observed on palladium,[81] ruthenium,[82] rhodium,[83] and nickel.[84, 85] This may be associated with the enhancement of the role of the hydrogenolysis of the hydrocarbons.[86]

The catalytic properties of the 5% $Re/\gamma\text{-}Al_2O_3$ system have been investigated in relation to the model ethyl acetate hydrogenation reaction.[87] The principal reaction product is ethanol, while diethyl ether, hydrocarbons, and water are formed as side products. A change in temperature from 190 to 250 °C, in the hydrogen pressure from 5 to 60 atm, and in the H_2 : EA molar ratio from 5 to 20 in the flow system after the catalyst had worked for 40 h did not affect its stationary activity. An increase in temperature from 250 to 270 °C did not entail an increase in the degree of conversion of ethyl acetate. The maximum degree of conversion of ethyl acetate into ethanol at 250 °C reached 40.9% for a diethyl ether content of 5.3%. It was shown that hydrocarbons are the products of the hydrogenolysis and not the dehydration of ethanol. Diethyl ether is formed from ethanol at a lower rate than from ethyl acetate. Under optimum conditions ($T = 230$ °C, $P_{H_2} = 60$ atm, H_2 : EA = 5, and $v_{mass} = 0.7\ h^{-1}$), the degree of conversion of ethyl acetate into ethanol is 49%, while the selectivity is 83.5%.

The nature of the support (θ-, δ-. and $\alpha\text{-}Al_2O_3$ or SiO_2) and the reduction conditions (reduction by the H_2 + EA mixture at 230 °C or by hydrogen at 500 °C) influence the hydrogenating properties of the supported rhenium catalyst in the conversion of ethyl acetate into ethanol[88] at 230 °C, $P_{H_2} = 30$ atm H_2 : EA = 5, and $v_{mass} = 0.7\ h^{-1}$. The following activity series was obtained: $Re/\theta\text{-}Al_2O_3 > Re/\alpha\text{-}Al_2O_3 > Re/\delta\text{-}Al_2O_3 > Re/SiO_2 \approx Re/\gamma\text{-}Al_2O_3$. The first catalyst of this series was three times more active than the last. Regardless of the reduction procedure, the maximum selectivity in the hydrogenation of ethyl acetate to ethanol is attained on the $Re/\alpha\text{-}Al_2O_3$ sample. Diethyl ether is formed in measurable amounts only on the $Re/\gamma\text{-}Al_2O_3$ and $Re/\theta\text{-}Al_2O_3$ catalysts. Its formation is appreciably promoted by treatment with hydrogen. On $Re/\gamma\text{-}Al_2O_3$, the yield of diethyl ether is 1.5 times greater than that of ethanol. After preliminary treatment with the H_2 + EA mixture at 230 °C, $C_1–C_4$ hydrocarbons are formed on all the catalysts (the maximum and minimum yields are on $Re/\gamma\text{-}Al_2O_3$ and $Re/\alpha\text{-}Al_2O_3$ respectively). Preliminary treatment with hydrogen at 500 °C induces a sharp decrease in the degree of conversion of ethyl acetate into hydrocarbons on the $Re/\gamma\text{-}Al_2O_3$ and $Re/\theta\text{-}Al_2O_3$ catalysts. On the remaining samples, the yield of hydrocarbons as well as the selectivity in their formation change insignificantly. Rhenium(-VII), supported on SiO_2 and $\theta\text{-}Al_2O_3$ (but not on $\gamma\text{-}Al_2O_3$), is fully reduced by hydrogen at 500 °C. The degree of dispersion of the metal diminishes in the sequence $Re/\gamma\text{-}Al_2O_3 > Re/\theta\text{-}Al_2O_3 > Re/SiO_2$. The temperature of the maximum desorption of hydrogen (200–300 °C), which can participate in the hydrogenation process, diminishes in the same sequence.[78] The maximum activity of the $Re/\theta\text{-}Al_2O_3$ catalyst can be explained by the higher degree of dispersion of rhenium in it compared with Re/SiO_2 and the higher oxidation state of the metal compared with $Re/\gamma\text{-}Al_2O_3$. The activity of the catalyst after preliminary treatment with the reaction mixture is as a rule higher than after treatment with hydrogen. This is manifested particularly strikingly in the case of the $Re/\gamma\text{-}Al_2O_3$ catalyst, in which rhenium interacts strongly with the support. Hence it is reduced with greater difficulty.[47] The H_2 + EA mixture probably reduces the supported Re(VII) more effectively at 230 °C than pure hydrogen at 500 °C.[87] The kinetic data obtained suggest the possibility of the formation of diethyl ether directly from ethyl acetate.

Diethyl ether is formed with participation of the acid centres on the $Re/\gamma\text{-}Al_2O_3$ surface, on which C_2 hydrocarbons may also be formed to some extent. The absence of acid centres from the surfaces of the supports in the Re/SiO_2 and $Re/\alpha\text{-}Al_2O_3$ catalysts promotes the manifestation of a higher selectivity by the latter but a lower hydrogenating activity than in the case of $Re/\theta\text{-}Al_2O_3$.[88, 89]

In order to discover the relation between the catalytic properties and the state of rhenium in the specimens containing 0.5% of Re on γ-, θ-, and $\alpha\text{-}Al_2O_3$, the kinetic data for the hydrogenation of ethyl acetate ($T = 230$ °C, $P_{H_2} = 30$ atm, H_2 : EA = 5) were compared with the results of an IR spectroscopic study of the chemisorption of carbon monoxide.[90] Comparison of data obtained before and after the reaction made it possible to postulate the existence of metallic rhenium in two main states on the catalyst surface — Re_x^0 and Re_y^0, differing in the degree of dispersion, the nature of the interaction with the support, and susceptibility to saturation by coke. On Re_x^0, ethyl acetate is converted into ethanol and hydrocarbons, whilst on Re_y^0 it is converted into ethanol and diethyl ether. On the $\gamma\text{-}Al_2O_3$-based samples, the ionic form Re^{n+} is also present and on it ethyl acetate is hydrogenated solely to diethyl ether. The ratio of the different states of rhenium determines their activity and selectivity in the ethyl acetate conversion reactions. The ideas described concerning the nature of the activity of rhenium/alumina catalysts for the hydrogenation of ethyl acetate are to some extent simplified. However, the observed features may prove useful for the development of more selective rhenium catalysts for the hydrogenation of carboxylic acid esters.

The addition of basic oxides — lithium or lanthanide oxides — affects the properties of the 2% $Re/\gamma\text{-}Al_2O_3$ catalyst in the hydrogenation of ethyl acetate.[91] Such additives are known to diminish the acid functions of the support in the $Pt/\gamma\text{-}Al_2O_3$ and $Pd/\gamma\text{-}Al_2O_3$ catalysts for the dehydrogenation of alkanes and cycloalkanes.[92, 93] The addition of 1% of lithium to the rhenium/alumina catalyst suppresses the Lewis centres of the $\gamma\text{-}Al_2O_3$ support, as a result of which the selectivity in the hydrogenation of ethyl acetate increases to 78%–81% and diethyl ether is hardly formed. However, the hydrogenating activity of the catalyst and its stability diminish simultaneously (Table 2).

The introduction of between 5% and 7% of the lanthanide oxide is accompanied by an appreciable decrease in the hydrogenating activity of the rhenium/alumina catalyst, while the yield of diethyl ether falls from 10.4% to 1.7% and 0.6% respectively. The selectivity in the formation of ethanol diminishes under these conditions. The maximum hydrogenating activity and selectivity was shown by the catalyst containing 2 mass % of Re, 7 mass % of a lanthanide oxide, and 91 mass % of $\gamma\text{-}Al_2O_3$: for an overall degree of conversion of 31.2%, the activity was 81.4% in the formation of ethanol, 0.6% in the formation of diethyl ether, and 16% in the formation of hydrocarbons. The formation of hydrocarbons is apparently unrelated to the acid centres of $\gamma\text{-}Al_2O_3$.

Table 2. The influence of lithium and lanthanide oxide additives on the properties of the 2% Re/γ-Al_2O_3 catalysts in the hydrogenation of ethyl acetate (T = 230 °C, P_{H_2} = 30 atm, v_{mass} = 0.72 h^{-1}, H_2 : EA = 5, τ = 4 h).[91]

Additive	Concentration of additive		Yield of product (mass %)					Selectivity (mass %)	
	mass %	mequiv. g^{-1}	C_2H_5OH	$(C_2H_5)_2O$	C_1-C_4	coke + losses	total	C_2H_5OH	C_1-C_4
None [a]	–	–	34.6	6.0	8.7	0.4	49.7	69.8	17.5
	–	–	29.1	10.4	6.8	0.2	46.5	62.6	14.6
Li	0.5	0.72	23.1	1.6	4.7	0.3	29.7	77.8	15.6
	1.0	1.44	21.4	traces	4.5	0.4	26.3	81.4	17.1
	2.0	2.88	15.1	"	3.3	0.8	19.1	78.6	17.2
Lanthanide	5.0	0.69	24.2	1.7	5.4	0.8	32.5	75.7	16.6
oxides [b]	7.0	0.99	25.4	0.6	5.0	0.2	31.2	81.4	16.0
	14.0	1.95	15.9	traces	2.9	–	18.8	84.6	15.4

[a] Re content in catalyst 5 mass %. [b] Composition (mass %): 28 La_2O_3, 49 CeO_2, 18 Nb_2O_3, 5 Pr_2O_3.

2. Hydrogenation of halogen-containing compounds

Rhenium catalysts have come to be used recently for the hydrogenation of halogen-containing compounds. A large number of various elements have been mentioned in the patent literature as catalysts for these processes: platinum group noble metals, Group VII and VIII elements, including rhenium, and certain Group II, IV, and V elements deposited on carbon. $CHCl_3$ and CH_2Cl_2 may be obtained from carbon tetrachloride in a flow system, the overall degree of conversion of CCl_4 amounting to 80%.[94,95] A catalyst containing $\geqslant$ 15% of Cr on TiO_2 and impregnated with $\geqslant$ 1% of Pt, Pd, Rh, Ru and Os, Re, or Ir has been used for the hydrogenation of halogen-containing hydrocarbons.[96] In the presence of metallic catalysts (Re, Co, Ni, Ru, Pd, Os, Ir, or Pt on carbon), fluoro-hydrocarbons are hydrogenated.[97] In particular, CF_3CHClF and CF_3CH_2F have been obtained from CF_3CCl_2F with selectivities of 11% and 87% respectively for an overall degree of conversion of 52.9%. There are data concerning the use of rhenium for the synthesis of 4-alkyl-2-fluorocyclohexanols.[98]

3. Hydrogenation of mixtures of oxygen-containing compounds

Higher alcohols are widely used in the manufacture of lubricating oils, high-quality detergents, plasticisers, *etc*. The direct hydrogenation of the $C_{10}-C_{16}$ fraction of synthetic aliphatic acids to the corresponding alcohols at T = 325–375 °C and P_{H_2} = 300–500 atm on copper–chromium and zinc–chromium catalysts is therefore of special interest. However, the rhenium sulfide/alumina catalyst containing 1.5% of rhenium has a higher hydrogenating activity than industrial oxide catalysts.[99] At 250 °C, P_{H_2} = 250 atm, and v = 0.13 h^{-1}, the degree of conversion of the $C_{10}-C_{16}$ fraction of synthetic aliphatic acids into the corresponding higher alcohols amounted to ~ 80% even after the rhenium catalysts had been operating for 750 h. The hydrogenating capacity of oxide catalysts falls to this level already after they have been used for 60 h. Rhenium sulfide/alumina catalysts containing 5%–8% of rhenium are not only more stable but also exhibit a higher productivity than the oxide catalysts.

The results obtained using supported rhenium catalysts in the hydrogenation reactions of the products of the hydroformylation of propene,[63,100] mainly with formation of an aldehyde, merit attention. Depending on the reaction conditions, isobutyraldehyde as well as (in amounts ranging from 10% to 20%) ethers, esters, acetals, aldols, and other oxygen-containing compounds are formed as side products. The hydrogenation of butyraldehyde is usually carried out at T = 120–320 °C and P_{H_2} = 250–300 atm in the presence of catalysts containing Co, W, Ni, Zr, Mo, Cu, and other elements in the metallic, oxide, or sulfide forms. Supported nickel and cobalt catalysts developed by various foreign companies contain at least 30%–60% of the metal. The hydrogenation of the hydroformylation products does not consist merely in the reduction of the carbonyl group to a hydroxy-group but, since the reaction

$$CH_3CH_2CH_2CHO + H_2 \longrightarrow CH_3CH_2CH_2CH_2OH$$

plays the main role, effective catalysts and optimum conditions are selected primarily for this reaction. When it was carried out on the hydrogen sulfide-treated 7% Re/γ-Al_2O_3 catalyst at T = 120 °C, P_{H_2} = 300 atm, and v = 4 h^{-1}, the content of butyraldehyde in the reaction mixture gradually fell from 37% to 2.3%, while the productivity of the process was fairly high.[100] An increase in temperature to 140–160 °C made it possible to attain a high degree of hydrogenation (98.7%) and high space velocities, up to 8.0 h^{-1}. The highest productivity (3219 g $litre^{-1}$ h^{-1}) was achieved at 180 °C and v = 10.5 h^{-1}. The residual content of butyraldehyde was 0.5% and there were virtually no oxygen-containing compounds in the catalyst apart from butyl alcohol. The catalyst retained its high hydrogenating activity throughout five months. At T = 120–160 °C, P_{H_2} = 300 atm, and v = 4–5 h^{-1}, the degree of conversion of butyraldehyde into butyl alcohol remained at the level of 99%–100%.

The hydrogen sulfide-treated bimetallic catalyst (5% Ni, 1% Re)/Al_2O_3 also possesses a high activity. The introduction of rhenium into the known nickel hydrogenation catalysts makes it possible to reduce its content by a factor of 6–10.

In terms of the degree of hydrogenation of the butyl esters of synthetic C_7-C_9 aliphatic acids, the (2% Re, 7% Ln)/γ-Al_2O_3 catalyst is superior to the industrial copper–chromium catalyst GIPKh-105 (flow-type apparatus, T = 210–218 °C, v = 0.40–0.45 h^{-1}, P_{H_2} = 300 atm, rate of consumption of hydrogen 900 litre h^{-1}).[91] On the rhenium catalyst, the esters are quantitatively converted into alcohols and the degree of conversion hardly changes throughout 450 h of continuous operation. This catalyst also exhibits a higher productivity (306–427 g $litre^{-1}$ h^{-1}) than the GIPKh-105 industrial hydrogenation catalyst (210–259 g $litre^{-1}$ h^{-1}).

4. Hydrogenation of other organic compounds

The hydrogenation of compounds of the type $RCOO(CH_2)_n$-COOH to $RCOO(CH_2)_nCH_2OH$ (R = alkyl, n = 8–16)[101] and of carboxylic acids to aromatic alcohols is carried out in an autoclave in the presence of ruthenium or Re/Al_2O_3 catalysts.[102] On catalysts containing Ru, Rh, Pd, Pt, or Re deposited on cobalt, it is possible to hydrogenate carboxylic acids or esters.[103] Lactones are obtained by hydrogenating dicarboxylic acids (saturated and unsaturated) and anhydrides in the presence of a Ni catalyst, supported on zirconium oxide or carbon, to which Group VIII noble metals and rhenium have been added.[104–106] Thus γ-butyrolactone has been obtained in 84.9% yield in the hydrogenation of succinic anhydride in the presence of tetrahydrofuran on the (10% Ni, 0.9% Pd, 0.6% Re)/ZrO_2 catalyst (specific surface 98 m^2 g^{-1}) in an autoclave at P_{H_2} = 50 atm and T = 200 °C for τ = 3 h.[104–106]

Vinyloxirane is hydrogenated to 1,2-epoxybutane in the presence of a catalyst containing Pd and Re on $BaSO_4$, ZrO_2, or TiO_2.[107]

Supported Group VIII metals and various rhenium compounds [Bu_4ReO_4, $Re_2(CO)_{10}$, Bu_4NReO_4, *etc.*] are used to obtain butane-1,4-diol by hydrogenating γ-butyrolactone, maleic or succinic anhydride, or the corresponding acids.[108–111] For example, butane-1,4-diol has been obtained in 66.0% yield from the lactone in an autoclave in the presence of zeolites of the alkaline type or water on Pd/C and Bu_4NReO_4 at $T = 180$ °C and $P_{H_2} = 50$ atm for $\tau = 16$ h.[108] The reaction is carried out in a solution of NEt_3 in dimethoxyethane. In the absence of NEt_3, the yield is 43.2%. An even higher yield (72.5%) is attained in the presence of Pd/C and $Re_2(CO)_{10}$ in ethanol at $T = 180$ °C and $P_{H_2} = 100$ atm for $\tau = 16$ h.[109] Butane-1,4-diol is formed in 70.0% yield from succinic anhydride or succinic acid in the presence of Ru/C, $Re_2(CO)_{10}$, and a 3 Å zeolite or water in dimethoxyethane ($T = 160$ °C and $P_{H_2} = 100$ atm, $\tau = 16$ h). The reaction does not take place in the absence of the zeolite.[110] Butane-1,4-diol has been obtained in 88.8% yield from succinic or maleic anhydride under similar conditions on Pt/C and Bu_4NReO_4 in Me_3COH at 180 °C.[111]

Tetrahydrofuran has been obtained with a selectivity of 90%–92% by hydrogenating maleic anhydride ($T = 250$ °C, $P_{H_2} = 140$ atm) on the (Co, Pd, Re)/C catalyst.[112] On a catalyst containing rhenium, Group VIII metals, and acid components (inorganic or organic acids), deposited on a metal oxide or a zeolite, tetrahydrofuran may be obtained by hydrogenating not only maleic anhydride but also succinic anhydride or γ-butyrolactone.[113]

The synthesis of γ-butyrolactone from water and 2,3- or 2,5-dihydrofurans in the presence or absence of hydrogen on hydrogenation catalysts, including a rhenium catalyst, at an elevated temperature has been described in a patent.[114] In the hydrogenation of 2,5-dihydrofuran in the presence of water on the 6% Re/TiO_2 catalyst ($T = 154$ °C, $P_{H_2} = 120$ atm), a mixture containing 85% of butane-1,4-diol, 6% of tetrahydrofuran, 3% of γ-butyrolactone, 1% of 4-hydroxybutanol, and 5% of butanol is formed in one stage with a 100% degree of conversion.[115]

The reduction of oleic acid to octadec-9-en-1-ol (*cis*- and *trans*-isomers) has been achieved with an appreciable yield in an organic solvent on a catalyst containing Re and Sn as well as Al, Si, or Ti compounds.[116,117] The reaction was carried out in an autoclave at $T = 250$ °C and $P_{H_2} = 56$ atm.

A new bimetallic rhenium–tin catalyst for the reduction of oleic acid to octadec-9-en-1-ol in a satisfactory yield under mild conditions has been proposed.[118] The catalyst was obtained by depositing NH_4ReO_4 and $SnCl_2$ on Al_2O_3. Its activity and selectivity depended on the type of support, the nature of the initial compound, the molar ratio of the metals, and the conditions in the activation and the reaction itself.

The hydrogenation of neocarboxylic acids leads to the formation of neoalcohols. For example, the corresponding alcohol has been obtained[119] from a 30% solution of pivalic acid in dioxane in a flow system on a catalyst containing 4.8% of Re and 0.5% of Pd on carbon at $T = 230$ °C, $P_{H_2} = 300$ atm, and $v = 0.15$ h^{-1}. The selectivity of the reaction reached 97% for a degree of conversion of 100%.

The influence of metallic promoting agents (Sn, Ge, Re) and various basic additives on the properties of Pt/SiO_2 catalysts has been investigated in relation to the alkylation of sterically hindered anilines in the vapour phase with formation of mono-*N*-alkylanilines. The reaction took place with a high selectivity and activity.[120] Doubly promoted Pt/SiO_2 catalysts accelerate the reaction of *ortho*-substituted anilines with primary and secondary alcohols. This distinguishes them from the copper–chromium catalysts, which make it possible to achieve N-alkylation by primary alcohols alone. The catalyst should be capable of activating three stages: the dehydrogenation of the alcohol, the condensation of the aniline with formation of carbonyl compounds, and the hydrogenation of the resulting imine to the final product — *N*-alkylaniline. When the reaction is carried out in the vapour phase, the hydrogenation stage is the most difficult.

3,5,5-Trialkyl-3-aminomethylcyclohexylamine, used to produce urethane elastomers, may be obtained in 78.5% yield by the catalytic hydrogenation of 3,5,5-trialkyl-5-cyanocyclohexanone in methanol on the Co, Re, Mo catalyst in the liquid phase in the presence of ammonia at 120 °C and 80 atm.[121] Diethylenetriamine and piperazine are formed in proportions of 15 : 62 by weight as a result of the hydrogenation of ethylenediamine on a catalyst having the following composition (mass %): 6.2 Ni, 4.4 Re, and 1.8 B.[122] The reaction is carried out in the liquid phase at ethylenediamine and hydrogen flow rates of 10.64 and 9.82 g mol h^{-1} kg^{-1} respectively and $P_{H_2} = 36$ atm. The reaction time at 138.2 °C is 705 h and the degree of conversion of ethylenediamine is 6.60%.

The influence of rhenium on the properties of the Pd/C catalyst in the hydrogenation reactions of *o*-, *m*-, and *p*-nitrobenzoic acids in an aqueous medium at 70 °C has been investigated.[123–125] Such catalysts are resistant to poisoning by S-containing impurities in the reaction solutions.[123]

The reactivity of nitrobenzoic acid diminishes in the sequence *para* > *ortho* > *meta* on the (Pd, Re)/Al_2O_3 catalyst.[124] The presence of rhenium as well as the texture of Al_2O_3 affect the state of palladium and the activity of bimetallic catalysts containing 4.0%–4.5% of Pd and 0.9%–1.0% of Re in the hydrogenation of *m*-nitrobenzoic acid, which reacts with much greater difficulty than *o*- and *p*-nitrobenzoic acids.[125] The texture of γ-Al_2O_3 was altered by means of a hydrothermal treatment. The hydrogenation was carried out in aqueous solutions with an acid concentration of 2.4×10^{-2}–1.3×10^{-1} M at $T = 70$–90 °C, $P_{H_2} = 5$–10 atm, and a *m*-nitrobenzoic acid : Pd molar ratio of 2000. The addition of rhenium to the palladium/alumina catalyst increases the yield of *m*-aminobenzoic acid after 30 min of the reaction from 70% to 91%, while the process selectivity rises from 88% to 93%. *m*-Azoxybenzoic acid is formed as a side product. The introduction of rhenium prevents the sintering of the palladium particles, which increases the degree of dispersion of the metal.[126] The hydrothermal treatment of Al_2O_3 alters the macrostructure of the support, makes it possible to optimise the Pt/Re ratio on the surface, and increases the content of the palladium–rhenium groups, which, like the (Pd, Re)-clusters,[127] exhibit an appreciable catalytic activity. Thus the higher activity and selectivity of the bimetallic systems compared with the catalyst to which no rhenium has been added is due to the increase in the degree of dispersion and in the thermal stability of palladium. As a result of the alteration of the macrostructure of the support during the hydrothermal treatment, the Pd/Re ratio on the catalyst surface decreases from 4 : 1 to 1 : 1.

5. Dehydrogenation of hydrocarbons

The dehydrogenation of n-dodecane[128–130] and cyclohexane[131] has been achieved on supported rhenium-containing catalysts. Comparison of the activities of the 0.5% Re/Al_2O_3 and 0.5% Pt/Al_2O_3 catalysts in the dehydrogenation of n-dodecane ($T = 480$ °C, $P_{H_2} = 2.5$ atm, $v_{vol} = 50$ h^{-1}, $C_{12}H_{26} : H_2 = 8$) showed that the yield of monoalkenes is 18.6% on the former catalyst and 12.1% on the latter. The selectivities in the formation of n-monoalkenes for degrees of conversion of 23.2% and 24.8% were 80% and 49% respectively. However, as a result of contact with air after the reduction of the rhenium catalyst at 900 °C and its cooling in hydrogen to 20 °C, the yield of monoalkenes fell from 9.8% to 4.4%. It was observed that preliminary treatment with hydrogen at 700–900 °C influences the activity of the rhenium/alumina catalyst.[128,129]

A similar effect, induced by the preliminary high-temperature treatment with hydrogen (900 °C, 3 h), was observed also when the 0.25% Re/Al_2O_3 catalyst was employed. After treatment at 600 °C, the selectivity in the formation of monoalkenes fell from 91% to 84% and their yield decreased from ~ 16% to ~ 15%. A

decrease in the concentration of rhenium to 0.1% and preliminary treatment with hydrogen at temperatures ranging from 700 to 900 °C increased the dehydrogenating activity and diminished the isomerising and cracking activities and there was an increase in selectivity. The selectivity in the formation of monoalkenes on catalysts containing 0.2% and 0.5% of rhenium also increased after the preliminary heat treatment of the support (Al_2O_3) in air at 900 °C.[127]

The preliminary treatment with hydrogen of the (0.2% Re, 0.2% Pb)/Al_2O_3 bimetallic catalyst at 700–900 °C instead of the usual temperature of 500 °C also had a positive effect.[128] The yields of n-monoalkenes formed from n-dodecane were respectively 5.4% and 12.4% after treatment with hydrogen at 500 and 700–900 °C, while the productivity of the catalyst was 2.5 and 8.3 g of n-monoalkenes per gram of the catalyst per hour. The selectivity remained at a high level (93%) in both cases.

Iron has a positive effect on the dehydrogenating activity of the rhenium/alumina catalyst.[130] The catalyst obtained by depositing NH_4ReO_4 on the $Fe(NO_3)_3/Al_2O_3$ system heat-treated beforehand in air showed the highest activity in the dehydrogenation of n-decane and n-dodecane ($T = 480$ °C, $P_{H_2} = 2–2.5$ atm, $v_{vol} = 35–80$ h^{-1}, molar ratio hydrocarbon : hydrogen = 8). The degree of conversion of n-dodecane may be increased by a factor of 2.5–3 if the catalyst is subjected to a preliminary treatment with hydrogen at 500–800 °C. The activity of the resulting catalyst is higher than that of the (Pt, Re)/Al_2O_3 specimen prepared similarly and reduced with hydrogen at the normally employed temperature of 500 °C. The dependence of the activity of the catalyst on the temperature of its preliminary treatment with hydrogen in the range from 500 to 900 °C passes through a minimum in the region of 600–700 °C.

The promoting effect of iron on rhenium is manifested for low iron contents. At an iron concentration of 3 at. %, the degree of conversion of n-dodecane increases by a factor of 1.7–2.0 if the preliminary activation of the sample with hydrogen is carried out at 900 °C and not 500 °C. However, for an iron content of 5 at. % and a reduction temperature in excess of 700 °C, the promoting effect vanishes. The highest degree of conversion is attained if the rhenium content is 0.25 mass %.

Modification with iron makes it possible to reduce by 150–200 °C the temperature at which the same effectiveness in the conversion of n-alkanes is reached as on the monometallic Re/Al_2O_3 specimen. It has been suggested[128] that, in order to overcome the strong interaction between the metal, activating the C—H bond in alkanes, and the support, it is necessary to reduce the metal to the zerovalent state. The formation of the Re^0 active centres on the Al_2O_3 surface is favoured by reduction at a temperature above 700 °C and, in the case of bimetallic catalysts, by the deposition of a compound of the active metal (by impregnation with NH_4ReO_4) on the modified Fe/Al_2O_3 supports subjected to preliminary thermal oxidation.

The state of rhenium in the 0.25% Re/Al_2O_3 catalyst reduced with hydrogen at 500–900 °C has been studied by analysing the diffuse reflection IR spectra of adsorbed CO.[131] Together with ionic forms of rhenium (+1 and +4 oxidation states), a highly disperse (possibly two-dimensional) metallic phase, the electron-donating capacity of which is reduced as a result of a strong metal–support interaction, is present on the surface. The CO adsorbed in a linear form on such a metal is removed by evacuation even at 20 °C. The amount of the highly disperse metallic phase on the support surface increases monotonically with increase in the activation temperature. The activity of the catalyst in the n-dodecane dehydrogenation reaction varies in parallel with the concentration of the electron-deficient highly disperse metallic phase. On this basis, it has been concluded that the highly disperse Re^0 formed during the high-temperature treatment in a stream of hydrogen is a precursor of the catalytically active centres for the alkane dehydrogenation reaction.

The dehydrogenation of cyclohexane to benzene ($T = 350$ °C, $v = 0.5$ h^{-1}) on a rhenium catalyst in which sibunit [a granulated pyrocarbon, bulk density 0.6 g cm^{-3}, S_{sp} (with respect to N_2) = 680 m^2 g^{-1}, S_{sp} (with respect to phenol) = 230 m^2 g^{-1}] was used as the support, proceeds at a higher rate than on the catalyst obtained by depositing rhenium on γ- and θ-Al_2O_3.[132] On the catalysts containing 2% of Re supported on sibunit, γ-Al_2O_3 and θ-Al_2O_3, the overall degrees of conversion of cyclohexane into benzene were 32.4 mass %, 15.2 mass %, and 9.7 mass % respectively. The selectivity of the catalysts at 350 °C diminished in the sequence Re/θ-Al_2O_3 > Re/sibunit > Re/γ-Al_2O_3. With increase in the reaction temperature to 400 °C, the selectivities for the formation of benzene on the same three specimens were respectively 37.9%, 42.4%, and 16.8%. Evidently, the Re/sibunit catalyst is more sensitive to an increase in temperature than the catalysts on aluminium oxide. The dehydrogenating activity of the 2% Re/sibunit catalyst prepared using $HReO_4$ is higher by a factor of 1.3 than in the case where NH_4ReO_4 is employed. This has been attributed to the greater ease of the reduction of the Re(VII) formed from perrhenic acid. In contrast to the rhenium oxide catalyst, there is no strong interaction between the metal and the support in the rhenium–carbon system. The dehydrogenating activity of the catalyst is influenced by the oxidative treatment of the support with nitric and oxalic acids. After treatment with 13% nitric acid for 1 h, the selectivity of the 2% Re/sibunit catalyst ($T = 400$ °C, $v = 0.5$ h^{-1}) increased from 35.2% to 61.7%. This may be explained by a decrease in the particle size of the reduced rhenium. Preliminary addition of oxalic acid to the support has a stronger effect on the sibunit catalyst than on the θ-aluminium oxide catalyst. The selectivity in the conversion of cyclohexane into benzene on the 2% Re/sibunit catalyst for an overall degree of 40% rose from 42.2% to 51.1%, *i.e.* by a factor of 1.35, whereas on the 2% Re/θ-Al_2O_3 catalyst the increase was from 50.5% to 61.2%, *i.e.* by a factor of 1.2.

6. Reactions with participation of CO, CO_2, and H_2O

Supported rhenium-containing catalysts have been used also in the hydrogenation of CO_2 to methanol,[133] which can proceed *via* the intermediate formation of CO. The rate of hydrogenation of CO on the Re/ZrO_2 catalyst is higher than on Re/CeO_2. In order to elucidate the reaction mechanism, a study was made of the conversion of formic acid and formaldehyde in the presence of hydrogen using ^{13}C as a tracer. It was shown that the surface formaldehyde participates in the methanol formation stage.

In contrast to the Co/SiO_2 and Re/SiO_2 catalysts the combined (Co, Re)/SiO_2 catalyst is active in the hydrogenation of CO to ethanol and hydrocarbons.[134] The introduction of strontium into the bimetallic system diminishes the yield of the hydrocarbons and increases the selectivity in the formation of the alcohol from 10% to 25%. It has been demonstrated by physical methods that strontium controls the reduction of Co^{2+} to Co^0 and that the basic active centres of the catalyst contain highly disperse metallic cobalt. Rhenium promotes the reduction of Co^{2+} to Co^0. The (Co, Re, Sr)/SiO_2 catalyst was prepared by employing cobalt acetate. If $Co(NO_3)_2$ or $CoCl_2$ is used to prepare the sample, then rhenium has no modifying effect on the hydrogenation of CO to methanol.[135] The use of $CoCl_2$ has a particularly negative effect on the formation of methanol. Rhenium promotes the reduction of Co^{2+} to the metal, facilitating the hydrogen spill over.

The addition of promoting agents (Re, Ru, Ir, Rh, Pt or Os) to the Co/SiO_2 catalyst obtained from $Co_2(CO)_8$ did not alter its activity in the CO hydrogenation reaction.[136]

An attempt has been made to use rhenium catalysts for the partial oxidation of methane by the oxygen in synthesis gas ($T = 1000$ °C, $v = 100\,000$ h^{-1}), but they were rapidly deactivated as a result of the volatilisation of the metal in the form of oxides.[137] Together with other metals (Ru, Rh, Ir), rhenium has been used as the catalyst of the reaction of methane with CO_2.[138] At 777 °C, the degree of conversion of methane on the Re/γ-Al_2O_3 system reached ~ 85%. However, at lower temperatures the activity of the rhenium catalyst diminished sharply. Thus at 500 °C the degree of conversion of methane was < 5%. The

authors explained this effect by the catalytic oxidation of the metal surface.

The characteristic features of the reduction of CO_2 under the conditions of the thermoprogrammed reaction have been investigated on the 3% Re/Al_2O_3 catalyst.[139] The rate of reaction increases sharply after the reduction of the catalyst and also as a result of the interaction of CO_2 with carbon fragments on addition of 1%–2% of hydrogen. It has been suggested that formate is formed as an intermediate in this process and that hydrogen has an initiating effect. At high hydrogen concentrations in the $CO_2 + H_2$ mixture, the conversion of carbon dioxide leads to the formation of CO and CH_4. The addition of formic acid to the reaction mixture increases the rate of formation of methane. It may be that the conversion of CO_2 proceeds *via* the formation of intermediate formate fragments, bypassing the CO_2 dissociation and CO hydrogenation stages. The reduction of CO_2 includes a stage in which surface carbonates are produced.

The acceleration of the Boudouard reaction ($CO_2 + C \rightleftharpoons 2CO$) has been observed on the 3% Re/Al_2O_3 catalyst in the presence of small amounts of hydrogen,[140] where it was less pronounced than on the 8% Fe/Al_2O_3 system. In the presence of the previously coke-saturated (in the isobutane conversion reaction) 3% Re/Al_2O_3 catalyst, the conversion of CO_2 under the conditions of thermoprogrammed heating occurred only at temperatures above 640 °C and the rate of formation of CO was low. The addition of 1%–3% of hydrogen to the stream of CO_2 induced a sharp acceleration of the reaction. The rate of conversion of CO_2 increased by a factor of 25, while the coke oxidation temperature fell by 200 °C. The activation energy for the formation of CO also decreased. The maximum rate of formation of CO was attained at 800 °C, while a further increase in temperature led to a decrease in rate. Under the conditions of thermoprogrammed cooling, the rate of conversion of CO_2 at temperatures below 800 °C was significantly higher than at the analogous temperatures under heating conditions. The authors explained this effect by a heterogeneous-chain mechanism of the reduction of CO_2 by rhenium or iron during the occurrence of the Boudouard reaction. The reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

takes place at similar hydrogen and CO_2 concentrations.

It has been suggested that, when a heterogeneous-chain mechanism operates, ReHCOO is formed as an intermediate complex. Thus the higher reactivity of CO_2 compared with CO in hydrogenation reactions can be accounted for by the formation of intermediate active species in which the dissociation of the C–O bond is facilitated.[139]

Together with other additives, rhenium improves the properties of Fischer–Tropsch catalysts containing 12%–20% of cobalt.[141] Vada *et al.*[142] added 1.0 mass % of Pt or Re to the catalyst containing 8.7% of Co and 91.3% of Al_2O_3 and carried out the hydrogenation of CO on it (T = 200 °C, P_{H_2} = 5 atm, and H_2/CO = 2 or T = 220 °C, P_{H_2} = 1 atm, and H_2/CO = 7.3). The introduction of Pt or Re appreciably increased the rate of reaction referred to unit mass of cobalt. The selectivity did not change under these conditions. The increase in the rate of reaction was induced by the fact that Pt and Re facilitate the reduction of Co atoms and increase their surface concentration.

The promoting effect of rhenium on the cobalt catalyst for the Fischer–Tropsch synthesis has been investigated by diffuse reflection IR spectroscopic methods.[143] Here it was also shown that rhenium promotes the reduction of cobalt. Rhenium is initially located in the surface layer and most probably forms the tricarbonyl.

Supported rhenium-containing catalysts are also used for the conversion of hydrocarbons by reaction with steam.

In terms of activity and selectivity in the conversion reactions of hydrocarbons with water vapour at temperatures above 600 °C, the 7% $Re/\gamma\text{-}Al_2O_3$ catalyst is not inferior to the industrial nickel-containing catalyst GIAP-3.[144] The following reactions take place under these conditions:

$$\text{iso-}C_4H_{10} + 4H_2O \longrightarrow 4CO + 9H_2,$$

$$\text{iso-}C_4H_{10} + 8H_2O \longrightarrow 4CO_2 + 13H_2.$$

Later the same investigators studied the activity of the $Re/\gamma\text{-}Al_2O_3$ catalyst containing 3% and 7.5% of rhenium in the conversion of isobutane by reaction with water vapour in the presence of the CS_2 catalytic poison.[145] The process was carried out in apparatus of the flow and flow-circulation types at atmospheric pressure. On the 3% $Re/\gamma\text{-}Al_2O_3$ catalyst at T = 700 °C and v_{vol} = 1500 h^{-1} and for a steam/isobutane ratio of 12, the addition of CS_2 in amounts corresponding to sulfur contents of 4 and 30 mg per m^3 of gas reduced the overall yield of the conversion product (H_2, CO, CO_2) from 95.7 vol.% (in the absence of sulfur) to 89.3 vol % and 89.4 vol % respectively. The introduction of 300 mg m^{-3} of sulfur not only reduced the content of H_2, CO, and CO_2 in the effluent gas but also led to the appearance of hydrocarbons with a lower molecular mass than that of the initial substance, including ethene and propene. The increase in the rhenium content from 3% to 7.5% did not improve the resistance of the catalyst to poisoning by sulfur.

The $(Re, Co)/Al_2O_3$ and $(Re, Ni)/Al_2O_3$ bimetallic catalysts have also been used for the conversion of isobutane.[146] The introduction of cobalt (3%) into the 1% $Re/\gamma\text{-}Al_2O_3$ catalyst lowered and the introduction of nickel (3%) increased its activity and selectivity in the formation of H_2, CO, CO_2, and CH_4. In contrast to the 3% $Ni/\gamma\text{-}Al_2O_3$ catalyst, the bimetallic catalysts containing 1% of Re and 3% of Ni on $\gamma\text{-}Al_2O_3$ ensured the full conversion of isobutane even at 500 °C. The gas formed had a nearly equilibrium composition, whereas in the presence of the industrial catalyst GIAP-3 as well as the nickel/alumina catalyst deviations from equilibrium towards the predominance of methane were observed. With increase in temperature, the compositions of the gas obtained on all three catalysts approached one another.

7. Oxidative dehydrogenation and acetoxylation reactions

The oxidative dehydrogenation of cyclohexane and ethylbenzene on rhenium-containing oxide systems has been investigated.[147] In the absence of air and water, the 2% $Re_2O_7/\gamma\text{-}Al_2O_3$ and 2% $Re_2O_7/\theta\text{-}Al_2O_3$ catalysts exhibited a low activity: the degree of conversion of cyclohexane at 420 °C was only 0.5% and that of ethylbenzene was 4% at 500 °C. In the presence of oxygen, the effectiveness of the dehydrogenation of cyclohexane was higher by a factor of 10–30. In the oxidative dehydrogenation of ethylbenzene without the addition of water vapour, the activity of the catalysts increased by an order of magnitude. In the course of half an hour, the degree of conversion of ethylbenzene into styrene reached 52% for a selectivity of 90% and then remained constant.

The modification of binary magnesium-containing oxide systems by the addition of Re_2O_7 increases the activity of the catalyst. The optimum catalyst for the oxidative dehydrogenation of ethylbenzene proved to be the system incorporating V_2O_5 (11.2%), Re_2O_7 (1.2%), and MgO (87.6%). The degree of conversion of ethylbenzene into styrene on this sample was higher than on the binary system and some suppression of the extensive oxidation processes was achieved. In the presence of an excess of atmospheric oxygen (molar ratio styrene : oxygen = 1 : 1.5–2), the yield of styrene at 500 °C was 70% for a selectivity of 87%–88%. An increase in temperature to 540 °C led to an appreciable rise in the degree of extensive oxidation. The addition of Re_2O_7 to the V–Mg binary oxide system apparently intensifies the dehydrogenating function of the catalyst.

The gas-phase oxidative acetoxylation of propene to allyl acetate has been achieved on supported Pd and Pd, Re catalysts.[148, 149] The reaction was carried out at atmospheric pressure, 180 °C, and a rate of supply of the acid of 2 h^{-1} using the ratios $C_3H_6 : AcOH : O_2$ = 2 : 1 : 0.5. The high-silica zeolite TsVM

($SiO_2 : Al_2O_3 = 29.6$),[148] γ-Al_2O_3, and $Al_2O_3 \cdot SiO_2$ were used as supports.[149] The activities of the 1.5% Pd/TsVM and (1.5% Pd, 1.5% Re)/TsVM catalysts were 5.89×10^{-3} and 9.06×10^{-3} mol g^{-1} h^{-1} for selectivities of 81% and 83% respectively. The introduction of rhenium increased the activity by a factor of 1.5. The activity of the (Pd, Re)/zeolite catalyst was influenced by the concentration of rhenium, the order in which it was introduced, and the composition of the initial perrhenate [NH_4ReO_4, $KReO_4$, $Ba(ReO_4)_2$, or $HReO_4$]. The bimetallic catalyst with the ratio Pd : Re = 1, prepared from ammonium perrhenate, had the highest activity. The introduction of 0.5% – 0.7% of Re into the 0.7% $Pd/Al_2O_3 \cdot SiO_2$ catalyst increased its activity without altering the selectivity ($\sim$ 80%). A further increase in the rhenium concentration to 1% – 1.5% diminished the activity and selectivity of the catalyst. The higher activity of the bimetallic catalysts, obtained as a result of the introduction of rhenium after the reduction of palladium, compared with the monometallic palladium sample, may be due to the interaction of rhenium oxides with the support surface, which depends on the degree of dehydroxylation of the surface.[150]

V. Mixed rhenium-containing catalysts

1. Reactions of hydrocarbons

The principal reactions of the reforming process are dehydrogenation, aromatisation, isomerisation, and hydrogenolysis. The properties of many rhenium-containing catalysts have been investigated in relation to these reactions.

The (Pt, Re)/Al_2O_3 bimetallic catalysts, prepared by precipitation, were investigated in the propane dehydrogenation reaction.[151] The (Pt, Re)/Al_2O_3 sample proved to be less active and selective in relation to the formation of propene than (Pt, Sn)/Al_2O_3. The hydrogenolysis of n-butane on Pt/Al_2O_3 catalysts involves the formation of adsorbed carbon particles, which influence the proportions of the products obtained.[152] The centres responsible for the dissociation of the central C – C bond are poisoned preferentially. Such species are not adsorbed on the (Pt, Re)Al_2O_3 catalysts.

The (Pt, Re)/Al_2O_3 catalyst proved to be less active under n-heptane reforming conditions than (Pt, Ir)/Al_2O_3 owing to cracking, which intensifies if the reduction takes place in the presence of water.[153] In order to facilitate the aromatisation of C_6 and C_7 alkanes on the Pt, Re reforming catalyst and to increase the selectivity of this reaction, it has been recommended that platinum deposited on the L-zeolite be introduced into the catalyst.[154] The catalyst is obtained by the mechanical mixing of the standard reforming catalyst with Pt/L-zeolite.

The aromatisation of n-hexane under reforming conditions using rhenium- and platinum-containing catalysts in proportions of 1 : 1 and 2 : 1 has been investigated.[155] Hydrogen has only a weak influence on the dehydrocyclisation of hexane to benzene. With increase in pressure, the selectivity of the reaction diminishes, which intensifies the isomerisation of n-hexane. However, this has little effect on the activity of the catalyst. The deposition of coke on both catalysts diminishes with increase in pressure and the $H_2 : C_6H_{14}$ molar ratio. On the catalyst with Re : Pt = 2 : 1, the extent of the deposition of coke was much smaller than on the catalyst with the 1 : 1 composition.

The activity of (Pt, Re)/Al_2O_3 catalysts depends on the method used for their preparation (joint or successive impregnation) and on the reduction procedure (direct reduction after the deposition of the metal, heat treatment with subsequent reduction).[156] Heat treatment appreciably diminishes the metal – metal interaction, which is indicated by the results obtained in the study of the hydrogenolysis of cyclopentane. Sulfiding of the catalysts increases their activity in the n-heptane dehydrocyclisation reaction.

The dehydrocyclising capacity of the Pt/Al_2O_3 and (Pt, Re)/Al_2O_3 metal cluster catalysts has been investigated in relation to the conversion of n-heptane into toluene under conditions close to those in reforming (T = 500 °C, P_{H_2} = 12 atm).[157] Platinum – rhenium metal cluster catalysts exhibited a higher selectivity and stability than the samples obtained by impregnating aluminium oxide with an aqueous solution of the initial platinum and rhenium compounds. The carbonyl complexes were decarbonised with formation of carbon particles and CO_2. The increased activity of the catalyst was associated with the formation on their surface of highly disperse carbon particles. The metal cluster Pt, Re catalysts were more stable than the analogous Pt catalysts and the standard (Pt, Re)/Al_2O_3 reforming catalysts.

The addition of boron and tin to the Pt/Al_2O_3 and (Pt, Re)/Al_2O_3 catalysts influences the activity of the latter in the dehydrogenation of cyclohexane, the dehydroisomerisation of methylcyclopentane, and the hydrocracking of 2,3-dimethylbutane.[158]

In order to eliminate alkenes from the reforming products, they are subjected to selective hydrogenation on a catalyst containing (mass %) 0.05 – 0.15 Pt, 0.001 – 0.05 Cd and/or 0.01 – 0.1 Re, and 0.01 – 0.1 Sb on γ-Al_2O_3.[159]

Group VIII metals (Pt, Rh, and Ru) supported on $Al_2O_3 \cdot TiO_2$ exhibit a high activity in the benzene, naphthalene, and biphenyl hydrogenation reactions at 300 °C and P_{H_2} = 65 atm.[160, 161]The activity of these catalysts increases after the addition of a second metal (Ir, Re, Pd). The bimetallic catalyst exhibits an enhanced resistance to poisoning by sulfur, the source of which may be thiophene. The activity of bimetallic catalysts on the TiO_2 support increases as a result of dispersion in combination with the addition of high-valence cations, for example W^{6+}. The bimetallic catalysts have a hydrogenating activity an order of magnitude higher than the usual hydrogenation catalyst (Co, Mo)/Al_2O_3.

In the study of the selective hydrogenation of *o*-xylene on metals deposited on SiO_2 (Pd, Ir, Pt, Ru, Os, Ni) in combination with rhenium, a correlation was observed between the electronic conductivity of the metal and the selectivity of the catalyst in relation to the formation of the *cis*-product.[162] The influence of heat treatment on the reactivity and selectivity of the bimetallic catalysts was noted.

2. The influence of chlorine, sulfur, and coke on the properties of the bimetallic catalysts

Chlorine and sulfur are known to be active modifying agents for supported Pt, Re catalysts for the conversion of hydrocarbons and the reforming of petrol fractions. The promotion of the (0.3% Pt, 0.3% Re)/Al_2O_3 catalyst was investigated by temperature-programmed reduction methods (TPR), analysis of the fine structure of X-ray absorption spectra (EXAFS), X-ray absorption near-edge structure spectroscopy (XANES), the oxygen adsorption method, and IR spectroscopy of adsorbed CO.[163, 164] It was found that the presence of chlorine promotes the formation of a Re^{4+}-containing phase in the course of the preliminary treatment of the catalyst at 450 °C. This phase interacts strongly with the surface layer of Al_2O_3, which prevents the formation of the Pt – Re alloy on reduction of the species, the specific role of chlorine in the interaction of the metal with the Al_2O_3 support has also been confirmed by other results.[165] In the absence of chlorine, such interaction may be fairly intense, but, when a solution of chloroplatinic acid is deposited, the surface hydroxy-groups are replaced by chloride ions and a stable metal-supported complex is formed.

It has been confirmed by the TPR and XANES methods that the chloride present on the Al_2O_3 surface plays the main role in the formation of an alloy between Pt and Re during the reduction process.[166] The rhenium on the Al_2O_3 surface (tentatively in the form of an oxide) is mobile. In the presence of sulfur, the activity of the Pt, Re catalyst in the hydrogenation – dehydrogenation reactions falls, The irreversibly adsorbed sulfur binds the entire rhenium in the form of Re_2S and $\sim$ 10% of platinum in the form of Pt_2S. With increase in the fraction of rhenium, the undesirable sensitivity of the catalyst to sulfur increases.

Rhenium, particularly in the form of the alloy with platinum, is a very active hydrogenolysis catalyst.[167] Sulfidation may decrease the activity of this catalyst to zero, since sulfur covers the rhenium surface. The sulfur compounds of rhenium themselves are incapable of accelerating the hydrogenolysis of hydrocarbons and act merely as diluents of the platinum. The addition of sulfur increases the resistance of the platinum catalyst to deactivation, but the adsorbed sulfur is rapidly lost. The introduction of rhenium influences the selectivity of the catalytic system, because it induces modification of the active centres of platinum and promotes the retention of sulfur on the surface. The probability of effecting reactions in which large ensembles of platinum atoms participate (hydrogenolysis, dehydrocyclisation, isomerisation, and cyclisation) diminishes as the latter are reduced. However, the alloying of platinum with rhenium does not influence the initial rate of hydrogenolysis.

Small ensembles of platinum atoms, formed on dilution of platinum by sulfur compounds of rhenium, are resistant to poisoning by carbon deposits, since there is no space on the catalyst surface for a large polymeric carbon structure to grow. Such a catalyst is very stable until the adjacent Pt, Re, S moieties lose their sulfur.

The reactions of cyclohexane and n-hexane have been investigated at 297–467 °C on platinum catalysts in which the support was a rhenium foil with an overall surface area of 0.5–1.0 cm^2.[168] The surface was sulfided before the reaction and under the reaction conditions by adding thiophene to the hydrocarbon. The ReS formed is catalytically inactive and only the dehydrogenation and hydrogenation reactions occur in the system, but the catalyst becomes more resistant to deactivation.

The problems of the deactivation of the (Pt, Re)/Al_2O_3 reforming catalysts by coke and sulfur have attracted the attention of investigators, since stability is one of the most important requirements which must be met by industrial catalysts. The content of residual coke, deposited on the (Pt, Re)/Al_2O_3 catalyst during the reforming of petroleum in the temperature range 350–650 °C has been determined.[169] The residual coke was investigated by the temperature-programmed oxidation method, X-ray diffraction, IR spectroscopy, chromatograph-linked mass spectroscopy, NMR, electronic spectroscopy, EPR, and chemical analysis. After the coke had been burnt away at 400 °C, the residual deposits were characterised by a minimal H : C ratio and a maximal concentration of C=O groups. At low temperatures, the most hydrogenated and amorphous carbon particles are the first to burn. At a high temperature, the combustion is nonselective and all the deposits burn simultaneously. In the course of combustion, coke is partly oxidised and intermediate species containing the C=O and C−OH groups are formed.

The effects of coating with rhenium and sulfidation of the surface of the platinum reforming catalyst have been investigated in relation to the reactions of n-hexane and cyclohexane on platinum without a support under the conditions of ultrahigh vacuum.[170] In the absence of sulfur, the degree of cyclisation of n-hexane diminished with increase in the rhenium content. The introduction of sulfur decreased the hydrogenolysis and increased the cyclising activity. The maximum cyclising activity of the sulfided catalyst was observed when the surface was coated by a monolayer of rhenium. Similar results have also been obtained under the conditions of the reactions of cyclohexane on the surface of the bimetallic Pt, Re catalyst: after sulfidation, the contribution of hydrogenolysis diminished, while that of dehydrogenation increased. The maximum rate of hydrogenation was attained on the sulfided catalyst with the platinum coated by 0.5 of a rhenium monolayer.

A multiflow reactor, which makes it possible to determine the composition of the gas phase along the catalyst bed and the coke deposition profile, has been used to investigate the deactivation of the Pt/Al_2O_3 and (Pt, Re)/Al_2O_3 catalysts in the reforming of n-heptane.[171] At a low pressure (1.05 atm), the coke content on the Pt catalyst increased, while at a high pressure (12.25 atm) it fell. The maximum deposition of coke was observed at an intermediate pressure. Correlations were noted between the coating of the surface by coke and the formation of C_5 naphthenes and also between the changes as a function of time in the supply of the starting material, pressure, and the location of the section on which coke is deposited. The C_5 naphthenes are apparently the main source for the formation of coke deactivating the catalyst. The addition of rhenium influences the deposition of coke and the formation of C_5 naphthenes. The form of the temperature-programmed oxidation (TPO) spectrum depends on the pressure at which the coke is deposited. An increase in the overall pressure leads to identical changes in the TPO spectra on the Pt and Pt, Re catalysts. The results confirm that rhenium increases the surface concentration of hydrogen on the Pt, Re catalyst and hence diminishes its dehydrocyclising and increases its hydrocyclising capacity. A smaller amount of dialkenes with a five-membered ring is formed on the Pt, Re catalyst than on Pt/Al_2O_3 and the (Pt, Re)/Al_2O_3 catalysts are therefore less coke-saturated and are more stable.

The sensitivity of the Pt/Al_2O_3, (Pt, Re)/Al_2O_3, (Pt, Ir)Al_2O_3, (Pt, Ge)Al_2O_3, and (Pt, Sn)/Al_2O_3 reforming catalysts to poisoning by sulfur has been investigated in relation to the model cyclohexane dehydrogenation reaction.[172] The permissible sulfur content in the starting material when the reaction was carried out on the above catalyst diminished in the sequence (Pt, Ge) > (Pt, Ir) ≃ Pt ≃ (Pt, Sn) > (Pt, Re). The resistance of the catalyst to sulfur decreased in the sequence (Pt, Ge) > (Pt, Ir) ≃ (Pt, Re) > (Pt, Sn). The (Pt, Ge)Al_2O_3, bimetallic catalyst thus proved to be the most resistant to sulfur and also permitted the highest sulfur content in the starting material.

The influence of the rhenium content on the activity, stability, and the resistance to poisoning by sulfur of the (Pt, Re)/Al_2O_3 reforming catalyst has also been investigated.[173] An increase in the rhenium content in the catalysts subjected to preliminary sulfidation suppressed the dehydrocyclisation of n-heptane to toluene but facilitated the conversion of methylcyclopentane into benzene without appreciable ring opening. Another result of the increase in the rhenium content was a gradual diminution of the deactivation of the catalyst and of the accumulation of coke on the surface. However, in the presence of a high rhenium content, the catalyst became more sensitive to poisoning by sulfur. The dehydrocyclisation of n-hexane was suppressed to a greater extent compared with other hydrocarbons. The different behaviour of the catalysts with high and low rhenium contents has been explained by the synergistic activity of rhenium and sulfur.

A comparative study of the noncoke-saturated and partially coke-saturated sulfided (Pt, Re)/Al_2O_3 reforming catalysts in the isomerisation and dehydrocyclisation of hexane, heptane, and methylcyclopentane showed that sulfur promotes the removal of coke from the metal surface.[174] The amount of irreversibly chemisorbed sulfur increases in the series of catalysts Pt/Al_2O_3 < (Pt, Re)/Al_2O_3 < Re/Al_2O_3. The ensembles of platinum atoms in the (Pt, Re, S)/Al_2O_3 bimetallic catalysts are larger and have a less distorted structure than in (Pt, S)/Al_2O_3.

3. Hydrogenation of hydrocarbon mixtures

In the 1970s, increased attention was devoted to the questions of the selection of effective catalysts for the hydrogenation of aromatic hydrocarbons in kerosene fractions. The 'Unisar' process was effected on platinum catalysts.[175] The modification of platinum catalysts with rhenium makes it possible to achieve the selective hydrogenation of the most undesirable hydrocarbons present in the middle petroleum fractions, namely bicyclic aromatic hydrocarbons and polysubstituted alkylbenzenes. An advantage of the bimetallic catalyst over the platinum catalyst is also its inertness to hydrocarbons of other classes — alkanes and isoalkanes, particularly in relation to their hydrocracking.[4]

The effective hydrogen sulfide-treated (1% Pd, 1% Re)/Al_2O_3 catalyst has been developed for the two-stage hydrogenation of middle petroleum fractions.[176] The optimum conditions

($T = 250$ °C, $P_{H_2} = 20$ atm, $v = 1.0-1.5$ h^{-1}, circulation of 800–1000 litres of hydrogen per litre of starting material), under which the degree of conversion of aromatic hydrocarbons is ~ 90% and the yield of the target product is ~ 98%, were found. A similar degree of conversion of aromatic hydrocarbons on the platinum/alumina catalyst was not attained until 300 °C and a hydrogen pressure of 40 atm.

4. Reforming

The greatest advance in the field of petroleum processing has been the achievement in 1968 of the rheniforming process using bimetallic Pt, Re catalysts on an oxide support, which are more active and stable than the platinum/alumina catalyst.[19] The improvement of these catalytic systems is being continued at the present time. The application of a new method for the modification of aluminium hydroxide made it possible to deposit on the latter ultrasmall amounts of platinum (0.15%) and rhenium (0.3%).[177] This catalyst, with the ratio Re : Pt = 2 : 1 shows a satisfactory activity as well as a high selectivity, stability, and mechanical strength and is readily regenerated. Among all the known reforming catalysts, it contains the smallest amount of platinum.

The productivity of the reforming catalyst can be increased by adding a zeolite of the pentasil type.[178] The chlorinated (Pt, Re)/Al_2O_3 catalyst mixed with HZSM-5 exhibits an increased activity and stability in the formation of aromatic compounds from n-heptane. A possible reaction mechanism involves the formation of intermediate carbonium and carbene ions.

The pressure dependence of the yield of hydrogen and of the octane number (o.n.) of the reformate has been investigated on the (Pt, Re)/Al_2O_3 catalysts.[179] The yield of the processing products and hydrogen increased as the pressure increased from 12 to 25 atm. The octane numbers varied linearly with the concentration of the aromatic hydrocarbons. At a pressure of 12 atm, the hydrodealkylation of C_8 and higher aromatic hydrocarbons proceeded with formation of xylenes and higher aromatic compounds.

The conditions for the regeneration of the coke-saturated (Pt, Re)/Al_2O_3 reforming catalyst by ozone–air and O_2-NO_2 mixtures were found.[180, 181] Coke was removed by ozone at low temperatures (since ozone decomposes at high temperatures) and then by oxygen. However, ozone removes coke nonselectively, whereas oxygen removes it selectively. In the first place, it was possible to eliminate coke deposited on metallic centres of the catalyst.

A special procedure for the 'minimisation of the sulfided support' is used in the regeneration of reforming catalysts containing chloride and sulfate ions.[182] In the presence of an amount of sulfate to which a sulfur concentration in excess of 0.08%–0.1% corresponds, the rate of deactivation as a consequence of the formation of coke increases. The intensification of the coke formation process is a result, firstly, of the blocking of the Lewis acid centres of aluminium oxide by sulfate ions and, secondly, of the excessive sulfidation of the metal particles by the hydrogen sulfide formed on reduction of the sulfided catalyst by hydrogen.

The Pt, Re bimetallic reforming catalyst of type IIP-IPCL (India), exhibited a high activity, selectivity, stability, and capacity for regeneration in tests on a pilot apparatus designed to generate motor fuel.[183] The first cycle of tests was interrupted after 13 experiments owing to the deposition of sulfur. In the second cycle, the catalytic activity was lower while the deactivation was very rapid owing to the sulfurisation of the catalyst in the course of the first regeneration. A special technology, involving the removal of sulfates by hydrogen at 490–510 °C and a pressure of 5–7 atm in the presence of ethylene chloride, was therefore used for the second regeneration. After such regeneration, the catalyst recovered its initial activity and stability and retained them in the course of three cycles.

The influence of temperature and of oxygen content, steam, and hydrocarbons in the gas phase on the initial characteristics of the CB-6 and CB-8 reforming catalysts (China) with a low platinum and rhenium content has been investigated.[184, 185] A deficiency of oxygen in the liquid phase leads to the formation of coke in the partial drying and regeneration stages, which induces a decrease in catalytic activity or complete deactivation.

The study of the influence of process parameters on the hydrocracking and isomerisation of petrol fractions on (Pt, Re)/Al_2O_3 catalysts (R-62 and R-16G)[186] in a flow system has been investigated at $T = 505-525$ °C and $v = 2.7-5.4$ h^{-1}. It was established that the yield of liquid products increases with increase in the space velocity. The R-16G catalyst exhibits a high activity in the formation of gaseous products, *i.e.* in the hydrocracking reaction. This is associated with the influence of the acid centres of aluminium oxide and the use in this case of a higher pressure (27 atm) than in the process on the R-62 catalyst (12 atm). On the other hand, the R-62 catalyst exhibits a higher activity than R-16G in the dehydrogenation of naphthenes to aromatic hydrocarbons. The reforming of mixed hydrorefined petroleums has been achieved on an industrial pilot apparatus on the same catalysts [$T = 490-525$ °C, $v = 2.7-5.4$ h^{-1}, hydrogen : hydrocarbon starting material = (5–7) : 1, $P_{H_2} = 27$ atm on the R-16G catalyst and 12 atm on the R-62 catalyst].[187, 188] An increase in temperature promotes an increase in the octane number of the processing product and the formation of high-quality petrol. The greater activity of the R-62 catalyst in the dehydrogenation of naphthenes to aromatic hydrocarbons noted above can be explained by the fact that the occurrence of this structure-insensitive reaction is promoted by a lower pressure. The catalyst was not deactivated by coke, since its residence in the reactor was brief (~ 23 h). The dehydroisomerisation and dehydrocyclisation of alkenes to aromatic hydrocarbons occurred to a lesser extent. An increase in temperature and a decrease in space velocity from 0.8 to 0.37 h^{-1} intensified the deposition of coke. The repeated regeneration of the catalyst led to an increase in the pore volume and in the overall porosity.[189]

The influence of the chlorine content on the properties of fresh, coke- saturated, and regenerated samples of the (0.3% Pt, 0.3% Re)/Al_2O_3 reforming catalyst has been investigated.[190] The equilibrium chlorine content was attained by treating the catalyst with the vapour of the H_2O-HCl mixture in a stream of air or hydrogen and was determined by the H_2O : HCl molar ratio and also by the temperature of the treatment. The equilibrium chlorine content in the fresh sample was independent of the nature of the chlorine compound introduced. The amount of chlorine retained by the support, calculated per unit surface area, was the same on the fresh and regenerated specimens. The presence of coke did not alter the amount of chlorine on the surface.

(Pt, Re)/Al_2O_3 catalysts have been tested on a pilot apparatus under the conditions of hydrocracking and isomerisation of n-heptane and also under the conditions of the reforming of the petrol fraction with $T_b = 77-155$ °C.[191] Problems arising in the use of chlorinated (Pt, Re)/Al_2O_3 catalysts under industrial conditions, problems of the recovery of the H_2O : HCl balance, problems in the monitoring of sulfur, *etc.* have been examined.[192] (Pt, Re)/Al_2O_3 catalysts prepared by the joint impregnation method and containing chlorine exhibit a high activity because of the decrease in the deposition of coke on their metallic centres.[193] The stronger the interaction of the metals in such a catalyst, the smaller the degree of its deactivation by coke.

The presence of fluorine on the Al_2O_3 surface prevents the formation of the strongly bound hexachloroplatinic acid complex PtO_xCl_y.[194] Heating in an inert gas leads to the removal of chlorine and the formation of metallic platinum. Treatment with hydrogen limits the possibility of the formation of a homogeneous Pt–Re solid solution. An increase in the amount of free rhenium in the catalyst promotes the intensification of its hydrogenolysing and the weakening of its aromatising capacities.

The properties of the CB-6 catalyst (China) reduced by electrolytic hydrogen and hydrogen obtained in the reforming process have been compared.[195] Reduction by electrolytic hydrogen led to an increase in the octane number of the petrol formed as a result of reforming by a factor of 2.2 and to a slight increase in the yield. The catalyst reduced by electrolytic hydrogen also possessed a greater stability. However, reduction of (Pt, Re)/Al_2O_3 catalyst by the hydrogen, evolved in the course of the reforming of petroleums, is more economical than the reduction by electrolytic hydrogen.[196]

Sixteen kinetic models were proposed,[197] which make it possible to describe the parameters of petroleum reforming processes in the presence of the (Pt, Sn)/Al_2O_3 and (Pt, Re)/Al_2O_3 catalysts.

Analysis of the patent literature of recent years [198–228] shows that the selection of effective regenerable rhenium-containing catalysts for the reforming processes is being continued. Pt, Re, Ir catalysts deposited on Al_2O_3, SiO_2, $Al_2O_3 \cdot SiO_2$, or a zeolite have been proposed.[198–200] Tin, cadmium, germanium,[201–205] as well as titanium [205] are used as promoting agents instead of iridium. Effective bimetallic platinum–rhenium supported catalysts, activated by chlorine or fluorine, have been developed.[206–211] Low-octane petrol fractions are subjected to reforming (220–260 °C, atmospheric pressure) in the presence of 0.1 mass %–0.3 mass % of Ni, Re, Os, Rh, Ir, Ru, Co, and/or Fe deposited on an oxide support.[212] W, V, Mo, Re, Ni, Co, Cr, Mn, and noble metals (Pt or Pd) can also serve as hydrogenating and dehydrogenating components.[213] The introduction of lanthanide oxides, for example Nd_2O_3, into an aluminosilicate support containing more than 50% of SiO_2 increases the activity of the platinum–rhenium catalyst in reforming and isomerisation processes.[214]

The combination of processes makes it possible to increase the octane numbers of the reforming products. For example, the product of the conversion of the starting material on the (Pt, Re)/Al_2O_3 catalyst is passed for this purpose over the (Pt, Sn)/Al_2O_3 catalyst.[215,216] Studies associated with the regeneration of the catalysts,[217,218] an increase in their useful lifetime, the reforming technology, *etc*.[219–228] are being continued.

Much attention has been devoted to the preparation and physicochemical methods for the analysis of monometallic Pt/Al_2O_3 catalysts [229,230] and also the commonest bimetallic reforming catalysts based on Pt and Re, Pt and Sn, Pt and Ir, and Pt and Ge.[229]

The interaction of the metals in (Pt, Re)/γ-Al_2O_3 bimetallic catalysts has been investigated by the EXAFS and other spectroscopic methods.[231] The likely usefulness of the employment of various Pt, Re clusters with a definite structure in heterogeneous catalysis has been demonstrated by comparing their properties with those of the usual (Pt, Re)/Al_2O_3 bimetallic reforming catalysts.[232]

The properties of the 0.3% Pt/Al_2O_3 (EUROPT-3) and (0.3% Pt, 0.3% Re)/Al_2O_3 (EUROPT-4) catalysts have been investigated in relation to the structure-sensitive hydrogenolysis reactions of alkanes (ethane, propane, n-butane, n-hexane, 2- and 3-methylpentanes, n-octane).[233] The rate and selectivity of the hydrogenolysis depend on the conditions in the preliminary treatment of the catalyst and the residual coke content on the surface. The bimetallic catalyst is more sensitive to the preliminary treatment than Pt/Al_2O_3, since rhenium-enriched phases or pure rhenium may be formed on its surface, which entails a change in the surface ratio Pt : Re. Under the conditions of vigorous hydrogenolysis of alkenes (ethene, butadiene) at 0 and 127 °C in a flow system, the (Pt, Re)/Al_2O_3 catalyst is rapidly deactivated, in contrast to Pt/Al_2O_3.

The methods for the preparation of bimetallic reforming catalysts, the conditions in their heat treatment, the role of the support, the impregnation methods, the selection of the initial solutions, the stability of the catalysts, and other problems have been discussed.[234] Methods for the extraction of rhenium and platinum from spent reforming catalysts have been examined.[235,236]

Polymetallic (Pt, Re, Cd)/Al_2O_3 catalysts of type K-104 have been tested under the conditions of reforming of petrol fractions.[237] During the initial period, coke is formed on the metallic centres of the RG-482 catalyst.[238] On regeneration, it is removed initially from the metallic and then from the acid centres.[239]

A new trimetallic reforming catalyst, which makes it possible to increase the yield of C_5 hydrocarbons and hydrogen compared with the usual (Pt, Re)/Al_2O_3 bimetallic catalyst, has been proposed in a patent.[240] Its stability is not inferior to that of the standard industrial catalyst.

Pt/Al_2O_3 and (Pt, Re)/Al_2O_3 mono- and bi-metallic catalysts, prepared by the methods used for the synthesis of industrial reforming catalysts, have been investigated by the EXAFS method.[241–243] Under the conditions in the reforming of n-heptane, the formation of Pt–C bonds was observed in both mono- and bi-metallic systems. The deposition of carbon was investigated.[242,243] The Pt–C bond is formed at 460 °C on the monometallic catalyst, whereas on (Pt, Re)/Al_2O_3 it is formed only at low temperatures, the process being accompanied by an appreciable change in the structure of the metallic particles. Modification of platinum with rhenium increases the stability of the catalyst and prevents the deposition of well structured carbon residues.

The results indicate also the presence of a long Re–O bond (2.20 Å) in the reduced (Pt, Re)/Al_2O_3 catalysts, which does not conflict with the idea that a structure formed as a result of the insertion of Re into Al_2O_3 exists. Such a structure emerges partly onto the surface and is reduced by the carbon–hydrogen mixture.

(Pt, Re)/Al_2O_3 catalysts have also been investigated by transmission electron microscopy combined with energy dispersive X-ray analysis.[244–246] Rhenium–platinum alloy is not formed in this catalyst and there is a wide size distribution of the rhenium crystals on the support surface.[244] Two types of platinum particles have been observed: three-dimensional metallic particles and small formations containing a few atoms. Some aggregation of the platinum particles in the course of the process has been observed under the conditions of the reforming of n-octane. The interaction of rhenium with Al_2O_3 and preliminary modification of platinum influence significantly the stability and selectivity of the catalyst in reactions involving cycloalkanes and in aromatisation processes. The distribution of active elements in (Pt, Re)/Al_2O_3 catalysts has been examined.[245,246]

The TAP method (Temporal Analysis of Products — analysis of reaction products as a function of time) has been used to investigate the conversion paths of C_6 hydrocarbons on the Pt/Mg(Al)O, Pt/KL (K is an ion-exchange zeolite), and Pd/Mg(Al)O catalysts, as well as (0.3% Pt, 0.3% Re)Al_2O_3 industrial catalysts (sulfided and nonsulfided).[247] The reactions were carried out under pulsed conditions at 477 and 510 °C, a pressure of 1 atm, and a H_2 flow rate of 0.25 ml min^{-1}. The reforming products were analysed mass-spectrometrically. It was found that only benzene is formed from cyclohexane, while hex-l-ene is either dehydrocyclised or is hydrogenated to n-hexane with subsequent dehydrogenation and ring closure. The possible dehydrogenation of hexane to hexadiene with subsequent cyclisation takes place at approximately the same rate as that of the dehydrogenation of cyclohexane to benzene. Under the chosen conditions, the sulfidation of the catalyst does not exert an appreciable influence on the course of the reaction.

Under industrial conditions at high pressures, the formation of benzene from alkanes on the (Pt, Re)/Al_2O_3 catalyst proceeds *via* a two-stage mechanism.[248]

The application of the oxygen–hydrogen titration method [249] made it possible to determine the degree of dispersion of platinum with a reproducibility of ±3% and of rhenium with a reproducibility of ±5%. Previously, the reproducibility was ±5% for platinum and ±10% for rhenium.[4]

IR spectroscopic study of the adsorption of NO and CO molecules showed that a Pt – Re alloy or metallic clusters are not formed on the surfaces of reduced (Pt, Re)/Al_2O_3 catalysts with a low concentration of the metal (0.22% of Pt and 0.43% of Re).[250]

The TPR and XANES methods have been used to estimate the influence of the content of the metal and of the Re : Pt ratio on the susceptibility of rhenium in (Pt, Re)/Al_2O_3 catalysts to reduction.[251] It was found that the final oxidation state of metallic rhenium depends on both these parameters. The catalysts were investigated with laboratory bench and pilot apparatus. The degree of reduction of rhenium determines the catalytic properties of bimetallic Pt – Re systems. With increase in the Re : Pt ratio, the lifetime of the catalyst increases and this trend is maintained so long as rhenium continues to be reduced. A second rhenium phase, the appearance of which increases the reduction temperature, arises when the Re : Pt ratio exceeds 2 : 1. In the presence of a controlled sulfur content in the starting material, the catalyst with the ratio Re : Pt = 2 : 1 works twice as long as the catalyst with the ratio Re : Pt = 1 : 1.

VI. Conclusion

The behaviour of rhenium-containing catalysts in a series of organic reactions is distinguished by specificity compared with the behaviour of other transition metals. The possibility of the modification, activation, and reduction of the concentration of rhenium in the Re_2O_7/γ-Al_2O_3 catalysts used for the metathesis of unsaturated compounds and functional alkenes has been demonstrated in recent years Unsaturated organic compounds which are difficult to obtain, including chlorine- and oxygen-containing ones, may be synthesised by reactions involving higher alkenes. The use of rhenium-containing catalysts permits metathesis or joint metathesis under milder conditions than on other catalytic systems.

Rhenocene hydride, rhenium pentacarbonyl, rhenium oxides with the perovskite structure, and rhenium heptasulfide are effective catalysts of the hydrogenation of a series of organic compounds and condensed nitrogen-containing aromatic ones. Supported rhenium catalysts exhibit a higher activity than the known industrial oxide catalysts in the hydrogenation reactions of oxygen-containing compounds (carboxylic acids, aldehydes, synthetic aliphatic acid esters, *etc*.).

The studies on rhenium-containing catalysts, especially bi- and poly-metallic ones, in which rhenium is used in combination with noble and Group VIII transition metals for hydrogenation, dehydrogenation, isomerisation, disproportionation, *etc*. reactions are being continued: the methods for the preparation, activation, regeneration, modification, and analysis of the catalysts are being improved and the mechanism of their action is being investigated. The range of physicochemical research methods is being constantly expanded. However, many questions concerning the unique role of rhenium, for example in bimetallic platinum – rhenium supported catalysts, remain unelucidated or controversial.

Rhenium-containing catalysts are widely used in two industrial processes — metathesis and reforming. Nowadays more than 30% of the total number of reforming catalysts employed throughout the world consist of Pt, Re catalysts.[236]

The most promising fields of application of rhenium and its compounds as catalysts still comprise diverse organic reactions as well as reactions with participation of CO, CO_2, O_2, H_2O, and chlorine-containing compounds.

The catalytic properties of rhenium have been discovered not long ago, so the possibilities for its employment in catalysis are still far from being exhausted.

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