CHEMISORPTION OF ETHYLENE ON NICKEL SURFACES WITH PREADSORBED OXYGEN

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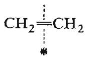
Received December 19th, 1976

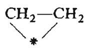
Chemisorption of ethylene was studied on thin polycrystalline layers of nickel prepared by metal deposition in high vacuum and modified by preadsorbed oxygen. The volumetric method combined with the gas-phase analysis and the measurement of the electrical resistance changes of these layers were used. Already small amounts of preadsorbed oxygen of the order of 10^{-2} of the monolayer affect rather substantially the extent of ethylene chemisorption. The extent of the initial irreversible chemisorption and also the total adsorption of ethylene as a function of the amount of preadsorbed oxygen have a maximum at the surface oxygen concentration of $3 \cdot 10^{13}$ molecule cm^{-2}. The adsorption accompanied by the extensive dissociation of ethylene C—H bonds proceeds predominantly on nickel atoms with lower coordination (atoms on the microcrystal edges, corner atoms, *etc.*), where also oxygen chemisorption proceeds preferentially. The complexes of chemisorbed ethylene on surfaces with preadsorbed hydrogen have a different structure than those formed on a clean surface or on a surface with preadsorbed oxygen.

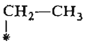
The adsorption of hydrocarbons on metal surfaces is a rather complex problem as the hydrocarbons can form various adsorption complexes that differ in their chemical structure.

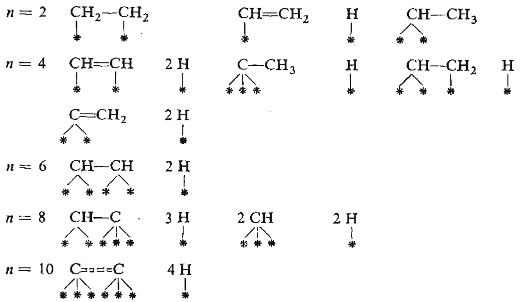
Ethylene hydrogenation and adsorption of ethylene and hydrogen that is associated with it belong to the most frequently studied processes in the field of the fundamental studies of catalysis by metal surfaces[1]. Among the metals of the VIII.A group of the periodic system nickel exhibits the maximum activity in the hydrogenation of ethylene[2]. For this reason the interaction of ethylene with nickel surfaces has been dealt with in a large number of theoretical and experimental studies[3-13] but so far only very little is known about the nature of the adsorbed complexes. From all the structures of adsorbed ethylene the π-adsorbed complex[4] and the dehydrogenated acetylene-like complex[9] are the most familiar. Let's summarize some possible surface complexes of ethylene (n is the number of occupied adsorption sites):

$n = 1$


$\underset{*}{\mathrm{CH_2 \overset{\vdots}{=} CH_2}}$


$\underset{*}{\mathrm{CH_2-CH_2}}$


$\underset{*}{\mathrm{CH_2}}\mathrm{-CH_3}$



The results obtained by various authors are very often different and they depend obviously on the experimental conditions and on the method used. Accordingly, one can assume that ethylene is adsorbed on the nickel surface in several different states the population of which depends on the surface coverage, temperature, surface topography, and on its cleanliness. Various adsorption states can therefore be expected on the surfaces of polycrystalline nickel films which – along with various crystal planes – contain many imperfections both in the microscopic and quasi-macroscopic scales. In addition to this initial heterogeneity the adsorption properties of the surfaces are also affected by the presence of preadsorbed atoms or molecules which may be contaminants or may originate in the initial stages of ethylene chemisorption (the so-called induced heterogeneity). These species can either act as catalytic poisons or they can promote the catalytic activity.

The surfaces of nickel are frequently contaminated by oxygen. The effect of oxygen on the catalytic activity of nickel has been studied only in few papers[14-19]. It has been reported that traces of oxygen enhance the catalytic activity of nickel in the hydrogenation of ethylene[19]. An analogous effect has also been observed in cyclopropane hydrogenation[20] and it seems that it is a quite general effect. According to certain authors[21] the mechanism of ethylene hydrogenation is similar to that of selfhydrogenation. It can be therefore expected that some valuable information on the effects of oxygen on the hydrogenation activity of nickel may be gained by studying the chemisorption and selfhydrogenation of ethylene on surfaces with preadsorbed oxygen. These experiments can presumably present an additional information on the structure of ethylene adsorption complexes.

EXPERIMENTAL

Thin nickel films prepared by vacuum sublimation were used as adsorbents. This technique insures the reproducibility of the preparation of the metal with a sufficiently clean surface[6].

The glass vacuum apparatus used for the preparation of films and for the adsorption measurements did not differ substantially from the apparatus described elsewhere[22]. During the evacuation of the apparatus, that lasted for about 100 h, the glass walls were heated to 630 K and the evaporation filament was degassed at a temperature just below that necessary for the sublimation of the metal. The residual gas pressure in the system prior to sublimation was better than 7 μPa. Spectral grade nickel (Johnson Matthey Metals Ltd., England) with the impurities content as determined by the spectral analysis (in ppm): Al, Ca < 1, Cu, Mg 1, Ag 2, Si 3, Fe 5) was evaporated on the inside walls of a spherical adsorption vessel kept at about 200 K during the vapour deposition. After the evaporation the films were annealed for 1 h at 360 K. After each experiment the weight of the deposited nickel was determined polarographically after dissolving the films in nitric acid. The mean thickness of the film, in most cases ~50 nm, was calculated from the weight and geometrical area.

The actual surface area of the films was determined by the physical adsorption of xenon at the liquid nitrogen temperature using BET method for the evaluation of the monolayer surface coverage. The ratio of the actual surface to the geometrical surface of the films was $R = 5{\cdot}95 \pm 0{\cdot}58$ (with the exception of the film No 15 for which $R = 3{\cdot}5$). During the deposition and adsorption measurements the films were protected against mercury vapours by two traps cooled with dry ice–acetone mixture.

The dead space of the apparatus during the measurements was 1380 ml. The equilibrium pressures in the range from 1·3 kPa to 133 μPa were measured with a McLeod gauge, the kinetics of pressure changes with a calibrated Pirani gauge. When necessary the adsorption data were corrected for the thermal transpiration using the method of Bennett and Tompkins[23]. The estimated error in the determination of the adsorbed amount is ±1·5%.

Ethylene was prepared by the catalytic dehydration of ethyl alcohol. Prior to admission into the adsorption vessel ethylene was purified by multiple vacuum distillation so that it contained 0·8% of ethane and 0·4% of butane as determined by mass spectrometry. No other impurities were found. The electrolytic hydrogen was purified by diffusion through a hot palladium thimble. Oxygen was prepared by the thermal decomposition of thoroughly outgassed potassium permanganate and it was further purified by passing through a trap cooled with liquid nitrogen. It contained about 1% of impurities (0·8% of carbon monoxide and 0·2% of carbon dioxide). The gas phase composition in various stages of the adsorption measurements was analyzed by thermal desorption from a thin layer of zeolite[24]. The analytical apparatus was directly connected with the adsorption apparatus. For control and also the calibration purposes typical samples of the gas phase were also analyzed with the LKB 9000 mass spectrometer. The changes of the electrical resistance of films were also monitored in the course of the adsorption measurements. For this purpose the adsorption vessel was equipped with platinum contacts fused in the glass wall.

RESULTS

Prior to chemisorption measurements the surface area of each film was determined by the BET method and this measurement was repeated at the end of the experiment. In agreement with the published data[3,25] the surface area determined at the end of the experiment was by 36 ± 8% lower than the initial value. The plausible explanation for the apparent decrease of the film surface area is discussed in detail in the paper[25].

The adsorbed amounts of gases given in this paper are given per unit surface area of the original film. This method of data presentation permits to compare the results obtained on different films.

Chemisorption of Ethylene on a Clean Film Surface at 273 K

Ethylene was admitted to the nickel films in discrete doses. The adsorption of the first doses proceeded rapidly leaving no products in the gas phase (Fig. 1). The subsequent uptake of ethylene was followed by a slow desorption of ethane. The ratio of the amount of the produced ethane to the consumed ethylene was $P = 1 : 1{\cdot}6$ and it differed from the value reported by Hirota and Teratani[16] who found $P = 1 : 2$. The adsorption rate decreased appreciably with the increasing surface coverage and it became negligible after the total surface coverage ($Q = Q_t$) had been reached. The experimental data allowed to determine rather accurately the extent of the initial irreversible chemisorption Q_i because of the qualitative and abrupt change of the adsorption process which obviously occurs at this coverage. On the other hand at the total surface coverage Q_t only quantitative aspects of adsorption change. This change proceeds gradually and the value of Q_t may be determined graphically as an intersection of the corresponding extrapolated linear parts of the dependence of N_R on N_D (Fig. 1). The electrical resistance of films increased during the adsorption of ethylene and its dependence on the adsorbed amount exhibited a break at $Q = Q_i$ (Fig. 2).

The value of the atomic ratio H/C calculated for the surface complex from the total mass balance was equal to unity at the complete surface coverage. The adsorption cross section of the surface complex formed by the adsorption of one ethylene molecule was calculated from the known surface area of the film and the values of Q_i and Q_t. The value corresponding to the coverage Q_i ($1{\cdot}145\ \text{nm}^2$) is in good agreement with the value calculated from the adsorption data published by Hirota and Teratani[16] that were obtained on nickel powder.

Assuming that the concentration of nickel atoms on the film surface is $1{\cdot}5 \,.\, 10^{15}$ cm^{-2} it is possible to calculate from the adsorption cross section the effective number of nickel atoms occupied by one adsorbed molecule of ethylene. This number is 17·2 atoms at the coverage Q_i. The adopted value for the concentration of surface nickel atoms has been calculated[26] as a mean value corresponding to equal extents of the (111), (110), and (100) planes that are assumed to be the most probable planes on the surface of the film. This number is also in good agreement with the number of oxygen atoms required for the formation of the monoatomic coverage of the surface[27].

For the coverages $Q \leqq Q_i$ the surface of nickel is not completely covered with the complexes of ethylene.

In order to make the correction for the uncovered part of the surface and to obtain a more realistic value of the effective number of nickel atoms occupied by one chemisorbed molecule of ethylene the following experiment was done. Ethylene was adsorbed at 273 K up to the surface coverage $Q < Q_i$. The film was then cooled down to the liquid nitrogen temperature and hydrogen was adsorbed. Assuming that the adsorption of hydrogen under these conditions proceeds predominantly on the free surface of the film it was possible to calculate from the amount of adsorbed hydrogen the corrected number of effective nickel atoms per complex formed by one adsorbed molecule of ethylene. The adsorption cross section of hydrogen atom depends on the type of the crystalline plane of the metal and for the three abovementioned planes it changes from 0·054 nm^2 to 0·088 nm^2. In our calculations we have used the value 0·084 nm^2.

The described method of titration of the free part of the metal surface by the adsorption of hydrogen at low temperatures must be – for various reasons – considered only as an approximate estimation. However, it is interesting that the value of about 13 nickel atoms per one ethylene molecule, obtained in this way, is close to the value obtained from the magnetic measurements[8] and points to a high degree of dissociation of the intramolecular bonds of ethylene during the initial stages of adsorption.

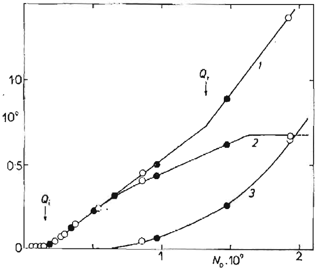


FIG. 1

Amount of the Gas Phase N_R (mol cm^{-2}) as a Function of the Amount of Added Ethylene N_D (mol cm^{-2})

1 The total amount of the gas phase, *2* the amount of the produced ethane, *3* the amount of the remaining ethylene. ○● the results of the measurement with two different films. The meaning of Q_i and Q_t is explained in the text.

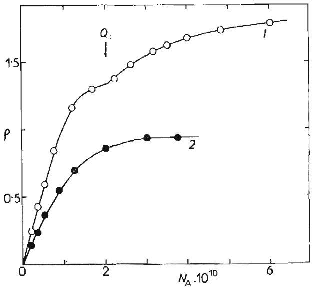


FIG. 2

Changes of the Electrical Resistance of the Film ϱ(%) as a Function of the Amount of Adsorbed Ethylene N_a (mol cm^{-2})

1 Adsorption on a clean surface of the nickel film, *2* adsorption on the surface with preadsorbed oxygen ($\phi(O_2) = 0·47$).

Chemisorption of Ethylene on the Surface with Preadsorbed Hydrogen

A clean nickel film was exposed to gaseous hydrogen at the pressure of 93 Pa and at the temperature of 273 K. After 30 min of contact the gaseous phase and the reversibly bound hydrogen were pumped off. The concentration of hydrogen that remained under these conditions irreversibly bound to the surface was $(3-4) . 10^{14}$ atoms cm^{-2} which is roughly 30% of the original adsorbed layer. Then ethylene was added in individual doses to such a modified surface. In contrast to the adsorption on the clean surface ethane was released into the gas phase already from the beginning of adsorption (*i.e.*, $Q_i \approx 0$, *cf.* Table I). The total amount of adsorbed ethylene was 3·3 times higher than in the case of the clean surface. On the other hand the change of the electrical resistance of the film corresponding to the total surface coverage by ethylene was the same for the film with preadsorbed hydrogen as for the adsorption on the film with a clean surface. In the case of the complete surface coverage each adsorbed molecule of ethylene occupies 1·3 nickel atoms. From the total mass balance the value of the atomic ratio $H/C = 1{\cdot}3$ has been calculated for the total surface coverage.

Chemisorption of Ethylene on Surfaces with Preadsorbed Oxygen

In another series of experiments a known amount of oxygen was preadsorbed on the nickel surface at 273K and chemisorption of ethylene was studied on such modified surfaces. The results are summarized in Table I. Ethane was the only product of self-hydrogenation, no other products were detected in the gas phase. Because the adsorption vessel was connected with the detection system *via* two cooled traps the presence of water, formed by a reaction of preadsorbed oxygen with hydrogen, released in the dissociative chemisorption of ethylene, cannot be excluded. The observed mean value of the atomic ratio H/C at the total surface coverage was slightly higher than that for the chemisorption on a clean surface and it varied from 1·0 to 1·2. The dependence of the electrical resistance of the films with preadsorbed oxygen on the amount of adsorbed ethylene exhibited no break typical for the film with clean surface (Fig. 2).

The observed dependences of Q_i and Q_t on the amount of preadsorbed oxygen (Fig. 3) showing a maximum at the oxygen concentration $Q(O_2) = 3 . 10^{13}$ molecules cm^{-2} seem to be the most interesting and important results of this study. Analogous maxima were also observed on the curves expressing the dependence of the electrical resistance changes of films at the total surface coverage on the amount of preadsorbed oxygen (Fig. 4). The decreasing parts of curves on Fig. 3 (*i.e.*, in the region of $Q(O_2) > 3 . 10^{13}\ cm^{-2}$) can be described by the equations

$$q_i(Et)/N_m(Xe) = (8{\cdot}7 \pm 0{\cdot}2) . 10^{-3} - (7{\cdot}8 \pm 0{\cdot}8) . 10^{-2} \ln \phi(O_2) \qquad (1)$$

$$q_t(\mathrm{Et})/\mathrm{N_m(Xe)} = (0{\cdot}3 \pm 0{\cdot}01) - (0{\cdot}19 \pm 0{\cdot}005) \ln \phi(\mathrm{O_2}) , \qquad (2)$$

where $N_m(\mathrm{Xe})$ is the monolayer capacity for xenon adsorption at the temperature of liquid nitrogen as determined by the BET method. The quantities $q_i(\mathrm{Et})$, $q_t(\mathrm{Et})$, and $\phi(\mathrm{O_2})$ are defined by the relations

$$q_i(\mathrm{Et}) = Q_i S , \quad q_t(\mathrm{Et}) = Q_t S , \quad \phi(\mathrm{O_2}) = Q(\mathrm{O_2})\, S/N_m(\mathrm{Xe}) , \qquad (3)$$

where S is the surface area of the film.

The saturation value of the quantity $\phi(\mathrm{O_2})$ for nickel films varies in the range 3·6–5·0 at 273 K and it depends on the pressure of oxygen, on the contact time and on the conditions during the film preparation, particularly on the temperature of the substrate during the deposition. The above-mentioned value of $\phi(\mathrm{O_2})$ includes

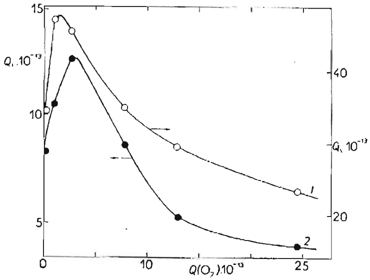


FIG. 3

The Values of Q_i (*1*) and Q_t (*2*) as Functions of the Amount of Preadsorbed Oxygen $Q(\mathrm{O_2})$ on the Surface of Nickel Films

All Q values are given as the number of molecules per cm^2 multiplied by 10^{13}.

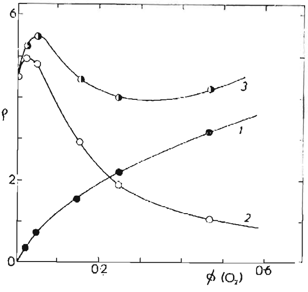


FIG. 4

The Relative Changes of the Electrical Resistance of Nickel Films ϱ (%) as a Function of the Amount of Preadsorbed Oxygen $\phi(\mathrm{O_2})$

1 The change caused only by the preadsorbed oxygen, *2* the change caused by the total coverage with ethylene of the surface with preadsorbed oxygen, *3* the sum of both changes.

TABLE I

Adsorption Data of Ethylene Obtained on Clean Nickel Surfaces and on Nickel Surfaces with Preadsorbed Oxygen

Film No	$Q(O_2) . 10^{-13}$	$N_m(Xe) . 10^{-17}$	$Q_i . 10^{-13}$	$Q_t . 10^{-13}$	Q_t/Q_i	P	n_t	n_{tc}	Z
1	0	5·9375	8·76	34·33	3·92	1 : 1·55	4·37	4·37	13
2	0	5·729	7·83	34·54	4·41	1 : 1·66	4·34	4·34	13
3	H (irr.)	6·250	0·44	115·34	262	1 : 1·53	1·30	1·30	10
15	1·042	3·542	10·50	47·28	4·50	1 : 1·56	3·17	3·13	20
14	2·604	5·885	12·60	45·77	3·63	1 : 1·69	3·28	3·17	21
13	7·813	5·573	8·59	34·93	4·07	1 : 1·85	4·29	3·84	16
6	13·020	7·1875	5·24	28·91	5·52	1 : 1·53	5·19	4·29	14
11	24·479	5·4167	3·90	23·37	5·99	1 : 1·90	6·42	4·30	9

$Q(O_2)$ is the amount of preadsorbed oxygen, $N_m(Xe)$ the monolayer coverage of physically adsorbed xenon, Z is the number of ethylene doses, n_t is the number of nickel atoms per one molecule of adsorbed ethylene at the total surface coverage, n_{tc} is the value of n_t corrected for the sites occupied by preadsorbed oxygen. The meaning of Q_i, Q_t, and P is given in the text. All adsorbed amounts are given by the number of molecules per cm^2.

also the partial incorporation of oxygen into the crystal lattice of nickel. From Eqs (*1*) and (*2*) it is possible to obtain the limit values of $\phi(O_2) = 1{\cdot}12$ and $\phi(O_2) = 4{\cdot}62$ corresponding to the zero values of Q_i and Q_t, respectively.

Hydrogenation of the Surface Complexes of Ethylene

Surfaces covered completely by the adsorption complexes of ethylene were – after the pumping off of the gas phase – put into contact with gaseous hydrogen at the pressure of 7 Pa. The slow decrease of the electrical resistance of the film indicated the proceeding reaction between hydrogen and the surface complexes of ethylene. After completing of the reaction, which lasted for about 10–12 h (at 273 K), the gas phase was analyzed. Along with the remaining hydrogen also ethane and butane in equimolar amounts were found in the gas phase. The fraction of ethylene that could be removed from the surface by the reaction with hydrogen was always approximately one tenth of the total coverage Q_t. The hydrogenation could be repeated several times on the same film and always the same amounts of hydrogen and readsorbed ethylene were consumed. The relative proportion of the interaction products was – within the error limits of the adopted analytical method – independent on the amount of preadsorbed oxygen.

DISCUSSION

The bonding of ethylene on clean nickel surfaces is a topic of numerous discussions. The photoetectron spectra (UPS) of ethylene adsorbed on nickel[9] at the temperature $T \geqq 230$ K are supposed to corroborate the idea of the formation of an acetylene-like complex adsorbed with the participation of π electrons of the hydrocarbon molecule. On the other hand, the infrared spectra of adsorbed ethylene are explained as due to the existence of associatively σ-bonded molecules. Recently Erkeleus and Liefkens[10] studied also the infrared spectra of ethylene adsorbed on silica supported nickel. Along with the absorption band characteristic for the associatively bonded ethylene the authors found also a band which they assigned to the half-hydrogenated ethylene and to the dimer products with the structure $Ni-(CH_2)_3CH_3$. Kesmodel and his coworkers[28] have shown by a theoretical analysis of results obtained with the LEED method that the π-complex coordinated on one metal atom similarly as the di-σ-complex may not be a favoured bonding modes on the fcc(111) crystal plane. Also Bond[4] has shown on the basis of a simple model of molecular orbitals that the fcc(111) plane is not suitable for the formation of π-complexes of adsorbed olefins.

In agreement with the results of magnetic measurements[8] our results seem to suggest that at the low surface coverage the chemisorption of ethylene proceeds dissociatively. This conclusion is also borne out by the experimentally observed dependence of the work function of nickel on the degree of surface coverage by ethylene[11,29]. This dependence has a maximum in the region of low coverage which can be most easily explained by the dissociation of C—H bonds of the ethylene molecule. The degree of dissociation is evidently different on different crystal planes of the metal and it is probably low on the (111) plane, the work function of which decreases monotonously during the adsorption of ethylene[12]. This conclusion is also in agreement with the observation[13] that the (111) plane of nickel is the most active plane for the hydrogenation of ethylene.

It appears that in the initial stages of adsorption, *i.e.*, at the low surface coverage, ethylene is preferentially adsorbed on sites formed by nickel atoms with low coordination which are capable to form multiple bonds[30] and consequently to bind more firmly the adsorbed molecules. The idea of high chemisorption activity of metal atoms with low coordination is in agreement with the results of the measurement on the stepped surfaces of single crystals[36] and it is also corroborated by the theoretical studies[31,32]. The degree of dissociation of C—H bonds of the ethylene molecule decreases with the increasing surface coverage and at the same time the molecules are chemisorbed less firmly. The selfhydrogenation reaction takes place on that part of the surface that is not covered with strongly chemisorbed species. The observed value of $P = 1 : 1{\cdot}6$ indicates that the mechanism of selfhydrogenation cannot be described by the simple reaction (*A*):

$$2\,C_2H_4 \rightarrow C_2H_6 + C_2H_2\,(\mathrm{ads}) \qquad (A)$$

that was assumed by several authors[16].

The results obtained in this study are best described by the reaction (*B*):

$$6\,\underset{*}{H} + 8\,C_2H_4 \rightarrow 5\,C_2H_6 + \underset{*}{CH_2}\text{—}\underset{*}{CH_2} + 2\,\underset{**}{CH}{=}\underset{**}{CH}\,, \qquad (B)$$

where the bond to the nickel surface is denoted by an asterisk. However, equation (*B*) is only a formal description of a more complicated reaction that proceeds in reality.

Hence, hydrogen transfer between adsorbed ethylene molecules takes place during the selfhydrogenation and at the same time also hydrogen, formed in the initial stage of the strongly dissociative adsorption of ethylene, is consumed (*i.e.*, at the coverage $Q < Q_i$).

The complexes of the chemisorbed ethylene on surfaces with preadsorbed hydrogen have a structure ($\underset{*}{C}H_2\text{—}CH_3$ or $\underset{*}{C}H{=}CH_2$) that is different from the complexes formed during the initial stages of adsorption. This result favours also the model proposed by Horiuti and Polanyi[3] according to which the halfhydrogenated state is an important intermediate in the hydrogenation of ethylene.

The magnitude of the final change of the electrical resistance of the film (*i.e.*, at the total surface coverage) was in the case of ethylene adsorption on the clean surface the same as in the adsorption on a surface with preadsorbed hydrogen in spite of the 3·3 times higher amount Q_t of adsorbed ethylene in the latter case. If we assume as the first approximation that the change of the electrical resistance of the film is proportional to the number of occupied adsorption sites, then this result means that the number of occupied sites is the same in both above-mentioned cases. Indeed, the number of nickel atoms occupied by one ethylene molecule at the total coverage of the film surface without preadsorbed hydrogen calculated from the above-quoted data (n_t = 1·3 . 3·3 = 4·3) agrees very well with the experimentally determined value (n_t = 4·37, Table I) and it is also consistent with the stoichiometric equation (*B*).

The obtained experimental results do not allow us to draw any definite conclusions about the mechanism of the formation of butane in the hydrogenation of surface complexes. It seems probable that butane is formed in the dimerization of multiple bonded complexes (Eq. (*B*)) that have a radical nature[30].

The main object of this study was the effect of the preadsorbed oxygen on the subsequent chemisorption and selfhydrogenation of ethylene. As it is evident from Fig. 3 this effect cannot be explained as a consequence of mere blocking of a part of the surface.

During the chemisorption on nickel oxygen is partly incorporated and these two processes are difficult to distinguish. However, according to the published data[33,34], no incorporation of oxygen and no nucleation of the oxide proceeds under the conditions used in this work, *i.e.*, at the low coverage and at the temperature of 273 K. The maximum adsorption capacity for ethylene is reached at the surface oxygen concentration of $3 . 10^{13}$ molecules cm^{-2}. Carbon dioxide has the same effect[16] as preadsorbed oxygen and the maximum adsorption capacity is in this case reached at the surface CO_2 concentration of $3·8 . 10^{13}$ molecules cm^{-2}. This result and also other our results indicate indirectly a possible dissociative nature of the carbon dioxide chemisorption under the given conditions. An analogous effect was found[18] also in the propylene adsorption on nickel films modified by preadsorbed oxygen. As shown by our calculations, the data of Kadlec and coworkers[18] obtained in the region of the surface coverage by preadsorbed oxygen $Q(O_2) > 6·2 . 10^{13}$ cm^{-2} can also be described by the logarithmic equations of the type (*1*) and (*2*).

At least two possible mechanisms exist that can explain the effect of preadsorbed oxygen on the subsequent chemisorption of ethylene: *a*) the competition for the active sites on the heterogeneous surface of the metal, *b*) the competition for hydrogen formed by the dissociative chemisorption of ethylene.

Assuming that oxygen is preferentially adsorbed on sites that are most active in the dissociative chemisorption of ethylene (*i.e.*, on the metal atoms with low coordination) then a higher surface coverage by ethylene is required if the surface concentration of the hydrogen active form, necessary for the production of ethane by selfhydrogenation, is to be achieved. This conclusion is also in agreement with the results of Miyahara[36] according to which the presence of impurities on the surface of nickel suppresses the dissociative chemisorption of ethylene.

It is well known that oxygen on the nickel surface reacts with hydrogen[37]. According to the results of Horgan and King[34] at the low coverage oxygen is present on the nickel surface in the β' state with relatively low adsorption heat (209 kJ mol^{-1}). With the increasing degree of coverage a phase transition with the formation of a new structure, denoted by these authors as the β_1 state, takes place. The adsorption heat increases and reaches the value of 460 kJ mol^{-1} for the β_1 state. The β' state is substantially more reactive than the β_1 state and it can, *e.g.*, react with carbon monoxide with the formation of carbon dioxide. Under the same conditions the β_1 state is inactive in this reaction. In line with these results it can be assumed that the β' state reacts with the hydrogen formed by the dissociative chemisorption of ethylene forming water which probably remains adsorbed under the conditions of the experiment. The adsorption sites freed in this way (*i.e.*, the sites where dissociated hydrogen would be bound in the case of a clean surface) are then accessible for another chemisorption of ethylene. The less reactive β_1 oxygen state can react with hydrogen only to form surface OH groups so that the adsorption capacity of the surface for ethylene decreases at higher coverage by oxygen.

However, the experimentally observed conspicuous decrease indicates that the existence of a special configuration of several nickel atoms (multiplets) is required for the chemisorption of ethylene. With the increasing amount of the preadsorbed oxygen, statistically distributed over the surface, blocking of multiplets, leading to a further decrease of the adsorption capacity of the surface, begins to accompany the reaction of this oxygen with hydrogen. This may be the reason why relatively low surface concentrations of oxygen can cause a substantial decrease of the adsorption capacity of the surface for the subsequent chemisorption of ethylene.

The difference between the extrapolated values of $\phi(O_2)$ corresponding to the zero values of Q_i and Q_t again indicates the difference in the structure of adsorption complexes formed in the initial stages of chemisorption and in the region of self-hydrogenation.

From these considerations it follows indirectly that the adsorption of ethylene, hydrogen, and oxygen proceeds probably on the same adsorption sites on the surface, which is in agreement with some results of other authors[38].

Also a number of other effects can participate on the complex behaviour of the nickel surfaces modified by preadsorbed oxygen. *E.g.*, during the formation of the adsorption bond O—Ni a modification of the adsorption properties of many other nickel atoms can take place due to the long-range interactions mediated by the conduction electrons of the metal[39]. Moreover, the chemisorption of oxygen leads to the reconstruction of the nickel surface[40] which may cause the formation of new adsorption sites.

The results of this work show that the surface of polycrystalline nickel can be formally regarded as formed by two regions. The first region adsorbs ethylene with a considerable dissociation of the C—H bonds. It is inactive in hydrogenation due to the preferential poisoning by carbonaceous species. This region is formed by nickel atoms with low coordination and it also preferentially adsorbs oxygen. It is also characterized by a low local value of the work function. The adsorption of ethylene on the second surface region is followed by selfhydrogenation and this region can also be active in hydrogenation.

It is interesting that the adsorption capacity of the surface for ethylene depends in an analogous way on the amount of preadsorbed oxygen as the hydrogenation activity of nickel depends on the oxygen content in the reaction mixture[19]. It is therefore possible that even in this case one of the reasons for the enhanced catalytic activity is the higher surface concentration of ethylene intermediates due to the presence of chemisorbed oxygen.

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Translated by Z. Prášil.