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The role of the adsorbed forms of hydrogen and oxygen in the reaction of oxygen-containing one-carbon molecules on membrane catalysts

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ABSTRACT. The role of various adsorbed forms of hydrogen and oxygen in hydrogenation and oxidation reactions respectively on palladium alloy and silver membrane catalysts is examined. The possibility of altering the ratio of the concentrations of hydrogen and oxygen on the working surface and in the layer near the surface of the catalyst after the introduction of these substances into the reaction zone, either by means of diffusion through the bulk of the metal or as part of a mixture with oxygen-containing one-carbon molecules, is demonstrated. When the above ratio is altered, there is a change in the selectivity and activity of the corresponding catalysts.
The bibliography includes 26 references.

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I. Introduction

The interaction of diatomic gases with the surface of a metal can be accompanied by their molecular adsorption, subsequent dissociation of the adsorbed molecules, and also surface diffusion of the adsorbed atoms and in certain cases their dissolution in the bulk of the metal. The last phenomenon is manifested most strikingly in the hydrogen–palladium and oxygen–silver systems. The high solubility and mobility of the hydrogen and oxygen atoms in palladium and silver respectively, combined with the catalytic activity of palladium in hydrogenation and dehydrogenation reactions and of silver in oxidation reactions, made it possible to create on the basis of these metals membrane catalysts which permit the introduction of one of the reactants into the reaction zone by diffusion through the metal.[1,2] Depending on the thickness of the membrane, the state of its entry and exit surfaces as regards the permeating gas, and the nature of the gases in contact with these surfaces, the rate of transfer of the gas through the metal may be limited[3] both by one of the stages indicated above and by the release of the diffuse species from the bulk of the metal onto the surface, surface diffusion, the recombination of atoms to molecules, and the desorption of the latter to the gas phase.

Thus, when a diatomic gas is introduced, it is possible to generate on the catalyst surface concentrations of adsorbed species which differ from the concentrations of the same species when hydrogen or oxygen are introduced in a mixture with substances to be hydrogenated or oxidised respectively.

The catalytic hydrogenation of carbon oxides is of interest in connection with the search for the possible replacement of the petroleum raw material, while the oxidation of methanol is an important industrial process requiring detailed investigation. When these reactions are carried out, the different ways of supplying hydrogen or oxygen to the catalyst surface can provide new information about the influence of the type of adsorbed forms on the catalytic reactions.

II. Diffusion of hydrogen through palladium membranes

For thick membranes at fairly high temperatures and hydrogen pressures, the rate-limiting stage is the diffusion of hydrogen through the bulk of the metal.[4] In the case of thin membranes at lower temperatures and low hydrogen pressures, the processes occurring at the gas–metal interface are rate-limiting.

The study of the interaction of hydrogen with the (110) and (111) faces of a palladium single crystal by the slow electron diffraction method[5] showed that the dissociative adsorption of hydrogen does not require an activation energy, while the presence of the hydrogen dissolved in palladium does not influence the structure of its adsorption layer. Moreover, it has been shown that the removal of the adsorbed hydrogen promotes its inflow to the surface from the bulk of the metal. On the other hand, the desorption of hydrogen at 368–413 K requires an activation energy of about 80 kJ mol^{-1} and takes place via the recombination of two adsorbed atoms, the adsorption centres being located in hollows between the surface palladium atoms.[6]

Data concerning the influence of the adsorbed hydrogen on the electronic work function[7–9] show that the sign of the charge on the adsorbed structures depends on the degree of surface coverage of palladium. At low coverages (up to 0.05), predominantly the negatively charged form $H^{\delta-}$ is formed, while with increasing coverage a layer of the positively charged form $H^{\delta+}$ is produced. The same result has been observed also on the exit surface of a palladium membrane in the diffusion of hydrogen. According to Cattania et al.,[10] the study of thermal desorption from the surface of palladium makes it possible to observe four different states of

hydrogen: two of these are the states of the surface chemisorbed forms and two others refer to hydrogen under the external layer of metal and are associated with the dissolution of hydrogen. According to Dus,[7] one of the surface forms of hydrogen, namely the positively charged form, can dissolve in palladium.

Thus one can postulate that the positively charged atomic form of hydrogen, which exists in the layer at the surface in a state subsequently designated by $H_b^{\delta+}$, participates in its transport through the palladium membrane. When thin palladium membranes are used, the transport process in the bulk of the metal can be fairly rapid, while the release from the surface layer onto the surface encounters certain difficulties. The concentration of the $H_b^{\delta+}$ species in the surface layer is then greater than under conditions where the exit surface of the membrane comes into contact with hydrogen at the same partial pressure in the absence of the diffusion flux. Probably, when the hydrogen pressure at the exit surface of the membrane is high and the degree of coverage of this surface by hydrogen is therefore considerable, the hydrogen is adsorbed mainly in the positively charged form which can be designated by $H_a^{\delta+}$.

III. The influence of the method of introduction of hydrogen into the reaction zone on the hydrogenation of carbon monoxide in the presence of palladium alloys

Since the permeation of hydrogen through thin membranes is limited by stages recurring at the gas–metal interface, the ratio of the concentrations of the hydrogen forms $H_a^{\delta+}$ and $H_b^{\delta+}$ depends on the composition of the membrane catalyst, the state of its surface, temperature, the partial pressures of the reactants, their adsorption capacities, and also on the method of introduction of the initial substances into the reaction zone. If hydrogen enters the reaction zone as a result of diffusion through the membrane catalyst, then the ratio $H_a^{\delta+}/H_b^{\delta+}$ is smaller than in the case where hydrogen is supplied to the working surface of the membrane catalyst in a mixture with the substance to be hydrogenated. This has been confirmed by data[11,12] obtained in a study of the hydrogenation of carbon oxides on a palladium alloy in membrane catalysts, where the method of supplying hydrogen to the working surface was varied.

The catalysts were foils and thin-walled tubes made of binary palladium alloys. In experiments with tubes when hydrogen was supplied to the reaction zone via diffusion, the inner surface of the tubes served as the entry side, while the substance to be hydrogenated was supplied to the outer side of the tube. In experiments on the hydrogenation of a mixture of the given substance with hydrogen, the gas having a specified composition passed to the outer surface of the tube while an inert gas was present inside the tube in a closed volume. The catalysts in the form of foil were placed in a stainless steel reactor and were fixed so that two identical chambers were formed. In order to carry out experiments under diffusion conditions, hydrogen was supplied to one of the chambers, while the substance to be hydrogenated was introduced into the other. The mixture was made to react in one of the chambers, while the other contained helium.

In the hydrogenation of carbon monoxide on binary palladium alloy membrane catalysts with 10 wt.% of ruthenium or with 6 wt.% of nickel[11] in the temperature range 523–683 K, methane, ethane, ethylene, water, and carbon dioxide were detected among the reaction products. The method of introduction of hydrogen into the reaction zone and the catalyst composition did not alter the nature of the products, but they did influence the rate of their formation (Tables 1 and 2).

Table 1. The rates of formation of hydrocarbons (10^3 mol h^{-1} m^{-2}) in the hydrogenation of CO on palladium–ruthenium and palladium–nickel alloys at different temperatures with hydrogen supplied to the reaction zone via diffusion through the catalyst (1) or in a mixture with CO (2).[11]

Alloy	T, K	CH_4		C_2H_6		C_2H_4	
		1	2	1	2	1	2
Pd—Ru	523	6.2	70.0	1.0	10.2	3.4	1.1
	583	7.5	80.4	2.3	10.1	6.2	1.4
	633	58.1	130.1	4.4	10.1	9.5	2.4
	683	83.4	310.4	3.4	30.5	7.6	2.7
Pd—Ni	523	2.6	2.4	1.4	0.6	0.8	0.2
	583	21.2	23.5	2.2	1.33	1.6	0.3
	633	49.7	41.1	3.8	2.9	3.4	0.4
	683	183.5	131.8	6.5	5.8	4.3	0.7

Table 2. The rates of formation of carbon dioxide (10^3 mol h^{-1} m^{-2}) on palladium–ruthenium and palladium–nickel alloys in the interaction of CO with hydrogen arriving in the reaction zone via diffusion through the catalyst (1) or in a mixture with CO (2) and also on contact of the working surface with CO alone (3).[11]

Alloy	T, K	1	2	3
Pd—Ru	523	29.4	65.1	98.2
	583	37.2	83.5	125.3
	633	48.6	125.2	263.9
	683	98.3	267.1	362.1
Pd—Ni	523	7.5	15.2	30.2
	583	21.2	27.6	37.1
	633	30.2	39.2	45.2
	683	42.0	47.1	53.1

The rate of formation of ethane and methane in the reaction of carbon monoxide with hydrogen diffusing through a palladium–ruthenium membrane catalyst was appreciably lower than in the hydrogenation of CO in a mixture with hydrogen (Table 1). Conversely, the rate of formation of ethylene when the reaction was carried out under diffusion conditions was much higher than in the hydrogenation of the mixture. It is quite likely that the $H_b^{\delta+}$ form present under the layer of surface atoms participates in the formation of the olefin, the amount of this form being greater when hydrogen is introduced into the reaction zone via diffusion through the membrane catalyst, while in the formation of alkanes the main role is assumed by hydrogen in the $H_a^{\delta+}$ form, the amount of which on the surface is greater in the hydrogenation of CO in a mixture with hydrogen. The fact that, regardless of the method of introduction of hydrogen into the reaction zone, the rate of formation of ethane is always lower than the rate of formation of methane evidently demonstrates that the addition of atomic hydrogen to the CH_3

radicals is faster than the dimerisation of the latter if it is assumed that CH_x radicals are formed via the hydrogenation of the surface carbon.

The differences between the hydrogen permeabilities of the palladium–ruthenium and palladium–nickel alloys[13] affect the concentrations of the adsorbed forms of hydrogen and their ratios. The activation energy for the permeation of hydrogen through a palladium–nickel alloy is greater than through a palladium–ruthenium alloy. This is apparently one of the main reasons why the rate of formation of methane when hydrogen is supplied via diffusion through a palladium–nickel alloy increases with increase in temperature to a greater extent than under analogous conditions on a palladium–ruthenium alloy (Table 1) and at 683 K exceeds the rate of formation of methane under the same conditions in the reaction of a mixture of CO and H_2.

The rates of formation of ethylene in the hydrogenation of carbon monoxide by diffusing hydrogen are higher on both catalysts over the entire experimental temperature range than in the case where a mixture of CO and H_2 is supplied. An analogous dependence of the rate of formation of ethane on the way in which the reaction is carried out on the palladium–nickel catalyst is probably due to the fact that the ethane is formed from ethylene via the hydrogenation of the latter.

Table 2 shows that the highest rates of formation of carbon dioxide were observed when carbon monoxide came into contact with palladium alloys in the absence of hydrogen. The latter suppressed the disproportionation of CO most effectively when it was introduced into the reaction zone via diffusion. The decrease in the rate of formation of carbon dioxide in the presence of hydrogen is apparently associated with the occurrence of a process in which the adsorbed oxygen species, formed on dissociation of CO, react with the hydrogen atoms to form water. The dependence of the rate of disproportionation of the way in which hydrogen is introduced into the contact zone also indicates a change in the ratio of the different adsorbed forms of hydrogen on the working surface. In all probability, adsorbed hydrogen atoms, localised in the surface layer of the alloy ($H_b^{\delta+}$), interact preferentially with the adsorbed atomic forms of oxygen.

The formation of carbon dioxide in the interaction of CO with palladium alloys in the absence of hydrogen indicates the dissociation of carbon monoxide. One can therefore postulate that hydrocarbons are formed from CO and H_2 on palladium alloys via the hydrogenation of the surface carbon formed on dissociation of carbon monoxide, which agrees with literature data.[14]. As shown above, the rate of formation of a particular hydrocarbon depends on the relative amounts of the different forms of hydrogen adsorbed on the working surface of the catalyst, which interact with the carbon monoxide dissociation products.

A study has been made to elucidate the role of the hydrogen entering the surface of the catalyst from its bulk phase.[15] A palladium–nickel foil was treated with hydrogen, after which its supply was stopped and CO was brought up to the working surface. Methane, ethane, ethylene, carbon dioxide, and water were found among the reaction products. As can be seen from Figure 1, a decrease in the rate of formation of methane and ethane begins immediately after the supply of carbon monoxide is begun, while the rate of formation of ethylene remains constant for almost 1.5 h and only then diminishes. This confirms the hypothesis that the $H_b^{\delta+}$ form of hydrogen participates in the formation of ethylene from carbon monoxide on the palladium–nickel catalyst. The decrease in the rate of formation of methane from the very beginning of the reaction indicates its involvement in the synthesis of the $H_a^{\delta+}$ form of hydrogen. The content of the latter on the surface diminishes rapidly after a time, since the $H_a^{\delta+}$ form is produced as a result of the transfer of the hydrogen dissolved in the metal onto the surface, which is in all probability the rate-limiting stage of the hydrogen transfer through a thin palladium–nickel membrane under the given conditions. The analogy in the character of the variation of the rates of formation of ethane and methane may be attributed to the fact that hydrogen adsorbed in the $H_a^{\delta+}$ form also participates in the formation of ethane from ethylene under the conditions investigated.

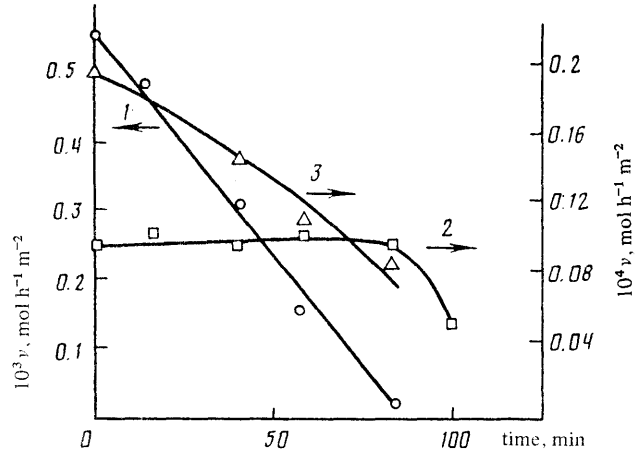


Figure 1. Time variation of the rates v of formation of methane (curve *1*), ethane (curve *2*), and ethylene (curve *3*) in the hydrogenation of carbon monoxide with hydrogen, dissolved beforehand in a palladium–nickel alloy, at 593 K.[15]

Table 3. Catalytic activity* of palladium–ruthenium and palladium–nickel alloys (10^3 mol h^{-1} m^{-2}) in the interaction of CO with hydrogen supplied to the reaction zone via diffusion through the catalyst (1) and in a mixture with CO (2).[11]

Alloy	T, K	1	2
Pd—Ru	523	73.1	222.8
	583	99.4	270.4
	633	182.9	406.4
	683	301.0	911.5
Pd—Ni	523	20.9	34.2
	583	70.9	80.6
	633	124.2	123.8
	683	288.7	238.7

*The activity was calculated from the sum of the rates of formation of the carbon-containing reaction products.

The overall catalytic activities of the binary palladium–ruthenium and palladium–nickel alloys (Table 3) can be calculated from the data presented in Tables 1 and 2. The overall activity of the palladium–nickel alloys depends only slightly on the way in which

hydrogen is introduced into the reaction zone, while the palladium–ruthenium catalyst is much more active in the hydrogenation of CO in a mixture with hydrogen than in its hydrogenation by the diffusing hydrogen, mainly as a result of the higher rate of formation of CO_2 and methane. In the reaction of a mixture of carbon monoxide and hydrogen, the activity of the palladium–nickel catalyst is much lower than that of the palladium–ruthenium alloy because of the lower rates of formation of carbon dioxide and methane in the presence of the former catalyst. When hydrogen is supplied into the reaction zone via diffusion, the activities of the palladium–nickel and palladium–ruthenium catalysts differ only slightly at 583–683 K.

The influence of the second component of the palladium alloy on its catalytic activity can be attributed both to a change in the concentrations of the different forms of adsorbed hydrogen and to the character of the adsorption of CO, which is indicated by data on the disproportionation of carbon monoxide in the absence of hydrogen (Table 2).

IV. Hydrogenation of carbon dioxide on membrane catalysts

The change in the ratio of the atomic forms of hydrogen on the working surface of the catalyst also affects the yield of the carbon dioxide hydrogenation products. It has been shown[16] that the maximum yield of methane when hydrogen is supplied via a palladium–ruthenium alloy membrane coated electrochemically by ruthenium is twice as high as in the hydrogenation of carbon dioxide in a mixture with hydrogen under the same conditions.

The state of the working surface of the catalyst and its chemical composition also influence the activity of the membrane catalyst. The study of the interaction of carbon dioxide with hydrogen which has diffused through a palladium–ruthenium alloy membrane catalyst showed that the activity of the latter is low in the hydrogenation of carbon dioxide to methane. The electrochemical deposition of a ruthenium layer[16] on the hydrogen exit surface of the palladium–ruthenium membrane catalyst increased sharply (by three orders of magnitude) the yield of the carbon dioxide hydrogenation products, among which ethane, carbon monoxide, and water were detected. Over the entire temperature range from 523 to 773 K, the rate of formation of methane increases with increase in the amount of hydrogen supplied through the membrane, which is consistent with literature data,[17] according to which the conversion of carbon dioxide into methane proceeds more vigorously on a ruthenium surface saturated beforehand with atomic hydrogen than on a clean ruthenium surface.

Thus the deposition of a layer of substance catalytically active in a specific reaction on a hydrogen-permeable membrane extends the possibilities of membrane catalysts. Nickel as well as ruthenium belongs to the group of the most active methane formation catalysts. The electrochemical deposition of a nickel layer 5×10^{-7} m thick on the exit surface of a palladium–ruthenium membrane catalyst[18] did not alter its permeability to hydrogen or the activation energy for the diffusion of hydrogen, which indicates a porous structure of the nickel layer and an insignificant influence of the latter on the transfer of hydrogen through the palladium–ruthenium alloy. During the hydrogenation of carbon dioxide with hydrogen, diffusing through such a catalyst, at 553 K and above, methane is formed, while an increase of temperature by a further 100 K leads to the appearance of carbon monoxide and small amounts of C_2–C_4 hydrocarbons. The rate of formation of methane in the hydrogenation of a mixture of carbon dioxide and hydrogen is always lower than the values obtained under the same conditions when hydrogen is supplied by diffusion.

The study of the temperature variation of the rate of formation of methane has shown[18] that the experimental activation energy for the reaction changes at 578 K, which may be due to a transition from the ferromagnetic to the paramagnetic state of the Ni–Pd–Ru layers formed near the nickel grains on the palladium–ruthenium foil as a consequence of the diffusion of the metal atoms. The change in activation energy may be associated with a magnetic transformation in pure nickel. Thus the presence of a thin layer of disperse nickel leads to magnetocatalytic effects without affecting the permeability of the palladium–ruthenium alloy to hydrogen.

The deposition of a lanthanum-containing nickel coating on the hydrogen exit surface of a palladium–ruthenium membrane catalyst[19] increased the rate of hydrogenation of carbon dioxide to methane compared with the rate of formation of methane on the same catalyst without the modifying element. However, the rate of reaction in the presence of lanthanum increased only in the temperature range from 573 to 663 K. Further increase of temperature resulted in a sharp fall of the rate of formation of methane, probably as a consequence of the formation of the catalytically inert lanthanum carbonate. The high stability of the latter precludes the regeneration of the catalyst.

As a result of the electrochemical deposition of a rhodium coating on a palladium–ruthenium membrane catalyst,[20] methane did not begin to form until 688 K, and although its content in the reaction products did increase with increase in temperature, it was appreciably (almost by a factor of four) smaller than the amount of carbon monoxide formed, traces of which were observed already at 473 K. An increase in the partial pressure of hydrogen at the hydrogen exit surface of the membrane catalyst from 200 to 725 mmHg increased somewhat the yield of methane and did not affect the yield of carbon monoxide. The formation of hydrocarbons with higher molecular weights was not observed.

Thus the method of introduction of hydrogen into the reaction zone as well as the deposition of dispersed layers of active metals on the hydrogen exit surface of the membrane catalyst influence the ratio of the concentrations of different forms of adsorbed hydrogen, which alters the selectivity and activity in the carbon dioxide hydrogenation process.

V. The role of adsorbed oxygen in the oxidation of methanol

Silver foil, which makes it possible to introduce oxygen into the reaction zone via diffusion through the metal, may be used as a membrane oxidation catalyst. The process involving oxygen transfer through silver membranes may include the same series of stages as the adsorption of oxygen on silver, in the forward and reverse sequences.[21] The adsorption of oxygen on silver in the temperature range from 453 to 623 K is known[22] to proceed in accordance with the scheme

$$O_{2\,gas} \rightarrow O_{2\,ads}^{-} \rightarrow 2O_{ads}^{-} \rightarrow 2O_{lat}^{2-}.$$

However, the rate-limiting stage in the transfer of oxygen through silver may not be the same as in the adsorption of oxygen from the gas phase.

The study of the permeability of silver tubes with walls 10^{-4} m thick to oxygen showed[23] that it is proportional to the square root of the oxygen pressure at the oxygen entry surface of the tube. This indicates the involvement of oxygen atoms in the rate-limiting stage of the transfer of oxygen through silver. The electrochemical deposition of a layer of silver on the oxygen exit surface of a silver membrane increases its permeability to oxygen by more than an order of magnitude,[24] but the linear dependence of this parameter on the square root of the oxygen pressure at the entry surface of the membrane is retained. All these factors show that the rate-limiting stage in the transfer of oxygen through thin silver membranes is the process occurring on the oxygen exit surface in which oxygen atoms participate.

The states of the oxygen, arriving via diffusion through membranes or as a result of adsorption from the gas phase, on the exit surface of the membrane have been investigated mass-spectrometrically[25] using a modernised ion source. In the immediate vicinity of the mass spectrometer ion source, a silver tube with walls 10^{-4} m thick was placed and the composition of the gas phase in contact with its outer surface was investigated. Furthermore, an additional cathode and potential-carrying grids were introduced into the ion source, which made it possible to investigate the species adsorbed on the outer surface of the silver tube by the method of the electron-stimulated desorption of ions (ESDI). Two peaks can be observed in the mass spectrum of gaseous oxygen: the molecular (O_2^+) peak with a mass number of 32 and a fragment (O^+) peak with a mass number of 16. The ratio of the intensities of these two peaks (I_{32}/I_{16}) was found to be close to 20 by the usual gas analysis. As can be seen from Table 4, approximately this value has been recorded when oxygen was admitted directly onto the outer surface of the silver membrane in the ionisation chamber. A similar value was also obtained when oxygen was supplied by diffusion through a silver tube at 665 K. However, in this case the decrease in the temperature of the membrane was accompanied by a decrease in the I_{32}/I_{16} ratio, which indicates the appearance in the gas phase of an additional source of oxygen atoms. These may be the atoms desorbed from the surface. The proximity of the membrane to the ionisation region makes it possible to record them. An analogous effect has been observed in a study by the ESDI method, which is probably associated with the enrichment of the exit surface of the silver membrane during the diffusion of oxygen through it in adsorbed forms, which on electron bombardment of the surface are capable of being desorbed to the gas phase in the form of the positively charged O^+ ions.

Since the entire oxygen which has diffused through the silver membrane passes to the ionisation chamber, the intensities of the molecular (O_2^+) and fragment (O^+) oxygen peaks are proportional to the permeability of the given silver membrane to oxygen under stationary conditions.

The activation energy calculated from the temperature variation of the intensity of the peak with a mass number of 32 exceeds the corresponding value found by measuring the height of the peak, with a mass number of 16, the same effect being observed for both methods of analysis. Presumably, in the diffusion of oxygen into a vacuum through a thin silver membrane, its exit surface is enriched in atoms capable of being desorbed into the gas phase on electron impact, the number of such species increasing with decrease in temperature. Furthermore, at low temperatures the surface diffusion process as a result of which the lattice oxygen passes to the adsorbed state, preceding the recombination stage, is hindered and the release of atoms into the gas phase becomes possible which, as already stated above, is the cause of the decrease in the ratio I_{32}/I_{16} (Table 4) and also of the lower activation energy calculated from the variation of the intensity of the peak with a mass number of 16.

Table 4. The ratios of the intensities of the mass spectrometric peaks with mass numbers 32 and 16 (I_{32}/I_{16}) for different methods of supplying oxygen to the exit surface of a silver membrane and at different temperatures.[25]

Method of introduction of oxygen	Analytical method	T, K						
		525	548	570	591	613	634	665
Diffusion through silver	analysis of gas phase	2	3	7	11	14	—	18
Direct injection	ditto	19	—	—	16	16	18	18
Diffusion through silver	ESDI	0.01	0.02	0.03	0.04	0.06	0.09	0.1
Direct injection	ditto	0.66	0.62	0.57	0.54	0.49	0.47	0.47

Methanol was oxidised[21] on the outer surface of a silver tube with walls 1×10^{-4} m thick. When a mixture of methanol and oxygen was supplied to the outer surface, the inner part of the tube was evacuated.

The permeability of silver to oxygen under the conditions of the oxidation of methanol by diffusing oxygen exceeded its permeability to oxygen in the diffusion of the latter into a vacuum under the same conditions to a greater extent the lower was the experimental temperature. In the interaction of methanol vapour with diffusing oxygen on the exit surface of the silver membrane catalyst, oxygen did not appear in the gas phase until 619 K. On further increase in temperature, its amount also rose and the permeability of the silver membrane catalyst to oxygen diminished, approaching the value obtained for the diffusion of oxygen into a vacuum. The activation energy for the transfer of oxygen through a silver membrane catalyst during the oxidation of methanol is smaller by 25 kJ g-atom^{-1} than in the diffusion of oxygen into a vaccum. This is in fact the difference between the activation energies calculated from the intensities of the O_2^+ and O^+ peaks in the analysis of the gas phase near the exit surface of the silver membrane.[25] The decrease in the activation energy for the transfer of oxygen through silver under methanol oxidation conditions can be due to the interaction of the substances being oxidised on the exit surface of the silver with oxygen species which participate in the stage preceding the rate-limiting stage of the transfer of oxygen to a vacuum. According to the scheme presented above, this form may be the lattice oxygen O_{lat}^{2-}.

The supply of oxygen by diffusion through a silver membrane catalyst evidently creates on the working surface, at temperatures below 619 K, a higher concentration of this form than in the adsorption of oxygen from the gas phase. Thus, in the oxidation of methanol by diffusing oxygen, the yield of formaldehyde at 619 K reached 85%, while in the case where a mixture of methanol with oxygen was used under the same conditions, the maximum yield of formaldehyde was 23 %. Apart from formaldehyde, carbon monoxide and dioxide as well as water were formed in the reaction.

The amount of carbon monoxide formed per unit time was independent of temperature, while the rate of formation of carbon dioxide increased on heating. However, the yield of carbon dioxide did not exceed 22% even at the highest experimental temperature (673 K).

Thus the ratio of different forms of oxygen on the silver surface depends on the method of supplying oxygen through the surface of the membrane catalyst and this affects the process selectivity, since oxygen species dissolved in the surface layer of the metal participate in all probability in the formation of formaldehyde from methanol on silver.

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