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The Reactions of Hydrocarbons on Membrane Catalysts

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The reactions of different classes of hydrocarbons on catalysts selectively permeable with respect to hydrogen are considered. The possibilities of membrane catalysts to increase the rate and selectivity of reactions, to obtain incomplete hydrogenation products, and to decrease the competition between the adsorption of the substance hydrogenated and hydrogen are demonstrated. The coupling of reactions on membrane catalysts whereby it is possible to achieve a reaction, which does not occur spontaneously, as a result of the decrease of the free energy of the coupled reaction when the substance common to the two reactions passes through the membrane catalyst is discussed.
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1. INTRODUCTION

Membrane catalysts differ from other heterogeneous catalysts in that they exhibit selective permeability with respect to only one reactant. The principal metals investigated as membrane catalysts are those which are to some extent permeable to hydrogen. Such metals have been used as cathodes on one surface of which hydrogen was obtained electrochemically and on the other a reaction with the hydrogen diffusing through the metal was carried out. Studies have also been made on the hydrogenation of olefins and of other reactions on a palladium membrane with gaseous hydrogen on its other side.

Even before the appearance of membrane catalysts, catalytic hydrogen redistribution processes between the molecules of the same or different substances were discovered (see Section 8). It was established that the best catalyst for such reactions is palladium, but the reason for this and also the mechanism of the redistribution of hydrogen remained obscure.

Studies on the redistribution of hydrogen in unsaturated cyclic hydrocarbons on palladium and platinum films showed (see Gryaznov's review[1]) that the process consists of a set of dehydrogenation and hydrogenation reactions. The ratios of the rates of these reactions depend on the ability of the catalyst to absorb hydrogen removed from the dehydrogenated molecules, to maintain it in an active state for hydrogenation, and to supply it to the molecules undergoing hydrogenation. This idea explains the advantages of palladium over other metals as hydrogen redistribution catalysts as well as many other experimental results.

Subsequently the reactions of hydrocarbons involving the elimination and addition of hydrogen were studied on membrane catalysts permeable with respect to hydrogen alone. This made it possible to achieve coupled reactions[2-6], occurring on different sides of the membrane catalyst, as a result of the transport through the catalyst of a substance, for example hydrogen, which is formed on one surface of the catalyst and is consumed on the other. Two reactions coupled in this way accelerate one another without mixing all the reactants involved in them, which was inevitable in coupled reactions known previously, occurring in a single reaction volume in the absence of a catalyst or on the same catalyst surface. Similar results were obtained independently[7] in the USA. In recent years new membrane catalysts and methods for the preparation on them of olefinic dienes, cyclo-olefins, and aromatic hydrocarbons were developed in the USSR[8-15].

This review surveys the journal and patent literature dealing with the reactions of hydrocarbons on membrane catalysts and with the coupling of reactions on such catalysts.

2. EFFECT OF THE HYDROGEN SORBED BY THE CATALYST ON REDUCTION REACTIONS

The catalytic activation of hydrogen dissolved in palladium was noted in a report[16] on the diffusion of hydrogen through palladium. In contact with hydrogen-saturated palladium, iron(III) salts were converted into iron(II) salts and hydrogen halides were obtained from the halogens. Certain organic compounds were reduced on palladium[17]. Granular zinc coated with palladium black and treated with hydrochloric acid to saturate the palladium with hydrogen was used for this purpose[18]. Subsequently the total hydrogenation of benzene, toluene, xylenes, and ethylbenzene was achieved on palladium black[19]. It was noted[20] that benzobicyclononene is hydrogenated to dicyclohexylmethane on palladised activated charcoal both in the presence and absence of free hydrogen.

It was shown in 1934[21] that below room temperature the hydrogen sorbed by a palladium film hydrogenates olefins faster than the hydrogen entering from the gas phase. The rate of hydrogenation of ethylene or butene under the experimental conditions[22] was not limited by the rate of hydrogen

transfer from the bulk of the palladium layer onto its surface. In the course of hydrogenation hydrogen is extracted from palladium faster than on evacuation with a high-vacuum pump. At higher temperatures the rate of hydrogenation of benzene is independent of the partial pressures of the reactants. On this basis, it was postulated that the hydrogen dissolved in palladium participates in the reaction with adsorbed benzene[23]. The constancy of the rate of hydrogenation of benzene (on raising the temperature from 120° to 220°C in the presence of a palladium catalyst deposited on silica gel[24] and from 168° to 220°C on palladium black[25]) was interpreted[25] as a consequence of phase transitions in the palladium–hydrogen system. When the palladium catalyst is saturated by hydrogen at room temperature in the course of several tens of hours, its activity with respect to the hydrogenation of benzene falls sharply. On treatment with benzene vapour, the activity of the catalyst is gradually restored, which was interpreted[26] as proof that the hydrogen-rich β-phase of the palladium–hydrogen system is catalytically inactive. The increase of the activation energy for the hydrogenation of benzene with decrease of temperature leads to the same conclusion[27]. On the basis of all these data for the hydrogenation of benzene, it was concluded[28] that pure palladium and the α-phase of the palladium–hydrogen system are catalytically active and that on formation of considerable amounts of the β-phase the activity falls sharply.

Nickel, platinum, copper, and tungsten films obtained by the condensation of their vapours in a high vacuum are inactive with respect to the hydrogenation of ethylene, but films of these metals prepared in the presence of specific amounts of hydrogen, oxygen, or nitrogen are catalytically active[29]. The promotion of Raney nickel catalysts by hydrogen was discovered[30–32] in the hydrogenation of various substances by the hydrogen retained in the catalysts. The hydrogen adsorbed by the catalyst was removed reversibly and without an appreciable decrease of the activity of the catalyst. The removal of the hydrogen dissolved in the metal was irreversible with deactivation of the catalyst, since the consumption of structural hydrogen in hydrogenation alters the composition of the active surface. The activity was restored[33] by heating Raney nickel at 300°C in hydrogen.

In contrast to Raney nickel, palladium black retains its catalytic activity and the capacity to sorb hydrogen at room temperature after the removal on hydrogenation of the hydrogen retained by it[34].

As a result of several extractions of hydrogen from Raney nickel by the substance hydrogenated, the active structure of the catalyst is completely disrupted[35]. After this, the time required to saturate the catalyst surface by hydrogen until the attainment of the reversible hydrogen potential increases sharply and the hydrogen deposited on the surface is not involved in hydrogenation. The ability of palladium to give up comparatively readily the adsorbed and dissolved hydrogen makes it one of the best catalysts for low-temperature hydrogenation. The rate of reaction increases with increase of pressure to 3 atm, despite the fact that the catalyst surface is covered by hydrogen at a pressure as low as 1.5–2 atm. At low temperatures an increase of hydrogen pressure increases the degree of involvement in the reaction of the hydrogen dissolved in palladium. To elucidate the state of the hydrogen sorbed by Raney nickel, a potentiometric method was used[36]. In the course of the hydrogenation of acetylene a constant potential of the nickel catalyst was rapidly reached and the removal of hydrogen from the catalyst continued at a high rate, which the authors[37] regarded as proof that the hydrogen dissolved in the catalyst is also involved in the reaction.

With increase of the palladium content on the surface of the carrier, there is initially a slow and then a rapid increase of the rate of hydrogenation of unsaturated compounds in solution, which was explained by the appearance[38] of palladium crystals in which hydrogen is dissolved. This is consistent with the finding that in the region of low surface coverages of the carrier by palladium the rate of hydrogenation of triple bonds is lower than that of double bonds. When the coverage of the carrier corresponds to a sharp increase of the rates of both these processes, triple bonds are hydrogenated more readily than double bonds, as on massive palladium. In the latter case the author[38] assumes that triple bonds are hydrogenated mainly by the dissolved hydrogen, while in the presence of a catalyst with a low percentage of palladium it involves adsorbed hydrogen. A similar explanation of the increase of the specific activity of palladium with respect to hydrogenation for high surface coverages of the carrier by palladium was given in an earlier study[39], where it was suggested that the formation of the palladium crystal lattice and the dissolution of hydrogen in it lead to a type of activation of hydrogen different from that on catalysts with a low percentage of palladium. Such increase of the specific catalytic activity with increase of the degree of coverage has not been observed in catalytic oxidation[40].

In view of the foregoing findings, data on the catalytic activities of palladium hydride phases are interesting, but few such results are available. When the α- and β-phases of the palladium–hydrogen system coexist, the rate of hydrogenation of ethylene and propene on palladium hydride increases according to Wicke's data[41] by a factor of two with increase of the hydrogen: palladium atomic ratio from 0.1 to 0.4. Under these conditions, the surface concentration of hydrogen is not determined by its partial pressure but by its volume concentration in palladium. The rate of hydrogenation is not limited by the diffusion of hydrogen from the bulk phase to the catalyst surface and the rate of sorption of hydrogen at -78°C by palladium powder falls by a factor of 100 on passing from pure hydrogen to an equimolar ethylene–hydrogen mixture. Data for the hydrogenation kinetics and even the results of experiments with palladium deuteride show that atomic hydrogen adds to adsorbed olefin molecules on the palladium surface in the rate-limiting stage[42].

As already mentioned, it has been concluded[28] that the formation of considerable amounts of the β-phase of the palladium–hydrogen system reduces sharply the catalytic activity for the hydrogenation of benzene. The rate of hydrogenation of propene on the palladium catalyst decreases[43] after the catalyst has been treated with hydrogen. A similar effect has been observed[44] in the hydrogenation of ethylene on nickel. On the other hand, the catalytic activity of a nickel–copper alloy increases after treatment with hydrogen. The catalytic activity of nickel–palladium alloys containing between 9.5 and 25 wt.% of palladium changes little[45] after treatment with hydrogen, while the activity of nickel films for the ethylene hydrogenation reaction decreases after treatment with hydrogen. Evidence has been obtained[46,47] for the decrease of the catalytic activity of nickel and nickel–copper films on formation of hydride phases.

Thus the activity of many metallic hydrogenation catalysts increases following the sorption by the catalyst of specific amounts of hydrogen, while the formation of hydrogen-rich phases can reduce the catalytic activity.

3. HYDROGENATION BY HYDROGEN SUPPLIED THROUGH THE MEMBRANE CATALYST

In a number of studies hydrogenation reactions were investigated on a catalyst cathode through which hydrogen, obtained electrolytically on the other surface of the same cathode, passed to the reaction zone. The hydrogenation was then achieved either electrocatalytically or by the usual catalytic procedure.

A study[48] of the electrodiffusion of hydrogen through a palladium cathode showed that the rate of permeation by hydrogen increases after the addition of substances such as pyridine, sodium arsenite, and hydrogen sulphide to the electrolyte from which hydrogen passed to the cathode. On the other hand, the addition of the same substances to the electrolyte in contact with the outlet surface of the membrane electrode decreased the rate of diffusion of hydrogen. Electrochemical reduction of pyridine to piperidine on a nickel catalyst was accelerated by the addition of mercury(II) chloride, in contrast to the usual catalysis. This was explained[48,49] by the fact that the adsorption of the poison molecules on the surface of the cathode reduces sharply its adsorption potential and facilitates the transfer of the hydrogen atoms adsorbed on the cathode to the molecules undergoing hydrogenation.

The reduction of various substances on membrane steel, palladium, and platinum foil catalysts has been studied[50] with the aid of a nickel test tube part of the lateral surface of which had been replaced by the foil. Within the tube, there was an axial platinum anode and the electrolyte. The tube was immersed in a hot solution of the substance to be hydrogenated. The tube broke up fairly rapidly in the course of the experiment and the principal results were obtained for membranes welded to the edges of a slot in a copper disc to which two glass cylinders with reflux condensers were clamped via polyethylene washers. One cylinder, fitted with a platinum anode, contained the electrolyte and the other a solution of the substance hydrogenated. One surface of the membrane was the cathode and the hydrogen evolved on it passed to the other surface, where catalytic reduction took place. However, such steel and palladium membranes too worked for only a short time owing to recrystallisation and chemical effects leading to the formation of a leak. A platinum membrane could be used much longer. Partial hydrogenation of oleic acid to stearic acid and the reduction of nitrobenzene to aniline were carried out on a platinum membrane at a rate of hydrogen transfer of 6×10^{-6} g-atom cm^{-2} min^{-1}.

Subsequently a study was made[51] of the interaction of oxygen with electrolytic hydrogen diffusing through a steel membrane. It was found that at low current densities the oxygen adsorbed on the outlet surface of the membrane reduces the rate of permeation of hydrogen and at higher current densities it increases the rate of permeation compared with experiments in which the recombining hydrogen was desorbed into a vacuum. The formation of water in the interaction between adsorbed oxygen and hydrogen diffusing through the membrane was observed only in certain experiments at the maximum experimental temperature of 180°C. When a mixture of gaseous hydrogen and oxygen was supplied to the hydrogen-saturated surface of the membrane, water was not formed. At temperatures up to 190°C molecular nitrogen did not react with the hydrogen diffusing through a steel membrane and did not affect the rate of permeation of hydrogen through it.

Cyclohexene was hydrogenated within a palladium–silver alloy tube on the outer surface of which hydrogen was obtained electrochemically[53]. The hydrogenation of ethylene in a palladium tube through the walls of which diffused hydrogen obtained by the electrolysis of a solution of alkali on the outer surface of the tube proceeds much faster at 50°C than in the absence of the supply of hydrogen through the catalyst[53,54]. The hydrogenation of acetylene is accelerated even more as a result of the diffusion of hydrogen through the walls of a palladium tube[55]. However, an increase of the rate of reaction was not observed in the hydrogenation of maleic acid[56] where hydrogen diffused through both a smooth palladium membrane and one coated with palladium black. The authors[56] noted that these results confirmed the conclusion[57] that an electron is initially supplied to the molecule being reduced and then a proton, which can migrate from solution in cathodic reduction and from palladium in the usual catalytic hydrogenation.

It was shown[58] that hydrogen atoms from the palladium membrane are not involved in chain reactions of hydrogen with chlorine and with oxygen. Subsequently[59] a palladium membrane in contact with hydrogen on one side and with an ethylene–hydrogen mixture on the other was used to investigate the steady-states of the catalyst in heterogeneous reactions. A decrease of the concentration of hydrogen in the palladium foil was observed in the hydrogenation of ethylene compared with the concentration in equilibrium with the partial pressure of hydrogen in a mixture of ethylene. These results led to the conclusion that hydrogen atoms are involved in the reaction, but ethylene is hydrogenated simultaneously also by molecular hydrogen adsorbed on palladium. The exchange of hydrogen and deuterium, the interaction of hydrogen and oxygen, and the hydrogenation of ethylene on a palladium membrane were investigated by a similar method[60,61]. These reactions have radical mechanisms. If the amount of oxygen in the mixture with hydrogen is much greater than required by stoichiometry, the steady-state concentration of atomic hydrogen on the surface of the membrane catalyst is found to be smaller by a power of ten than the equilibrium concentration. No deviations from the steady-state concentration of atomic hydrogen from the equilibrium value were observed in the course of the hydrogenation of ethylene at temperatures from 200° to 300°C. This result, which differs sharply from that obtained at much lower temperatures[22], shows that at 200°C the rate of dissociation of hydrogen molecules and of recombination of hydrogen atoms on the palladium surface is greater by a power of ten than the rate of hydrogenation, while below room temperature the rates are comparable. A method has been developed[62,63] for the investigation of the mechanism of heterogeneous catalytic reactions with the supply and removal of hydrogen through a palladium capillary. In particular, the hydrogenation of ethylene in a gradient-free system was studied on the surface of this capillary. The kinetic data obtained at 200°C are consistent with the hypothesis of the consecutive addition of hydrogen atoms to the ethylene molecule. At higher temperatures the reaction mechanism changes.

A membrane consisting of a porous partition on which the catalytically active substance is deposited has been suggested for the liquid-phase hydrogenation of organic substances[64]. Hydrogen is supplied on one side of this partition, for example a glass sinter with a layer of nickel, and on the other side the substance to be hydrogenated, for example cottonseed oil, is present. The catalyst is not mixed with the hydrogenation products and the process can be made continuous and not cyclic. Later it was noted[65] that porous membrane catalysts can be used in principle also for the dehydrogenation and oxidation of organic compounds in the liquid phase. However, porous membrane catalysts are unsuitable for gas-phase processes, since

not only hydrogen but also the substance hydrogenated or oxidised can diffuse through the pores to the second reactor zone. Moreover, one loses an important advantage of non-porous membrane catalysts, namely that the hydrogen (or oxygen) transferred through them enters the reaction zone in the active, atomic state.

A study[66] of the diffusion of oxygen through a palladium membrane showed that the oxygen supplied via the membrane increases the catalytic and electrochemical activity of the membrane, in contrast to adsorbed oxygen, which inhibits electrochemical oxidation (for example of formic acid). The diffusion through the same membrane of part of the hydrogen formed in the dehydrogenation of formic acid decreases the oxidation current. It has been established[67,68] that, in the oxidation of hydrazine on a palladium membrane, the hydrogen formed as an intermediate in the electrochemical process is sorbed. Sorption of hydrogen can occur in the dissociation of the intermediates in the oxidation of hydrazine.

To transfer atomic hydrogen through palladium and palladium alloy partitions to the substance hydrogenated, a reactor with a spiral palladium tube was employed[69]. Hydrogen was supplied within the spiral and ethylene or styrene was hydrogenated on its outer surface by the hydrogen diffusing through palladium. A tube made of palladium alloy containing 23% silver, coated on the outside by a layer of gold 0.025 mm thick, served as the catalyst for the hydrogenation of cyclohexene[70]. The gold layer prevents the diffusion of hydrogen through the membrane from the side in contact with cyclohexene vapour, while hydrogen within the tube can diffuse through the walls. It was found that the rate of hydrogenation is proportional to the olefin pressure and the square of the degree of surface coverage of the catalyst by atomic hydrogen. The isomerisation of but-1-ene and *trans*-but-2-ene was not observed at 300°C on a palladium–silver tube which had no gold coating and was permeable to hydrogen from both sides[71], while the introduction of hydrogen into the tube caused rapid isomerisation of both hydrocarbons on the outer surface of the tube. With increase of the amount of hydrogen which has diffused, the hydrogenation of the butenes to butane became the dominant process. The removal of hydrogen via the membrane catalyst led to the dehydrogenation of butane, but the catalyst lost its activity after the complete removal of hydrogen. The supply of hydrogen through the membrane catalyst restored its activity, while gaseous hydrogen did not have this effect. The authors[71] explained this by the stable adsorption of olefins on the catalyst, which prevents the adsorption of hydrogen from the gas phase. According to their data[71], the first stage in the isomerisation of olefins is the addition of a hydrogen atom to the olefin molecule, after which hydrogen is split off. The diffusion of hydrogen formed in the dissociative adsorption of olefins on a palladium–silver alloy into the bulk of the alloy reduces the surface concentration of atomic hydrogen and the catalytic activity of the alloy with respect to isomerisation. The alloy consisting of 40% of palladium and 60% of gold, which dissolves much less hydrogen, exhibits a steady activity with respect to isomerisation.

The hydrogenation of but-1-ene and cyclohexene on the gold-plated surface of a palladium–silver tube with hydrogen supplied via its walls is slower by a factor of 60–200 than the diffusion of hydrogen through the same palladium alloy (with 23% of silver) alone. The rate of hydrogenation increases with increase of the rate of diffusion of hydrogen, which was explained[72] by a change in the distribution of hydrogen concentrations in the membrane.

Experiments with a thin-walled tube made of a palladium alloy containing 25% of silver, where the vapour of the substance to be hydrogenated was supplied inside the tube and hydrogen at a pressure of 3.5 atm was on the outside, showed[73] that, despite the low surface area of the membrane catalyst (9.8 cm^2), but-1-ene is hydrogenated to the extent of 82% at a temperature as low as 50°C. At this temperature the rate of diffusion of hydrogen through the catalyst (2.5 ml min^{-1}) does not reach the rate of supply of butene (3 ml min^{-1}). It is suggested[73] that in the presence of the olefin at the outlet surface of the membrane the permeability with respect to hydrogen may be enhanced by its rapid removal from the surface by the molecules being hydrogenated. After passing butene for 10 h, no decrease of catalytic activity was observed. At 250°C olefinic and acetylenic compounds, including even di-t-butylethylene which is sterically hindered, were hydrogenated quantitatively.

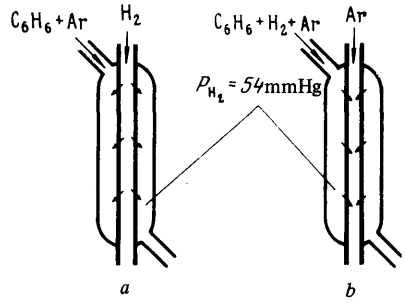


Figure 1. Schematic illustration of the supply (*a*) and removal (*b*) of hydrogen through a membrane catalyst in the course of the hydrogenation of benzene at a constant hydrogen partial pressure in the reaction zone.

The hydrogenation of benzene on the palladium alloy with 5% of nickel and the effect of the adsorption of benzene and cyclohexane vapours on the permeability of this membrane catalyst with respect to hydrogen and on its activity have been investigated[74,75]. It was established that the adsorption of cyclohexane vapour has little effect on the diffusion of hydrogen through the palladium–nickel alloy, while the adsorption of benzene vapour reduces the permeability. At a constant temperature and constant benzene and hydrogen partial pressures in the reaction zone the rates of hydrogenation are not the same for the supply and removal of hydrogen through the membrane catalyst (see the schematic arrangement in Fig. 1). This indicates the absence of equilibrium between the adsorbed hydrogen and the gas phase. The supply of hydrogen through the membrane catalyst increases the rate of hydrogenation of benzene only for a low ratio of the partial pressures of hydrogen and benzene in the reaction zone. If, on the other hand, the ratio is sufficiently high to ensure the required concentration of adsorbed hydrogen, then the supply of hydrogen via the membrane catalyst decreases the rate of hydrogenation, probably as a result of the displacement of some of the benzene molecules from the catalyst surface. The hydrogenation of benzene on the membrane catalyst leads not only to cyclohexane but also to cyclohexene, which is thermodynamically unstable under these conditions.

The high selectivity of hydrogenation on a membrane catalyst is due to the fact that the concentration of hydrogen adsorbed on its surface can be regulated by altering the hydrogen pressure on the opposite side. For this reason, membrane catalysts make it possible to obtain incomplete hydrogenation products and lead to new possibilities for reducing the competition between the adsorption of the substance hydrogenated and hydrogen, for estimating their surface concentrations, and for investigating the mechanism of reactions involving the addition of hydrogen.

4. HYDRODEALKYLATION OF BENZENE AND NAPHTHALENE HOMOLOGUES ON PALLADIUM ALLOYS

The hydrodealkylation reaction of benzene and naphthalene homologues is important not only in connection with the growing production of benzene from toluene and naphthalene derived from petroleum but also for the partial elimination of alkyl groups, for example in order to convert dimethylnaphthalenes into methylnaphthalenes. It was particularly important to elucidate the possibility of hydrodealkylation on palladium alloys suitable for use as membrane catalysts, because this is one of the few reactions involving the addition of hydrogen which is thermodynamically feasible at the temperatures of the dehydrogenation of alkanes and alkenes considered in the subsequent sections.

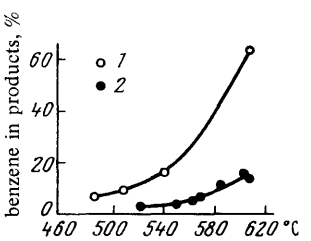


Figure 2. Variation of the benzene content in toluene hydrodealkylation products on the quenched (1) and unquenched (2) palladium–10% rhodium alloy.

It was found[76] that the rate of hydrodemethylation of toluene on the palladium alloy with 10% of rhodium increases by a factor of 6 with increase of temperature from 500° to 590°C. The activity of the catalyst can be increased by special heat treatment before the experiments, as was observed previously[77–79] for platinum films. Fig. 2 shows that after "quenching", the exposure of the palladium–rhodium alloy to a stream of hydrogen at 700°C for 20 min, and rapid cooling to the temperatures of the catalytic experiments, the rate of hydrodemethylation of toluene increases by a factor of 4 compared with the value before the heat treatment. The activity of the palladium alloy with 5.5% of nickel in relation to the hydrodemethylation of toluene proved to be lower than that of the alloy with 10% of rhodium, but after the above heat treatment of the catalyst the yield of benzene from toluene reaches 65% at 605°C.

The palladium alloy with 5% of rhenium catalyses the hydrodemethylation of toluene at a temperature as low as 320°C, but the yields are low and increase little with increase of temperature[80]. Toluene is converted into benzene to the extent of 21% at 547°C on the palladium alloy with 2% of molybdenum[81].

In a study of the effect of the substituent position in methyl- and dimethyl- naphthalenes on the rate of their hydrodemethylation binary alloys of palladium with molybdenum, rhenium, and nickel, consisting of solid solutions, were employed[82,83]. In the presence of alloys with 2.5 and 15% of molybdenum, 5% of rhenium, and 5% of nickel, the methyl groups of alkylnaphthalenes are eliminated more readily from the β-positions than from the α-positions. For example, at 527°C on the palladium–nickel alloy α-methylnaphthalene is converted into naphthalene to the extent of 29%, while the conversion of β-methylnaphthalene is 36%. Under the same conditions, the 1,6-dimethylnaphthalene conversion products were found to contain 1.5 times more α-methylnaphthalene than β-methylnaphthalene. These results are not complicated by isomerisation. In particular, the hydrodemethylation of 1,4- and 1,5-dimethylnaphthalene does not lead to the formation of β-methylnaphthalene.

The higher rate of elimination of groups in the β-positions and the absence of the isomerisation of α-methylnapthalene to β-methylnaphthalene were explained by postulating that alkylnaphthalene molecules are adsorbed via the plane of the ring on the flat sections of the catalyst surface. The carbon atoms of the methyl groups in the α-positions which deviate according to Coulson[84] from the plane of the naphthalene ring owing to the overlapping of the van der Waal's spheres of the methyl group and the hydrogen atom in the peri-position, are more remote under these conditions from the catalyst surface than the carbon atoms of the β-methyl groups in the plane of the naphthalene ring (Fig. 3).

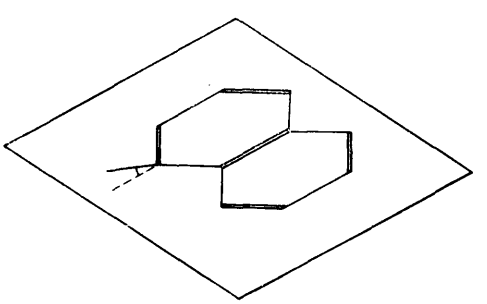


Figure 3. Schematic illustration of the adsorption of an α-methylnaphthalene molecule on a planar section of the catalyst surface.

This model suggests that the dimethylnaphthalenes in which the deviations of the methyl groups from the plane of the ring are particularly marked would be most difficult to demethylate. The available data[85] show that these deviations are maximum in 1,8-dimethylnaphthalene, the deviations of the two adjacent α- and β-methyl groups in 1,2-dimethylnaphthalene are somewhat smaller, and the deviations of the two adjacent β- and β′-methyl groups in 2,3-dimethylnaphthalene are smaller still. It has been stated[83] that the rate of hydrodemethylation should increase

in the following sequences of dimethylnaphthalenes: 1,8 < 1,2- < 2,3- < 1,4-, 1,5- < 1,3-, and 1,6- < 2,6- and 2,7-. The experimental data for the palladium alloy with 5% of nickel at 525°C are consistent with the above sequences (Table 1).

Table 1.

Dimethylnaphthalene	2,3-	1,4-	1,5-	1,6-	1,3-	2,6-
Yield of hydrodemethylation products, %	27,8	35,5	36,3	36,8	37,0	42,4

Experiments with dimethylnaphthalenes on the palladium–2% molybdenum alloy at 477°C also confirmed[81] the above reactivity series (Table 2).

Table 2.

Dimethylnaphthalene	1,8-	1,2-	2,3-	1,6-	2,6-
Yield of hydrodemethylation products, %	8	10	13	24	31

5. DEHYDROGENATION OF ALKANES AND ALKENES WITH ELIMINATION OF THE HYDROGEN FORMED THROUGH MEMBRANES

Many investigators attempted to increase the degree of dehydrogenation reactions by removing the hydrogen formed through membranes. Thin-walled platinum or palladium tubes, heated to 800°C, which were not used as dehydrogenation catalysts but merely as membranes permeable to hydrogen, were suggested for this purpose[86].

Porous partitions[87] obtained by subliming zinc from the walls of a brass tube were used as the catalytic membranes (cf. Warrick and Mack[88]). Palladium was also tested as the refractory component of the alloy; zinc was sublimed from a palladium–copper–zinc alloy. Such porous membranes were naturally not permeable to hydrogen alone and in addition they lost their permeability on contact with the vapours of hydrocarbons and other organic compounds. Porous tubes in which iron(III) and chromium oxides were deposited on the walls of the pores as well as perforated tubes where iron(III), molybdenum, aluminium, and chromium oxides were pressed into the apertures suffered from the same disadvantages[89].

Oxygen-permeable membranes have been proposed[90] to increase the degree of dehydrogenation of hydrocarbons. The reactor is divided into two zones by thin-walled silver tubes. The initial hydrocarbon is supplied to one zone filled with an alumina–chromium oxide catalyst or another dehydrogenation catalyst. The hydrogen formed on dehydrogenation is partly oxidised by the oxygen diffusing through the walls of the silver tubes from the other zone of the reactor where air is admitted. The decrease of the partial pressure of hydrogen achieved in this way in the dehydrogenation zone ensures a 20% conversion of butene into butadiene with a selectivity of 0.94 at 538°C and a pressure of 1.2 atm, whereas under the same conditions but in the absence of silver membranes dehydrogenation does not take place at all. It is noteworthy that the authors[90] failed to say anything about the diffusion of hydrogen from the dehydrogenation zone via the walls of the silver tubes, although the permeability of silver to hydrogen is greater by a factor of 3 than the permeability to oxygen. For this reason, the above effect might have been caused by the diffusion of hydrogen through the silver membranes and not of oxygen. The high selectivity, which is usually not observed in oxidative dehydrogenation, can also be explained from this point of view.

The method of preparation of hydrogen from hydrogen-containing substances[91], for example by the conversion of methane in a mixture with water vapour on a nickel catalyst at 450°C, provides for the removal of the hydrogen formed via the walls of tubes made of the palladium–25% silver alloy. The tubes are threaded through the catalyst bed in such a way that no point on the surface of the granular catalyst is further than 6 mm from the surface of the tubes. It is emphasised[91] that the tubes serve only as membranes permeable to hydrogen but do not exhibit a catalytic effect, since they cannot compete with the granular catalyst, which has a much greater surface area.

In contrast to the methods for the removal of hydrogen from the dehydrogenation zone[86–91], other workers[92,93] used foils made of binary alloys of palladium with nickel, ruthenium, rhodium, rhenium, silver, and platinum as membrane catalysts permeable to hydrogen alone. It was found[92] that, in the presence of the palladium alloy with 5.5 wt.% of nickel, isopentane is converted into isoprene and isopentenes. With increase of temperature to 558°C, the content of isoprene in the product reaches 18.6% and that of isopentenes 10.5%. On the palladium alloy with 10% of rhodium, 23.9% of isoprene and 6% of isopentenes were obtained from isopentane at 588°C. The dehydrogenation of 2-methylbut-1-ene on the palladium alloy with 5.5% of nickel at 287°C led to 81% of isoprene without side products[8]. A similar high activity and selectivity in the dehydrogenation of 2-methylbut-1-ene was shown by the palladium alloy with 10% of rhodium in the presence of which 78.7% of isoprene was obtained at 271°C.

The kinetics of the dehydrogenation of chromatographically pure 2-methylbut-1-ene, 2-methylbut-2-ene, and 3-methylbut-1-ene were investigated[93] on the palladium–5.89% nickel alloy. With increase of temperature from 340° to 400°C, the yield of isoprene from 3-methylbut-1-ene was found to be higher than for other isopentenes and to increase for a virtually constant content of the remaining isopentenes in the products. Consequently under these conditions isoprene is obtained from 3-methylbut-1-ene and not from its isomerisation products. At higher temperatures isoprene is formed mainly from 2-methylbut-2-ene produced by the isomerisation of 3-methylbut-1-ene. The dehydrogenation of pure 2-methylbut-2-ene to isoprene is complicated to a relatively small extent by isomerisation, since the change in the content of the 2-methylbut-2-ene isomerisation products is small compared with the increase in the content of isoprene when the temperature is increased. On the other hand, the isomerisation of 2-methylbut-1-ene to 2-methylbut-2-ene is much faster than dehydrogenation: the contents of 2-methylbut-2-ene and isoprene in the reaction products of 2-methylbut-1-ene and 2-methylbut-2-ene are almost the same.

A mixture of 95% of 2-methylbut-2-ene and 5% of 2-methylbut-1-ene was dehydrogenated at the Sterlitamak experimental SKI-3 synthetic rubber factory in enlarged reactors with membrane catalysts made of the same alloy[93]. At 430°C, a rate of supply of the mixture of the vapours of isopentenes and argon of 2.4 litre h^{-1}, and a partial pressure of isopentenes of 3 mmHg the yield of isoprene in the initial period of the experiment was 38.8%. The hydrogen evolved diffused through the membrane catalyst and was removed by the carrier gas. After 6 h of operation of the system, the yield of isoprene fell to 16.6%. Regeneration of the catalyst with air not only restored but also enhanced its activity. After operating for 20 h and four regenerations of the palladium–nickel foil catalyst, the maximum yield of isoprene at 430°C and a partial pressure of isopentenes of 3 mmHg was 54%.

The foregoing findings show that palladium alloy membrane catalysts exhibit a high activity and selectivity in the formation of isoprene and other dienes by dehydrogenation.

6. DEHYDROGENATION OF CYCLOHEXANE ON PALLADIUM AND PALLADIUM ALLOYS

The dehydrogenation of cyclohexane was investigated on palladium–ruthenium[94], palladium–silver[95,96], palladium–nickel and palladium–platinum[96], and palladium–tungsten and palladium–ruthenium[97] alloys, which are permeable to hydrogen alone, as well as on palladium foil[98]. Experiments[95] with a tube made of the palladium–23% silver alloy around which the required hydrogen pressure or a vacuum was established while the external surface served as the catalyst showed that the dehydrogenation of cyclohexane results in the formation of cyclohexene, the content of which increases at low hydrogen pressures in the reaction zone and at high rates of elimination of hydrogen from this zone. It is interesting that in the complete absence of hydrogen the catalyst did not show any activity in relation to the dehydrogenation of cyclohexane. The results led to the following mechanism for the dehydrogenation involving adsorbed hydrogen atoms and hydrogen atoms dissolved in the catalyst:

$$C_6H_{12} + H_{ads.} \xrightarrow{k_1} C_6H_{11}^{\cdot} + H_{ads.} + H_{soln.},$$

$$C_6H_{11}^{\cdot} + H_{ads.} \xrightarrow{k_2} C_6H_{12},$$

$$C_6H_{11}^{\cdot} \underset{k_4}{\overset{k_3}{\rightleftarrows}} C_6H_{10} + H_{ads.}.$$

Having assumed that cyclohexane molecules, the cyclohexyl radicals formed them, and cyclohexene molecules are adsorbed on the catalyst, it was found that in the steady state the concentration ratio $[C_6H_{10}]/[C_6H_{12}] = k_1k_3/k_2k_4[H_{ads}]$, i.e. is inversely proportional to the concentration of adsorbed hydrogen atoms. This is consistent with experimental data. After prolonged contact of the reaction mixture with the membrane catalyst, benzene was found in the products.

A study of the dehydrogenation of cyclohexane to benzene on palladium foil in a flow-circulation system showed[98] that the rate of reaction is described satisfactorily by the equation $w = kp^m_{C_6H_{12}}p^n_{H_2}$, where $m = 0.5$ and $n = 0.2$ at 250°C and $m = 0.6$ and $n = 0.5$ at 322°C. The fact that the p_{H_2} exponent is positive and does not exceed 0.5 under the conditions indicated suggests, in agreement with Gryaznov et al.[96], that hydrogen atoms adsorbed on the catalyst are involved in the dehydrogenation of cyclohexane. Together with hydrogen molecules, cyclohexane molecules, whose adsorption with the dissociation of one C–H bond can lead to the formation of cyclohexyl radicals, can serve as a source of hydrogen atoms. Further removal of hydrogen atoms led to the formation of species still more depleted in hydrogen until the formation of benzene molecules. Only benzene was found in the desorbed cyclohexane dehydrogenation products at temperatures below 350°C. If the rate-limiting stage is the conversion of the complex formed by a cyclohexane molecule from the gas phase and an adsorbed hydrogen atom into a hydrogen molecule and an adsorbed cyclohexyl radical and the subsequent conversion of the latter into benzene virtually corresponds to equilibrium (like the adsorption of cyclohexane molecules on hydrogen atoms), then the rate of dehydrogenation should be proportional to the degree of surface coverage of the catalyst by the complex $C_6H_{12}.H_{ads}$. Using the Langmuir equation, it is possible to obtain the following expression for the reaction rate:

$$w = \frac{k\,a\,a_{H_2}p_{C_6H_{12}}\sqrt{p_{H_2}}}{1 + a\,p_{C_6H_{12}} + a_{H_2}\sqrt{p_{H_2}}},$$

where k is the rate constant and a and a_{H_2} are the adsorption coefficients of cyclohexane and hydrogen respectively. The term including the partial pressure of benzene does not enter into the equation owing to the low degrees of dehydrogenation of cyclohexane. The linear relations between $p_{C_6H_{12}}/w$ and $p_{C_6H_{12}}$ and between $\sqrt{p_{H_2}}/w$ and $\sqrt{p_{H_2}}$ correspond to this equation. The experimental data, some of which are presented in Fig. 4, are indeed described by linear plots in terms of the above variables (Figs. 5 and 6). The kinetic equations derived on the assumption that the rate-limiting stage is the interaction of an adsorbed hydrogen atom and a cyclohexane molecule with formation of an adsorbed C_6H_{11} radical and an H_2 molecule are also consistent with the experimental data. On the other hand, if the rate-limiting stage is assumed to be, following Kiperman[99], the adsorption of cyclohexane molecule with elimination of a hydrogen atom or the interaction of an adsorbed hydrogen atom and one of the intermediates in the dehydrogenation of cyclohexane, then it follows from the resulting kinetic equations that the reaction should be inhibited by hydrogen. This has not been observed experimentally[98].

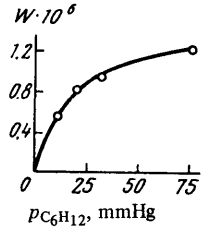


Figure 4. Variation of the rate of dehydrogenation of cyclohexane (C_6H_{12}) on palladium foil with its vapour pressure (250°C, hydrogen pressure 350 mmHg).

The catalytic activity of binary palladium alloys in relation to the dehydrogenation of cyclohexane depends in a complex manner on the nature and amount of the second alloy component[96]. Palladium alloys containing 20, 40, and 50% of silver are less active than pure palladium. The formation of the Kurnakov compounds Pd_3Ag_2 and PdAg does not

lead to an enhancement of catalytic activity. The introduction of between 0.1 and 1.5% of platinum into the palladium alloy results in an improvement of the catalytic activity of palladium at temperatures below 400°C and the palladium alloy with 5% of nickel is more active over the entire experimental temperature range than pure palladium. On the other hand, the alloy with 10% of nickel is inferior to pure palladium as regards activity. Consequently the catalytic activity of palladium–nickel alloys in the dehydrogenation of cyclohexane passes through a maximum as the nickel content in the solid solution is increased. A similar relation has been found[94] for palladium–ruthenium alloys: the most active alloy in the dehydrogenation of cyclohexane contains 8.36% of ruthenium, while those with 7.0 and 9.2% of ruthenium are somewhat less active.

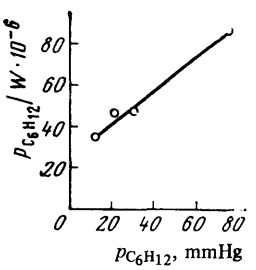


Figure 5. Variation of $p_{C_6H_{12}}/w$ with cyclohexane vapour pressure (250°C, hydrogen pressure 90 mmHg).

It has been noted that, with increase of the ruthenium content from 1 to 9%, the permeability of the palladium–ruthenium alloys to hydrogen, measured by the method of Mishchenko and Gryaznov[100], passes through a maximum for a ruthenium content of about 6%. The long-term tensile strength of this alloy at 550°C amounted to 11 kgf mm^{-2} over a period of 1000 h, [94] which is higher by a factor of almost 5 than that of pure palladium. The short-term tensile strength of deformed palladium–ruthenium alloys extended *in vacuo* increases with increase of the ruthenium content to 9% at 500° and 900°C. The above data lead to the conclusion that palladium alloys containing between 6 and 9% of ruthenium are optimal as regards catalytic activity in the dehydrogenation of cyclohexane, permeability to hydrogen, and mechanical properties. One must emphasize that, together with a high activity, the membrane catalyst must exhibit an adequate permeability to hydrogen and mechanical strength, so that thin-walled designs can be employed.

7. DEHYDROCYCLISATION OF *n*-ALKANES ON PALLADIUM ALLOYS

The dehydrocyclisation of straight-chain hexane, heptane, octane[9], and decane[82] under non-chromatographic pulse conditions was investigated on a foil made of the palladium alloy with 5.5% of nickel. At 618°C 9% of benzene was formed from hexane in a stream of hydrogen and cleavage to methane, which occurred at higher temperatures, was not observed. Heptane in a stream of argon at 587°C gave rise to 65% of aromatic hydrocarbons, including 50% toluene and 15% of benzene. The main octane dehydrocyclisation product on the same alloy proved to be *o*-xylene. *n*-Decane was converted into naphthalene to the extent of 3% at 553°C, while at higher and lower temperatures the yields of naphthalene were smaller.

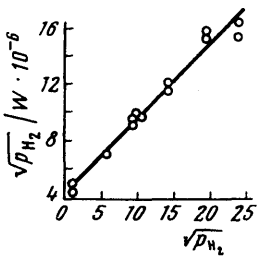


Figure 6. Variation of $\sqrt{p_{H_2}}/w$ with $\sqrt{p_{H_2}}$ at 250°C and a cyclohexane vapour pressure of 60 mmHg.

The palladium alloy with 10% of rhodium[76] showed a higher activity with respect to the dehydrocyclisation of *n*-heptane than the palladium alloy with 5.5% of nickel: 46% of toluene and 24% of benzene were obtained at 550°C on the palladium–rhodium, while on the palladium–nickel alloy under the same conditions the yields were 37% of toluene and 8% of benzene.

Palladium–rhenium alloys were tried as catalysts for the dehydrocyclisation of *n*-alkanes[101,102]. The product obtained from heptane at 625°C on the alloy containing 5% of rhenium consisted of 14% of toluene and 34% of benzene. The dehydrocyclisation of octane on the same catalyst is accompanied to an even greater extent by the hydrodealkylation of the aromatic hydrocarbon products to benzene.

The palladium alloy with 5% of ruthenium proved to be one of the most active catalysts of the dehydrocyclisation of *n*-alkanes[103]. Hexane, which, as shown by the experiments described previously, is dehydrocyclised with greater difficulty than *n*-alkanes with a higher molecular weight, gave rise to 58% of benzene at 575°C on a foil made of this alloy. In the presence of the palladium alloy containing 5% of tungsten and 1% of ruthenium, 54.7% of benzene and 2.6% of toluene were obtained from *n*-heptane at 590°C.

The high activity of palladium alloys used as hydrogen-permeable membrane dehydrocyclisation catalysts is particularly important, since alkanes widely occurring in different types of petroleum are converted by this reaction into more valuable aromatic hydrocarbons and the formation of one mole of such hydrocarbons is accompanied by the generation of four moles of hydrogen, which can be used on the other side of the same membrane catalyst for hydrodealkylation and other reactions.

8. THE COUPLING OF CATALYTIC HYDROGEN ELIMINATION AND ADDITION REACTIONS

By definition[104] coupled reactions consist of a system of two reactions occurring in the same medium the course of one of which depends on the other. A study of coupled oxidation reactions in solution showed[104] that coupling is possible only for complex processes with formation of an

intermediate which constitutes a link between the primary and secondary reactions. The conclusion reached in a monograph[104] that in coupled reactions chemical energy is transferred as such from one process to another must be regarded as even more general. We shall return to this conclusion after a brief survey of the results of studies of coupled reactions on the same surface of a heterogeneous catalyst.

The coupling of catalytic hydrogen elimination and addition reactions has been observed[105] in the hydrogenation of methyl tetrahydroterephthalate. It was found that at room temperature in the presence of palladium foil the hydrogenation process is accompanied by the dehydrogenation of part of the starting material to the terephthalate ester. The authors[105] noted that palladium black having lost its hydrogen in the hydrogenation reaction is again saturated with hydrogen from the tetrahydroterephthalate ester and not the hydrogen present in a free state. In the presence of a large amount of palladium black at room temperature the dehydrogenation of dihydronaphthalene predominates[106] over the thermodynamically unavoidable hydrogenation, since the absorption of hydrogen by palladium displaces the equilibrium. Cyclohexadiene has been converted into benzene and cyclohexene and the latter to benzene and cyclohexane on the palladised asbestos at temperatures below 130°C in a stream of carbon dioxide[107]. In these "irreversible catalytic" reactions (as defined by Zelinskii) hydrogen is not evolved, since the hydrogenation of one molecule of cyclohexene causes the hydrogenation of two other such molecules and the dehydrogenation of one cyclohexadiene molecule causes the hydrogenation of another such molecule. Similar reactions of hydrocarbons of different classes with double bonds in the rings and in side chains, with a triple bond in the side chain, and in bicyclic hydrocarbons with and without bridging groups have been investigated[108–124]. The conversion of ethylene into ethane and acetylene and of propene into propane and propyne has been observed[125] on palladium films and to a lesser extent on platinum films.

Various substances can serve as hydrogen donors and acceptors. In particular it has been stated[126] that between 240° and 260°C methylcyclohexane behaves as a donor and benzene as an acceptor of hydrogen. This pair of coupled reactions was subsequently investigated[127] on palladised silica gel. Petroleum naphthenes, which can be converted into valuable aromatic hydrocarbons, have been noted as particularly interesting hydrogen donors[126] and liquid vegetable oils have been noted as interesting hydrogen acceptors. However, this system has not been investigated and the possibility of the hydrogenation of unsaturated acids by the hydrogen obtained in the dehydrogenation of ethanol was confirmed by experiments using a nickel catalyst.

On the hypothesis that the energy required for the endothermic dehydrogenation of the hydrogen donor is provided by the exothermic hydrogenation of the hydrogen acceptor. Vesterberg and Braun[128] explained certain experimental data and calculated the ΔG°_{298} for pairs of coupled reactions: dehydrogenation of cyclohexane or methylcyclohexane–hydrogenation of maleic or fumaric acid, dehydrogenation of bibenzyl–hydrogenation of trimethylethylene. It was noted that the predominance of the maximum useful work obtained in the hydrogenation of the hydrogen acceptor over the corresponding quantity obtained in the dehydrogenation of the donor is a necessary but naturally not a sufficient condition for coupling. Another problem is to ensure a sufficient rate of the coupled reactions in the presence of the given catalyst.

The hydrodecyclisation (ring hydrogenolysis) of ethylcyclopentane coupled with the dehydrogenation of cyclohexane has been achieved[129,130] on platinised charcoal. The same hydrogen donor has been used[131] for the coupled hydrogenation of propenylbenzene to propylbenzene, of *trans*-stilbene to bibenzyl, of 1,1-diphenylethylene to 1,1-diphenylethane, etc. The use of ethylene as the acceptor of the hydrogen evolved in the dehydrogenation of n-butane on an alumina–chromium oxide catalyst increased[132] the yield of butadiene from 9.3 to 16.4%.

In all the studies described in this section the coupling of the reactions made it possible to increase their rate or selectivity. However, all the components of coupled reactions were present in the same volume and the separation of the resulting multicomponent mixtures frequently proved to be difficult and reduced the advantages of coupling.

9. THE COUPLING OF REACTIONS ON MEMBRANE CATALYSTS

It was suggested in 1964[2,3,5,11] that, in order to increase the efficiency of catalytic processes, two reactions be carried out on different sides of a partition made of a catalytically active substance or one coated by catalyst layers. Three types of coupling of catalytic reactions are then possible.

1. In the absence of the transfer of reactants through the catalyst the heat evolved in any exothermic reaction occurring on one catalyst surface can be used to carry out any endothermic reaction on the other catalyst surface. Any catalyst with adequate thermal conductivity can be used for such energy coupling of catalytic processes. Catalysts with low thermal conductivity can be deposited in the form of thin layers on the surface of a heat conducting partition.

2. When the substance formed as a result of the reaction on one catalyst surface and consumed in the reaction on the other surface is transferred through the catalyst, the thermodynamic equilibria in both reactions will be displaced and the degrees of conversion will increase. A catalyst permeable to the chosen substance alone is necessary for such thermodynamic coupling.

3. If the substance formed on one side of the catalyst and consumed on the other is transferred through the catalyst in an active, for example atomic, state, a specific (kinetic) coupling of the reactions is possible. To remove the substance from the catalyst surface where it is formed, the recombination and desorption stages are no longer required and its reaction on the other catalyst surface does not need activation.

The above types of coupling of catalytic processes can occur both separately and in combination with one another. The degree of coupling of two reactions is chosen in such a way that the steady-state process is stable. A distinctive feature of the coupling of reactions on a membrane catalyst is that the transfer of chemical energy from one process to the other[104] with minimal dissipation of energy is possible. The non-spontaneous reaction ($\Delta G_1^\circ > 0$) can be achieved as the result of the free energy of the other reaction ($\Delta G_2 < 0$), provided that $|\Delta G_2^\circ| > |\Delta G_1^\circ|$.

The use of hydrogen formed in the reaction on one side of the partition of a palladium or palladium alloy tube to carry out on the other side of the partition a reaction involving the addition of hydrogen is an example of the coupling of catalytic reactions. Thermodynamic calculations have shown[5] which hydrogen addition reactions are possible at temperatures sufficiently high for industrially important dehydrogenation reactions. In particular at 427°C (700°K)

ΔG° for the hydrodemethylation of toluene is negative and its absolute value is higher than the positive ΔG° for the dehydrogenation of butene to butadiene. Therefore thermodynamic limitations are lifted from the latter reaction when it is coupled with the hydrodemethylation of toluene.

The removal of hydrogen from the dehydrogenation of dehydrocyclisation zone via the membrane catalyst increases the equilibrium degree of conversion. At 527°C (800°K) and an overall pressure of 1 atm the equilibrium yield of butadiene from but-2-ene is 15%. If 90% of the hydrogen formed is removed from the reaction zone, the yield of butadiene increases to 38% and after the elimination of 98% of the hydrogen the equilibrium yield rises to 73%.

A palladium foil dividing the reactor in half can be used as the simplest example of a membrane catalyst. If the upper half of the reactor contains butene, the latter will be dehydrogenated to butadiene on the upper surface of the palladium foil, as shown in Fig. 7. The hydrogen formed in the dehydrogenation process dissolves in the palladium and migrates in an atomic form across the foil, whose cross-section is illustrated in Fig. 7 by a shaded band. On the lower surface of the palladium foil, atomic hydrogen can be used, for example, for the hydrodemethylation of toluene or for other hydrogen addition reactions.

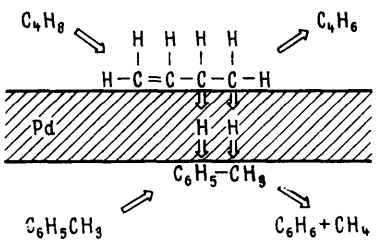


Figure 7. Schematic illustration of the coupling of butene dehydrogenation and toluene hydrodemethylation reactions on a palladium membrane catalyst.

In the general case any reaction involving the formation of hydrogen can take place on one surface of a membrane catalyst permeable to hydrogen alone:

$$A \rightarrow B + H_2 \quad , \qquad (1)$$

while on the other surface any hydrogen addition reaction can occur:

$$C + H_2 \rightarrow E \quad . \qquad (2)$$

It is of course necessary that reactions (1) and (2) should proceed at the same temperatures and pressures, since the thermal conductivity of a thin membrane is high and its strength is low. If reaction (1) is carried out separately from reaction (2), then a specific degree of surface coverage of the catalyst by hydrogen Θ_1^* is established under the specified conditions and, when reaction (2) takes place separately from reaction (1), the degree of surface coverage is Θ_2^*. The rates of these reactions can be expressed by the equation

$$w_i = k_i f_i(\mathbf{p}_j)\left[1 - \frac{\varphi_i(\mathbf{p}_j)}{K_{pi}}\right],$$

where i is the number of the reaction, j the reactant index, $\mathbf{p}_j$ the vector of the reaction mixture composition, $k_i f_i(\mathbf{p}_j)$ the rate of reaction disregarding its reversibility, $\varphi_i(\mathbf{p}_j)$ the expression of the law of mass action, and K_{pi} the equilibrium constant for the ith reaction.

If reactions (1) and (2) are carried out on a membrane catalyst, then under the same conditions the degree of surface converages of the two catalyst surfaces will be different (Θ_1 and Θ_2 respectively) owing to the transfer of hydrogen through the catalyst. The rate of transfer of hydrogen is determined by Θ_1 and Θ_2 and the coefficient β:

$$w_H = \beta(\theta_1 - \theta_2) \quad .$$

If the rate of transfer of hydrogen is higher than the rate of its formation by reaction (1), then the inequalities

$$\theta_1^* > \theta_1 > \theta_2 > \theta_2^*$$

constitute the main condition for the coupling of the reactions on a membrane catalyst permeable to hydrogen alone[133].

The three types of coupling discussed above involve (1) the maintenance of isothermal conditions owing to the transfer of heat from the exothermic hydrogen addition reaction zone to the endothermic hydrogen elimination reaction zone (energy effect), (2) an increase of the quantity $(1-\varphi_i(\mathbf{p}_j)/K_{pi})$ in consequence of changes in the equilibrium conditions (thermodynamic effect), and (3) an increase of the rate of reaction $k_i f_i(\mathbf{p}_j)$ when no account is taken of its reversibility (kinetic effect).

A mathematical model of the coupling of reactions on a membrane catalyst can be constructed taking into account three levels: (a) the molecular level including the stages of catalytic reactions; (b) the element of the membrane catalyst where catalytic reactions are combined with hydrogen and heat transfer through the catalyst; (c) the reactor with the membrane catalyst.

The first level is described by the kinetic equations for the corresponding reactions and the second level by a combination of these equations, the heat balance equation, and the equation for mass transfer through the catalyst. Analysis of these equations showed[133] that they have a steady-state solution characterising the stability of the coupling of the two reactions on the membrane catalyst.

The experimental evidence for the coupling of reactions, one of which involves the evolution and the other the addition of hydrogen, on different sides of a catalyst selectively permeable to hydrogen alone was obtained[4] in the dehydrogenation of cyclohexane within a palladium tube and in the hydrodealkylation of toluene or *o*-xylene on its outer surface by the diffusing hydrogen. Both reactions and hydrogen transfer are accelerated under the conditions of such coupling compared with the conditions where the reactions are carried out separately. The coupling of the dehydrogenation of *trans*-but-2-ene at 380°C and a pressure of 1.4 atm with the hydrogenation of benzene on the other surface of a palladium tube resulted in the formation of 6.1% of butadiene. This yield is three times higher than the equilibrium yield at the given temperature and a pressure of 1 atm without the removal of the hydrogen formed. The amount of butadiene collected from a unit geometrical surface area of the palladium membrane catalyst was 2000 times greater than for the K-16 industrial catalyst (according to Tyuryaev and Kolobikhin's data[134]).

The efficiency of the coupling of heterogeneous catalytic reactions is much higher than that of the simple removal of the hydrogen formed from the dehydrogenation zone. For example, the rate of formation of butadiene increases by a factor of five when a stream of argon onto the other side of

the membrane catalyst is replaced by a stream of a mixture of toluene vapour and argon, i.e. when the diffusing hydrogen is combined.

The use of membrane catalysts permeable to hydrogen in processes involving the evolution of hydrogen not only accelerates them but also suppresses side reactions. For example, in the dehydrogenation of isopentenes under flow conditions at 410°C on the surface of a thin-walled tube made of 94.5% palladium–5.5% nickel alloy with an inert gas flowing along its other surface, the yield of isoprene increases from 14 to 21%, without the formation of undesirable impurities (penta-1,3-diene and cyclopentadiene), as a result of the decrease of the partial pressure of hydrogen in the dehydrogenation zone from 15 to 5 mmHg.[133]

As shown in Sections 3–7, binary alloys of palladium with nickel, ruthenium, rhodium, rhenium, molybdenum, and other metals can be used as membrane catalysts permeable to hydrogen alone. These alloys exhibit a high permeability to hydrogen and are superior to pure palladium as regards catalytic activity with respect to dehydrogenation, dehydrocyclisation, hydrogenation, and hydrodealkylation of hydrocarbons.

For the continuous removal of the hydrogen formed in the dehydrogenation of alkanes, it has been suggested[7] that the hydrogen diffusing through a palladium or palladium alloy membrane be burnt. The heat of combustion of hydrogen makes it possible to reduce the supply of heat needed to carry out the endothermic dehydrogenation reaction. In the dehydrogenation of ethane under a pressure of 8.6 atm at 452°C up to 0.7 vol.% of ethylene was obtained on the inner walls of a palladium–25% – silver alloy tube when a mixture of nitrogen with 0.7 vol.% of oxygen was present outside the tube at a pressure of 7 atm. The combustion of the hydrogen removed from the dehydrogenation zone is not an optimal method for its combination, since the hydrogen which has migrated to the palladium alloy is extremely active in hydrogenation and other hydrogen addition reactions. Moreover the hydrogen obtained in the dehydrogenation of hydrocarbons on palladium membrane catalysts is sufficiently pure for the manufacture of semiconductor devices. Nowadays millions of cubic metres of hydrogen are purified daily for such purposes by diffusion through palladium without the synthesis of any other products.

In the industrial manufacture of vitamins and pharmaceutical preparations the hydrogenation or dehydrogenation processes are frequently carried out on porous (Raney) metals, blacks, and other catalysts whose fine particles contaminate the products. The greater mechanical strengths of membrane catalysts makes it possible to prevent the contamination of products by catalyst particles and to avoid the loss of catalysts, for example palladium.

It was discovered in recent years that catalysts for many industrial processes are best prepared by depositing the metals onto the surface of alumina or aluminium silicate blocks resembling honeycombs in shape. Such block catalyst offer a resistance to the flow of gas which is even lower than that of spherical catalysts, which were the best known previously. Block catalysts make it possible to reduce the volume of the reactor and the consumption of noble metals. A change from granulated catalysts in tubes or on reactor shelves to catalysts consisting of the constructional elements of the reactor has been suggested. It is easy to assess the prospects opened up by the next stage in this development— the creation of a reactor with a membrane catalyst for carrying out simultaneously two coupled processes.

Reactor designs with a membrane catalyst in the form of tubes have been proposed[135]. This system resembles a heat exchanger with a floating head, which eliminates the deformation of thin-walled palladium alloy tubes owing to differences between the thermal expansion coefficients of the alloy and the material of the reactor shell. Thin-walled tubes are welded to two collectors, one of which serves as the lid of the reactor shell and is fitted with a partition ensuring that the initial substance flows from above downwards in one half of the total number of tubes and from below upwards in the other half.

To increase the surface area of the membrane catalyst per unit volume of the reactor, reactors have been developed with a membrane catalyst in the form of flat or corrugated plates and also in the form of a double helix. To prevent the deformation of the membrane catalyst, specially corrugated sheets of a stronger material, inert with respect to hydrocarbons or coated by a thin layer of the catalytically active substance, can be inserted between the plates or the turns of the helix.

Membrane catalysts may consist of a combination of a selectively permeable but catalytically relatively inactive substance and the catalytically active component. When the active component (metal) is sufficiently dispersed and the reactant, for example hydrogen, is transferred from the metal to the carrier (membrane), the limitations due to the rate of diffusion of the given reactant through the massive metal are lifted. This can ensure the operation of membrane catalysts at low temperatures. Moreover, a membrane with different metal or alloy particles attached to its two sides makes it possible to extend the range of reactions capable of being coupled. Such a membrane can serve as a model for biological membrane-enzyme system.

Membrane catalysts make it possible to investigate heterogeneous catalysts in open systems. When the zones of two reactions coupled as a result of the transfer through the catalyst of the substance evolved in one reaction and consumed in the other is separated by a membrane catalyst, not only is the mixing of the reactants of the two reactions prevented but it is also possible to obtain more complete data for the elementary stages of these reactions, which is very important in view of the decisive role of the coupling of the stages in catalysis.

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