THE INFLUENCE OF TEMPERATURE AND STRUCTURE OF PALLADIUM SURFACES ON THE ADSORPTION OF ETHYLENE AND HYDROGENATION OF ADSORPTION COMPLEXES BY MOLECULAR AND ATOMIC HYDROGEN

Josef KOPEŠŤANSKÝ

J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2

A measurement of the work-function change, combined with the volumetric method and gas product analysis were used for investigation of the influence of temperature and palladium surface structure on the adsorption of ethylene and hydrogenation of its adsorption complexes by molecular and atomic hydrogen. It was verified that on palladium the highest activity for the C—H bond splitting of hydrocarbons is found on the adsorption sites corresponding to low-coordination surface atoms. The activation energy of the C—H bond dissociation is very low ($E_D \approx \approx 2$ kJ/mol); as a result, in the early stages of surface coverage, hydrogen appears on the surface — together with the formation of surface adsorption complexes. The presence of hydrogen is the main reason for the non-linearity of the work-function changes, observed for ethylene adsorption in the low-coverage region. Stable dehydrogenated surface particles are formed also by self--hydrogenation of ethylene in the higher-coverage region. With increasing temperature, the extent of dehydrogenation of the adsorbed complexes also increases — while the influence of molecular hydrogen on the work-function of the surface with pre-adsorbed ethylene becomes less significant. The interaction of atomic hydrogen with ethylene adsorption-complexes caused in all cases irreversible changes of the surface work-function.

The adsorption and catalytic reactions of hydrocarbons on transition metals have been for a long time a subject of intensive studies. Among the most frequently studied systems was the adsorption of ethylene and reactions of its adsorption complexes with hydrogen. The results obtained by various authors differed frequently, depending on the method applied and the experimental conditions used. Recent papers have shown that the topography of the metal surface has a significant effect on behaviour of the adsorbate[1-10].

The chemical composition and structure of the particles adsorbed on the surfaces with microcrystalline deffects can be very different from those adsorbed on ideal surfaces. The surface lattice-defects are also sometimes the reason, why the formed complexes have a reversed orientation of the dipole moment — compared with complexes formed on ideal surfaces[2-3].

The properties of such surfaces were studied by means of LEED and also by other techniques[1-10]. It was observed that on the adsorption sites formed by surface defects — expecially on those containing low-coordination atoms — diatomic molecules are dissociated during the adsorption and in the case of hydrocarbons, C—H bonds (with some metals even C—C bonds) are splitted. The formed hydrocarbon complexes exhibit large bond strengths and very often they have a strongly dehydrogenated composition.

The influence of electrons, photons and electromagnetic field on the composition and structure of the surface complexes is not yet entirely clarified especially when the adsorption of complex molecules (*e.g.* hydrocarbons) is concerned. The results in papers[11-13] have shown that the above mentioned factors can be in many cases the reason for irreversible changes in the adsorbed layer.

This paper presents the results of investigation of the influence of lattice deffects on the hydrogenation and dehydrogenation of hydrocarbons — under conditions, where the above mentioned complicating factors (surface bombardement by electrons and photons and the influence of electromagnetic field) can be excluded. The measurement of the metal work-function change is a suitable method for the above purpose, since it enables to select such an experimental arrangement, in which no side effects can influence either the structure and composition of the adsorbed layers or the gas phase composition of the reaction products. The Kelvin vibrating-capacitor method represents such a type of arrangement[14-17].

Palladium is a suitable metal for this type of investigation. There are several reasons for this selection. First of all — at all temperatures — the palladium work-function increases[18-20] with the adsorption of hydrogen while the adsorption of surface hydrocarbon complexes always leads to decrease of its value[21-24]. On some low-indexed planes (*e.g.* 111), some of the hydrocarbons are adsorbed without a change of their chemical composition (*e.g.* ethylene). In addition, this metal allows also to study the effect of dissolved hydrogen on the adsorption and reactions of hydrocarbons.

Evaporation of the films represents the most simple way of preparation of clean metal surface. Their microcrystalline structure can be, for example varied by deposition of the films on substrates kept at different temperatures[25] or by using different types of sintering[25,26]. Ethylene and the reactions of its adsorption complexes with molecular and atomic hydrogen were chosen for the experimental work. The aim of the experiments with different film-deposition temperatures T_d was to prove the influence of microcrystalline film structure on the changes of the work-function $\Delta\varphi$ in the process of ethylene adsorption. The adsorption measurements carried out for different film temperatures T_a, were intended to clarify the dependence of $\Delta\varphi$ on the extent of dehydrogenation of the adsorbed ethylene molecule, which was determined from the known amounts and composition of the reaction products and adsorbed ethylene (determined was the average atomic ratio H/C of the surface complexes).

The aim of these experiments was to prove that also in the case of ethylene adsorption on palladium, the surface sites which are exhibiting the greatest activity in C—H bond splitting of the chemisorbed hydrocarbon molecules are formed by lattice defects of the surface crystal structure.

EXPERIMENTAL

The adsorption of ethylene and reactions of its adsorption complexes with hydrogen were studied in the ultra-high vacuum system, the construction of which is similar to the system described in paper[17]. The residual gas pressure before evaporation of the films was in all experiments $p \leqq 5 . 10^{-7}$ Pa and in the course of evaporation in no case exceeded the value $1 \cdot 6 . 10^{-6}$ Pa (the residual atmosphere consisted mainly of CO and H_2O (ref.[17]). The films were prepared from palladium of spectral purity (Jonson Matthey Metals, Ltd) which was evaporated from a tungsten support, heated by electric current. Before the evaporation, both the tungsten support and palladium were thoroughly degassed in ultra-high vacuum conditions. The films were deposited on the walls of the adsorption vessel, the construction of which resembled the one described in paper[27]. The vessel walls were kept at temperature 0°C and −195°C, respectively. After the end of evaporation, the pressure above the film surfaces gradually decreased and in all experiments remained below $5 . 10^{-7}$ Pa.

The adsorption of ethylene and reactions of its adsorption complexes with hydrogen were carried out at temperatures −80, 25, 100 and 200°C; before the adsorption, the films were thermally stabilized for at least 15 minutes — always at temperatures exceeding at least 30°C the temperature of the film used in the adsorption. The average time of film deposition varied around 4 hours (with average evaporation rate around $1 \cdot 5$ mg/hour) and the interval between the end of film deposition and the beginning of interaction of the first dose of the adsorbate with a surface never exceeded one hour.

The purification of the adsorbates — ethylene and hydrogen — was similar to the procedure described in paper[17] and in detail is published elsewhere[23]. The atomic hydrogen was obtained by atomization of H_2 on an incondenscent tungsten filament.

The work-function changes were measured in the Kelvin vibrating capacitor arrangement with a phase-sensitive detection of the measured signal. The values of the contact-potential difference which were used for the determination of the work-function (and of its change), were measured with the accuracy better than ±5 mV.

The gas pressure during the adsorption was measured by means of a calibrated Pirani-gauge manometer. The adsorbed amounts were measured volumetrically and the film surfaces were determined by means of xenon adsorption, using the BET and Dubinin–Radushkevich method[28,29].

The gas phase composition above the adsorbed layer was analyzed using the method of desorption[23,30] and also by the analysis of gas phase samples on a JEOL 100 mass-spectrometer.

RESULTS

Ethylene Adsorption

The dependence of the work-function change of the film ($\Delta\varphi = \varphi_a - \varphi_0$, where φ_a is the work-function after adsorption of the particles on the surface, φ_0 is the work-function before the interaction of the particles with the surface) is plotted against the adsorbed amount of ethylene N_a in Fig. 1 and Fig. 2; in Fig. 1 the measured dependence $\Delta\varphi = f(N_a)$ is shown for different film temperatures during the adsorption while in Fig. 2 for different temperatures of film deposition. Ethylene —

in the case of a saturated adsorption layer — decreases the work-function of palladium, independently on temperatures T_d and T_a.

The adsorbed ethylene shows remarkably different behaviour in the different stages of surface coverage: the experimental plot of the work-function change against the amount adsorbed shows a remarkable difference between the low and high coverage region and this difference is even more enhanced by a change of temperature T_a and T_d. Especially in the low coverage region of ethylene adsorption, a change in deposition temperature T_d and an increase of film temperatue T_a, results not only in a change of the absolute value of the slope $\partial(\Delta\varphi)/\partial N_a$ (of the dependence $\Delta\varphi = f(N_a)$) but it reverses also the slope-value sign.

At all temperatures, the ethylene adsorption proceeded in a following way: With adsorbed amounts smaller than N_a^x (where N_a^x corresponds to coverage Q^x, the definition of which was given in ref.[31]), all ethylene from the individual doses was fully adsorbed and no products of surface-interaction appeared in the gas phase. With the adsorbed amounts larger than N_a^x, a self-hydrogenation reaction occurred on the surface - leading to appearance of ethane in the gas phase, the amount of which went up linearly with the increasing coverage (the slope of this linear dependence $\Delta N_{nf}/\Delta N_1$ equaled ≈ 0.5; N_{nf} is the total amount of ethane in the gas phase and N_1

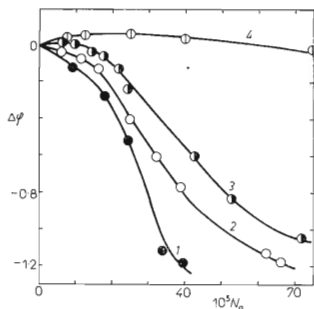

Fig. 1

Plot of the work-function change $\Delta\varphi$ (eV) against the amount of adsorbed ethylene N_a (μ mol cm^{-2}), for different film temperature T_a (deposition temperature of the film $T_d = 0°C$): 1 $T_a = -80°C$; 2 $T_a = 25°C$; 3 $T_a = 100°C$; 4 $T_a = 200°C$
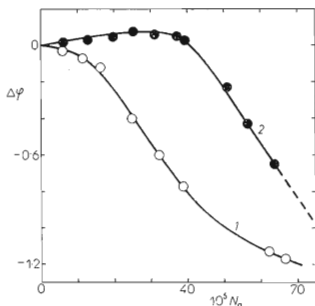
Fig. 2

Plot of the work-function change $\Delta\varphi$ (eV) against the amount of adsorbed ethylene N_a (μmol cm^{-2}), for different film-deposition temperatures T_d (temperature of the film during the adsorption of ethylene $T_a = 25°C$) 1 $T_d = 0°C$; 2 $T_d = -195°C$

is the total amount of ethylene which interacted with the surface). The self-hydro-genation reaction ends after the adsorbed amount N_a^t is reached. In this case, the surface interaction of further ethylene doses resulted in the appearance of unconsumed ethylene in the gas phase (in addition to ethane).

In these three different regions of surface coverage, which were observed at all temperatures T_d and T_a, the time-dependence curves of the work-function changes $\Delta\varphi_i$ showed a remarkably different behaviour for the interaction of the film with individual ethylene doses (the adsorption kinetics in the individual regions has changed). This showed that different surface processes occurred in these three different stages of coverage.

A typical time-dependence plot of the work-function change of a film, corresponding to the interactions of individual ethylene doses (at $T_a = 25°C$ and two different temperatures T_d: 0 and $-195°C$), is given in Fig. 3. The Fig. 4 shows schematically the typical form of $\Delta\varphi_i = f(t)$ for the interaction of ethylene with palladium films in the three above mentioned regions of coverage ($\Delta\varphi_i$ — is the work-function change at time t, in the course of the interaction of the ith dose with the metal surface): In the initial stages of coverage (up to the adsorbed amounts N_a^x) the forms of $\Delta\varphi_i = f(t)$ depended very much on the film temperature during the adsorption of discrete doses, as well as on the deposition temperature of the film. In the self-hydrogenation
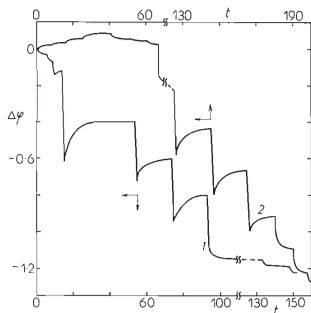

FIG. 3

The form of the work-function change $\Delta\varphi$ (eV) plotted against time t (min), for the interaction of individual ethylene doses with palladium films ($T_a = 25°C$): *1* $T_d = 0°C$; *2* $T_d = -195°C$
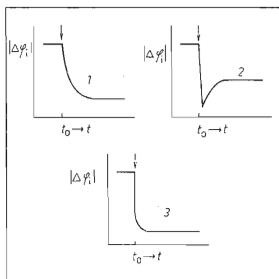
FIG. 4

Typical time-dependence of the absolute value of the work-function change $\Delta\varphi_i = f(t)$, for the interaction of an ethylene dose with palladium, in different regions of the adsorbed amount N_a: *1* $0 \leqq N_a \leqq N_a^x$; *2* $N_a^x \leqq N_a \leqq N_a^t$; *3* $N_a > N_a^t$. Value of $|\varphi_i|$ increases in the direction shown by arrows in the picture

region $\left(N_a^x \leqq N_a \leqq N_a^t\right)$ the curves passed in all cases through a minimum. In the $\left(N_a > N_a^t\right)$ region, $\Delta\varphi_i$ in the time-dependence decreased monotonously until it reached the limiting value $\Delta\varphi_{is}$, typical for the given dose. In the region of surface coverage, the absolute value of $\left|\Delta\varphi_{is}\right|$ decreased (for the interactions of individual ethylene doses) with increasing coverage, until a stage was reached where the addition of a further dose resulted into a practically zero change of $\Delta\varphi_i$. This zero change of $\Delta\varphi_i$ defines the saturated values of the total work-function change $\Delta\varphi_s$ due to the adsorption. For the adsorption of ethylene, this value $\Delta\varphi_s$ did not depend on temperatures T_a and T_d and equaled $1\cdot31 \pm 0\cdot05$ eV (obtained from 10 experiments).

Evacuation of the gaseous reaction products changed the obtained value $\Delta\varphi_s$ by less than $0\cdot1$ eV, which showed that a part of the ethylene adsorption complexes is bound on the palladium surface reversibly.

The coverage interval, in which the slope $\partial(\Delta\varphi)/\partial N_a$ reaches a low absolute value is not identical with the interval of the adsorbed amounts $\left(0 - N_a^x\right)$: at room temperature and at $-80°C$, the interval $\left(0 - N_a^x\right)$ substantially exceeds the interval corresponding to the low value of the slope $\partial(\Delta\varphi)/\partial N_a$. With increasing temperature T_a, the relation between the sizes of those two intervals changes, as a result of the increased degree of dehydrogenation of the adsorption complexes: it was found that the interval $\left(0 - N_a^x\right)$ becomes smaller with increasing temperatures T_a and T_d. On the other hand, the interval of the low absolute slope-value practically does not change with the increase of temperature T_a (with the exception of temperature $200°C$, at which a decomposition of the adsorption complexes takes place) but it increases with the decrease of temperature T_d — which is in addition followed by a change of the slope-value sign.

The H/C atomic ratio of the adsorbed ethylene layers (estimated from the known amounts of reaction products and the amount of ethylene interacting with the film) decreased with increasing temperature T_a. For the adsorbed amount N_a^t, the following H/C ratios were obtained (in parentheses are given the temperatures at which the H/C ratios were determined): $1\cdot8$ $(-80°C)$; $1\cdot2$ $(25°C)$; $1\cdot1$ $(100°C)$; $0\cdot5$ $(200°C)$. With changing temperature T_d, the H/C ratio changed in the following way (at $T_a = 25°C$): $1\cdot0$ $(-195°C)$; $1\cdot2$ $(0°C)$.

Interaction of Ethylene Adsorption Complexes with Molecular Hydrogen

After evacuation of the products present in the gas phase, hydrogen was introduced into the reaction vessel in discrete doses. As a result of its interaction with the adsorption layer, the work-function of the film increased and the composition of the gas phase changed.

At $25°C$, the work-function φ linearly increased with the rising amount of hydrogen consumed in the interaction with the surface and this change was independent on the temperature of film deposition T_d. The final value of $\Delta\varphi$, in the interaction of the ad-

sorption layer with hydrogen (related to the work-function value of the saturated ethylene adlayer on the palladium surface — measured after evacuation of the reversibly bound fraction), equalled roughly $+0.8$ eV. This fact proves that a part of the ethylene adsorption complexes remains in the films bound in such a form that either these complexes do not react with hydrogen or their interaction with molecular hydrogen does not influence any more the work-function of the surface. The gas phase consisted, in addition to hydrogen, from saturated hydrocarbons — ethane and butane. The amount of butane formed represented only several % from the overall amount of hydrogenated products. Independently on the temperature T_d, roughly 1.8 hydrogen molecules were consumed for each molecule of the product which was desorbed into the gas phase, as a result of this interaction. The highest hydrogen consumption was observed for the small total amounts of hydrogen interacting with the surface, probably as the result of its adsorption on the remaining vacant sites in the ethylene adlayer on the surface. The reaction of hydrogen with the adsorption complexes was visibly slower than the adsorption of ethylene on both ypes of the films.

At temperature 100°C, molecular hydrogen had practically no influence on the work-function change, not even at pressure in the range of 10^2 Pa. The maximal detected work-function increase in these cases, did not exceed 30 meV.

Neglecting a very small change of φ, a consumption of hydrogen and hydrogenation of adsorption complexes were observed during this interaction. The gas phase consisted of ethane and butane, both present approximately in the same amount and relative abundance as observed at room temperature. In addition to these products, a very small amount of a higher hydrocarbon (or C_4H_{10} isomer with a higher boiling point) was detected.

At 200°C no consumption of molecular hydrogen was observed, even after a very long time of interaction (around 12 hours). Also, no products of hydrogenation were found in the gas phase and the work-function change was zero.

Interaction of Adsorption Complexes with Atomic Hydrogen

After a stage was reached, in which the work-function did not change any more under the influence of molecular hydrogen, the unconsumed hydrogen and reaction products were pumped away. The atomic hydrogen was prepared on an incondescent tungsten wire, after a hydrogen dose was introduced into the reaction vessel. The initial pressure of molecular hydrogen which was used for the preparation of all doses of atomic hydrogen — as well as the temperature of the filament — were identical. The time of generation of the individual H atom doses was 2 minutes and was constant in all experiments (with the exception of $T_a = 100$ and 200°C, where also longer intervals of generation were used). The heating of the filament, in the absence of hydrogen in the reaction vessel, did not effect the work-function of the film.

The products of the interaction of the adsorbed complexes with atomic hydrogen were condensed in the course of the reaction in a trap which was placed in the vicinity of the reaction vessel and kept at $-195°C$. It is probable that a part of the products in the gas phase could have been decomposed by the interaction with incondescent wire, so that the true composition of the products might have been slightly different from the composition of the condensate. In addition to that, the gas phase might have contained also some uncondensable methane. However, at $T_a \leqq 100°C$, the amount of the eventually formed methane is negligibly low, due to a low effficiency of C—C bond splitting on the palladium. It can be also assumed that the effect of the glowing tungsten wire does not substantially change the distribution of the hydrogenated products, since such an interaction would, most probably, lead to the decomposition of the hydrocarbon molecule — yielding hydrogen (desorbing into the gas phase) and carbon (remaining on the tungsten surface). It can be therefore assumed that the condensable product as a whole originates from the interaction of hydrocarbon adsorption-complexes with atomic hydrogen.

The effect of atomic hydrogen on the work-function changes is shown in Fig. 5 for $T_d = 0°C$ and different temperatures T_a. At $T_d = -195°C$ and $T_a = 25°C$ the atomic hydrogen did not influence the work-function of the surface.

The analysis of the condensable products showed the following composition: at $T_a = 25°C$: ethane only, at $T_a = 100$ and $200°C$: ethane and small amount of a larger hydrocarbon — corresponding by its composition — to the product observed already in the interaction of molecular hydrogen with the adsorption layer at $T_a = 100°C$. For $T_d = -195°C$ and $T_a = 25°C$, the amount of the condensable product was negligible.
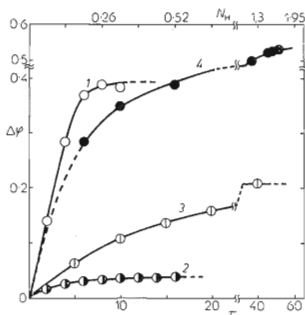

Fig. 5

Dependence of the work-function change $\Delta\varphi$ (eV) on the total amount of interacting atomic hydrogen N_H (μmol cm^{-2}) and on the time of hydrogen generation τ (min), for the hydrogenation of ethylene adsorption complexes with atomic hydrogen: *1* $T_a = 25°C$, time of generation of individual doses $\tau_1 = 2$ min; *2* $T_a = 100°C$, $\tau_1 = 2$ min; $T_a = 100°C$, $\tau_2 = 5$ min; *4* $T_a = 200°C$, $\tau_2 = 5$ min

DISCUSSION

The effect of temperatures T_a and T_d on the work-function of the films was significant, especially in the region of low-coverage — *i.e.* on surfaces where the adsorption is not yet affected by pre-adsorbed complexes[32]. In order to interpret the experimental dependence $\Delta\varphi = f(N_a)$ one can neglect, in the first approximation, for this coverage region the mutual interactions of the adsorbed particles and regard them as completely isolated. On the other side, in the high coverage region it is the mutual interaction of the particles which determines to large extent their adsorption state[33-37].

The differences in the forms of the $\Delta\varphi = f(N_a)$ curves observed in the regions of small and large adsorbed amounts, can be most probably explained by a formation of different adsorption complexes in the different stages of surface coverage[22,23]. The most probable reason for a formation of different surface complexes in different coverage regions can be either the adsorption of ethylene on non-equivalent adsorption surface sites or these different particles can be formed as a result of the passing surface reactions. In each case, the formed surface complexes can differ in structure or even in their chemical composition and they can have therefore different effects on the change of the work-function.

Adsorption of Ethylene in the Low-Coverage Region

The effect of dehydrogenation of the adsorbed ethylene (effect of tempeature T_a):
The form of the measured work-function changes $\Delta\varphi$, plotted against the adsorbed amount N_a (for hydrocarbon adsorption on transition metals), is in some cases explained as a result of dissociative adsorption in the low coverage region of the polycrystalline surface and by a superposition of the effects of the formed surface particles, on the measured value $\Delta\varphi$ (ref.[17,21,23]). This interpretation is based on the observation that hydrogen adsorbed on clean surfaces of some transition metals (*e.g.* Pd, Mo, Ni), at pressures up to 10^{-3} Pa, increases their corresponding work-functions, while the hydrocarbon-complexes usually lead to a decrease of the work-function values[5,17,21-24].

Under the assumption of validity of the above facts, the measured curves $\Delta\varphi = f(N_a)$ (in the low-coverage region) must reflect with increasing temperature T_a (Fig. 1) the influence of the increasing extent of dehydrogenation of the adsorbed molecules and thus of an increasing amount of surface hydrogen atoms formed by the dissociation of ethylene: with the same amounts of adsorbed ethylene — the increase of temperature T_a must result in an increase of the work-function, in agreement with the results in Fig. 1.

If we neglect the mutual interaction between the surface particles in the low-coverage region ("the isolated-particles approximation"), one can assume that the probability of C—H bond dissociation for ethylene molecules interacting with the

surface depends only on the type of the metal and on its temperature T_a during the adsorption. If such C—H bond dissociation requires some activation energy, then the dissociation probability A can be expressed by an exponential function $A = A_0 \exp\left(-E_D/RT_a\right)$, where E_D is the activation energy of C—H bond dissociation for ethylene interacting with the metal surface, $\boldsymbol{R}$ is the gas constant and A_0 a factor independent on temperature T_a.

For $A \neq 0$, following particles can be expected on the film-surface in the adsorption of ethylene; adsorbed hydrogen, dehydrogenated hydrocarbon remainders of a C_2H_x composition and, finally, non-dissociatively adsorbed ethylene (it is assumed that only C—H bonds are splitted on the palladium). The amounts of these, during the adsorption formed particles - denoted as $N_a(H)$, $N_a(C_2H_x)$ and $N_a(C_2H_4)$ — are determined only by the probability A (and thus by temperature T_a):

$$N_a(H) = (4 - x) A N_a \; ; \quad N_a(C_2H_x) = A N_a \; ; \quad N_a(C_2H_4) = (1 - A) N_a \; , \quad (1)$$

where x signifies the amount of hydrogen atoms present in one adsorbed dehydrogenated two-carbon-atom complex C_2H_x. If the dipole moments of these adsorbed particles are denoted as $\mu(H)$, $\mu(C_2H_x)$ and $\mu(C_2H_4)$ then for the relative effective dipole moment, which is defined by the relation

$$\frac{\mu_{ef}}{|\mu(C_2H_4)|} = \frac{1}{4\pi e |\mu(C_2H_4)|} \frac{\partial(\Delta\varphi)}{\partial N_a} \qquad (2)$$

we can write[23]:

$$\frac{\mu_{ef}}{|\mu(C_2H_4)|} = -1 + B A_0 \exp\left(-E_D/RT_a\right) . \qquad (3)$$

$|\mu(C_2H_4)|$ signifies in expressions (2) and (3) the absolute value of the dipole moment of non-dissociatively adsorbed ethylene in the given coverage region; the term B is given by the expression:

$$B = 1 + \frac{\mu(C_2H_x)}{|\mu(C_2H_4)|} + (4 - x) \frac{\mu(H)}{|\mu(C_2H_4)|} . \qquad (4)$$

Expression (3) is based on the assumed superposition of the effects of individual surface particles on $\Delta\varphi$ — and it was obtained after the values for the adsorbed amounts (1) and corresponding dipole moments (2) were substituted in the Helmholtz equation — and using expressions (2) and $A = A_0 \exp\left(-E_D/RT_a\right)$.

The term B is under all circumstances equal or larger than zero. This follows from the fact that the minimum value of the relative effective dipole moment equals -1

i.e. to the value of the dipole-moment for non-dissociatively adsorbed ethylene. Increasing temperature T_a has a much smaller effect on term B than on the exponential factor $\exp(-E_D/RT_a)$. Therefore, if the above mentioned assumption of dissociative adsorption of ethylene for the low coverage region is valid, than the dependence

$$\ln(\mu_{ef}/|\mu(C_2H_4)| + 1) = f(1/T_a) \tag{5}$$

must be (after filling in the experimental data) close to a straight-line, with a negative value of the slope — in agreement with the experiment. The low value obtained for E_D (approximately equal 2 kJ/mol) is consistent with the assumed easy dissociation of ethylene molecules on polycrystalline surfaces, in the low-coverage regions. This result is in agreement with the conclusions in paper[17,21,23].

It can be concluded, that one of the main reasons for the change of the effective--dipole-moment (which is observed with increasing temperature T_a in the low coverage region) is the presence of hydrogen atoms on the surface. These are formed as a result of dehydrogenation of ethylene molecules due to the adsorption.

The Effect of Microcrystalline Structure of the Films (effect of temperature T_d)
As mentioned above, predominately two types of adsorption sites play a role in the adsorption of ethylene on polycrystalline palladium surfaces. From the previous part of discussion (concerning the effect of temperature T_a) it followed that the sites which were responsible for the intensive dehydrogenation of the chemisorbed ethylene molecules were in fact those sites, which were preferentially filled during the adsorption.

For the adsorption of ethylene on these adsorption sites is typical the preferential coverage of these sites and a low absolute value of the effective dipole-moment. The results in Fig. 2 show that the coverage region which corresponds to the low absolute value of the effective dipole moment, increases in size when the film-deposition temperature T_d drops (from 0°C to -195°C). This means that the number of the mentioned adsorption sites on the surface of such films increases. In addition, compared with the films deposited at higher temperatures T_d ($T_d = 0°C$), the orientation of the effective dipole is reversed.

It can be assumed that a change in temperature T_d leads to a change of the microcrystalline structure of the film[25,26]. A lower temperature of metal-film deposition T_d results in a smaller size of the continuous surface regions — containing well-developed crystal planes. Besides, these films have (compared with the films obtained at higher temperatures T_d) a higher proportion of high-indexed crystal planes and also an increased amount of conglomerates or even individually surface-bound metallic atoms. On the other hand, the increasing temperature T_d (or increasing temperature at which the films are stabilized — *i.e.* increasing temperature of film sintering) leads to a formation of "smoother" metal films — *i.e.* the proportion of the well-

-developed, preferentially low-indexed planes, increases[7,36]. The high-indexed planes, which are also present in the evaporated films, are formed by terraces and mono-atomic steps of low-indexed planes. Individual metal atoms bound on the terraces, so as the adjacent atoms surrounding the vacancies and the corner and kink atoms — are denoted as low-coordination atoms. These atoms exhibit a specific behaviour in the interactions with the chemisorbing molecules[1,2,4,5,17]: the interaction of these atoms leads, in general, to intensive fragmentation of molecules and to formation of a very strong adsorption bond. With hydrocarbons, both the C—H and C—C bonds can be splitted[4].

In the basis of the above presented considerations one can assume that a decrease of temperature T_d leads to an increased number of low-coordination surface atoms. Therefore, the adsorption sites in the coverage region corresponding to the low absolute value of effective dipole moment in the ethylene adsorption, can be regarded as identical with the adsorption sites formed by the above low-coordination surface atoms. The shape of the $\Delta\varphi = f(N_a)$ curves at lower temperatures T_d (shown in Fig. 2) can be thus explained (in agreement with the conclusions in paper[4]) by increasing dehydrogenation of ethylene — which is in the interaction with surface, preferentially adsorbed on the low-coordination adsorption sites.

Adsorption of Ethylene in the Medium and High-Coverage Regions

The effect of temperatures T_a and T_d on the shape of $\Delta\varphi = f(N_a)$ curves in this region is not so expressive. Certain differences in features of the curves — corresponding to different applied temperatures T_a and T_d — can be explained by a different pattern of individual crystal planes of the films.

In this coverage region — all adsorption sites formed by low-coordination atoms are already occupied and therefore, the additional adsorbing ethylene covers further sites on the surface. These can be the centres on the well-developed crystal planes. The adsorbing ethylene can form on these sites various surface particles of different structure and stability, possibly even of different chemical composition. In this region, both the direct and indirect interactions between the surface complexes become playing a role[2,37]. A part of the formed particles represents relatively very reactive complexes of low stability, which, due to their presence on the surface, initiate, starting from the point of complete coverage N_a^x, a self-hydrogenation surface reaction, *i.e.* they are precursors of self-hydrogenation. The coverage region, in which this reaction takes place, shows a minimum in the $\Delta\varphi_i = f(t)$ dependence when discrete ethylene doses interact with the surface. This fact reflects the kinetics of the surface processes which involves the adsorption of C_2H_4 molecules, the surface reaction and the desorption of the products into the gas phase. Simultaneously, ethane appears in the gas phase and the metal surface is covered with stable dehydrogenated particles of a C_2H_y $(y \leqq 4)$ composition[23]. Approximately equal values of the ef-

fective dipole-moment in the high-coverage at different temperatures T_a (with the exception of $T_a = 200°C$, where a very intensive thermal decomposition of hydro-carbon complexes is observed — accompanied by evolution of vast amounts of hydrogen into the gas phase[23]) shows that due to self-hydrogenation — stable, identical dehydrogenated particles might have been formed. After the amount N_a^t was adsorbed, the reaction of self-hydrogenation ends. This means that at N_a^t they are no more vacant sites on the studied surface on which the above reactive particles could be further formed. With increasing coverage, further less suitable adsorption sites are occupied on the surface until a saturated adsorption layer is formed. This is evidenced also by the form of the $\Delta\varphi_i$ time-dependence, which shows further only a monotonous decrease. Besides ethane, the unconsumed ethylene is detected in the gas phase. More details concerning the possible types of mechanisms of the self-hydrogenation reaction will be discussed elsewhere[35].

On the basis of the papers[17,32,36], it is possible to assume that the surface complexes in the region $N_a > N_a^t$ are particles with a very low degree of dehydrogenation (practically with the C_2H_4 chemical composition), because in these coverage stages, the dissociative adsorption of ethylene is substantially suppressed.

At the point of saturation of the adlayer, the change of the work-function reaches its limiting value $\Delta\varphi_s$.

In addition to the above mentioned processes, other, polymerization reactions (especially dimerization) proceed on the polycrystalline surface, as it is evidenced by the results obtained in the interaction of hydrogen with adsorbed ethylene layers.

Interaction of Ethylene Adsorption Complexes with Hydrogen

Interaction with molecular hydrogen: The results show that the work-function changes of the films caused by the interaction of the adsorption complexes with molecular hydrogen, become much smaller with increasing temperature T_a. While at room temperature this change — after the addition of hydrogen — varies around one eV, at 100°C it equals only about 30 meV and at 200°C it is practically zero. These data show that not all types of adsorption complexes are hydrogenated by molecular hydrogen and besides that, some types of complexes hinder the adsorption of hydrogen on the surface. The fact that at increased temperatures the resulting work-function change (in the interaction of adsorbed layers with hydrogen) drops to zero, shows, that the above complexes could be precisely those dehydrogenated complexes, which cannot be removed from the surface by hydrogen. If this is true, then the complexes which can be removed from the surface, are those with a low--degree of dehydrogenation — corresponding closely to the formula C_2H_4. According to the above presented discussion these should be the complexes which are formed in the region $N_a > N_a^t$, because at lower coverage the stable surface particles are dehydrogenated.

As a consequence of the hydrogenation of the hydrocarbon complexes, some adsorption sites become free and they are subsequently covered with hydrogen which occupies also other free sites not suitable for ethylene adsorption.

The experimental results in Fig. 3 show that the increase in the amount of adsorbed ethylene from N_a^i up to the saturated layer causes a change in the work-function, varying in its absolute value between $0.4 - 0.5$ eV — depending on temperature T_d. The change of the palladium work-function, due to the hydrogen adsorption, can reach the values between $0.2 - 0.35$ (ref.[19-21]), depending on a type of the crystal plane. It can be therefore expected that at 25°C, the limiting change of φ, observed for the interaction of the adsorption-complexes with molecular hydrogen, should vary between $0.6 - 0.8$ eV, which is in satisfactory agreement with the experimental data.

The product of this hydrogenation is ethane; at high pressure of the interacting hydrogen above the adlayer — besides ethane — also a hydrocarbon of a C_4H_{10} composition is detected.

A more detailed description of the probable mechanism of hydrogenation of the ethylene adsorption-complexes layers will be given elsewhere[35].

Interaction with atomic hydrogen: On the basis of the above discussion it can be assumed that the surface contains already before the interaction with atomic hydrogen a large amount of adsorbed hydrogen (respectively of hydrogen dissolved in the metal) which does not react with the adsorbed ethylene complexes in the considered interval of temperatures T_a. Therefore, in order to explain the hydrogenation of surface complexes with atomic hydrogen one has to consider also other types of interactions, than those, that would occur between the adsorbed hydrocarbon complexes and adsorbed hydrogen atoms. On basis of the obtained result it is possible to assume that the most probable mechanism is the interaction between free hydrogen atoms from the gas phase and the surface complexes of a C_2H_y composition:

$$C_2H_y \, (a) \; + \; H \, (g) \quad \rightarrow \quad C_2H_{y+1} \, (a) \, ,$$
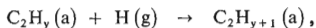
(where a and g signify the particles adsorbed and free in the gas phase, respectively). Only some types of surface complexes can participate in these reactions — such for which the above reaction will not have a very high potential barrier. Thence, this addition of reactive hydrogen atoms can explain the appearance of ethane and polymers, as well as, the increase of the work-function change with the increasing overall amount of interacting atomic hydrogen. In the case of the films with the deposition temperature $T_d = -195$°C, the change of the work-function in the interaction of atomic hydrogen with ethylene adsorption-complexes was zero. These films, compared to the films with deposition temperature $T_d = 0$°C, possess a higher proportion of adsorption sites formed by low-coordination atoms. As mentioned

before, ethylene is adsorbed on these sites with a high extent of dissociation and the formed surface complexes are under the conditions used in this work, practically unreactive.

The overall change of the work-function observed in the interaction of the adsorption-complexes with hydrogen (both molecular and atomic) was, however, in all cases lower than the absolute value of the change of φ, found in the adsorption of ethylene. This fact shows that even after the hydrogenation, the film surface is covered with a significant amount of strongly bonded hydrocarbon residues.

REFERENCES

1. Derochette J. M.: Bull. Soc. Chim. Belg. *88*, 549 (1979).
2. Ertl G.: J. Vac. Sci. Technol. *14*, 435 (1977).
3. Derochette J. M., Marien J.: Phys. Stat. Solidi (a) *39*, 281 (1977).
4. Somorjai G. A.: Advan. Catal. Relat. Subj. *26*, 1 (1977).
5. Lang B., Joyner R. W., Somorjai G. A.: Surface Sci. *30*, 440 (1972).
6. Jobic M.: Proc. 4th Intern. Conference on Solid Surfaces, Cannes, September 22—26, 1980 (D. A. Degras, M. Costa, Eds), Vol. 2, p. 746, Suppl. a la Revue: *Le Vide les Couches Minces* No 201, Paris 1980.
7. Yasumuori I., Kabe T., Inoue Y.: J. Phys. Chem. *78*, 583 (1974).
8. Baron K., Blakely D. W., Somorjai G. A.: Surface Sci. *41*, 45 (1974).
9. Bernasek S. L., Sickhaus W. L., Somorjai G. A.: Phys. Rev. Lett. *30*, 1202 (1973).
10. Somorjai G. A.: Surface Sci. *34*, 156 (1973).
11. Demuth J. E., Eastman D. E.: J. Vac. Sci. Technol. *13*, 283 (1976).
12. Ibach H., Lehwald H.: J. Vac. Sci. Technol. *15*, 407 (1978).
13. Lo W. J., Chung Y. W., Kesmodel L. L., Stair P. L., Somorjai G. A.: Solid State Commun. *22*, 335 (1977).
14. Culver R. V., Tompkins F. C.: Advan. Catal. Relat. Subj. *11*, 67 (1959).
15. D'Arcy R. J., Surplice N. A.: J. Phys. Appl. Phys. *3*, 482 (1970).
16. Rivière J. C. in the book: *Solid State Surface Science* (M. Green, Ed), Vol. 1, p. 180. Dekker, New York 1969.
17. Bastl Z.: This Journal *43*, 1665 (1978).
18. Conrad H., Ertl G., Latta E. E.: Surface Sci. *41*, 435 (1974).
19. Duś R.: Surface Sci. *42*, 324 (1973).
20. Duś R.: J. Catal. *42*, 334 (1976).
21. Bastl Z.: This Journal *43*, 1943 (1978).
22. Duś R., Lisowski W.: Surface Sci. *85*, 183 (1979).
23. Kopešťanský J.: *Thesis.* Czechoslovak Academy of Sciences, Praha 1981.
24. Inoue Y., Kojima I., Moriki S., Yasumuori I.: Proc. 6th Int. Congr. Catalysis, London 1976, preprint A6.
25. Anderson J. R.: *Structure of Metallic Catalysts*, Academic Press, London, New York, San Francisco 1975.
26. Nieuwenhuys B. E., Bouwman R., Sachtler W. M. H.: Thin Solid Films *21*, 51 (1974).
27. Alexander C. S., Pritchard J.: J. Chem. Soc., Faraday Trans. 1 *68*, 203 (1972).

28. Thomas J. M., Thomas W. J.: *Introduction to the Principles of Heterogeneous Catalysis*, Academic Press, London and New York 1967.
29. Bastlová H.: This Journal *40*, 3100 (1975).
30. Bastl Z., Cuřínová A.: This Journal *37*, 1490 (1972).
31. Merta R., Ponec V.: J. Catal. *17*, 79 (1970).
32. Miyahara K.: J. Res. Inst. Catal. Hokkaido University *14*, 134 (1964).
33. Ito M., Mori I., Kato T., Suetaka W.: Appl. Surface Sci. *2*, 543 (1979).
34. Abon M., Teichner S. J.: Nuovo Cimento, Suppl. *5*, 521 (1967).
35. Kopešťanský J.: This Journal, in press.
36. Zachař P., Bastl Z., Adámek J.: This Journal *46*, 340 (1981).
37. Benziger J. B.: J. Chem. Soc., Faraday Trans. 1 *76*, 49 (1980).

Translated by Z. Dolejšek.