ACETYLENE CHEMISORPTION AT PALLADIUM: EFFECT OF TEMPERATURE AND STRUCTURE OF THE SURFACE

Josef KOPEŠŤANSKÝ

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

The effect of temperature and structure of the palladium surfaces on acetylene chemisorption was studied along with the interaction of the adsorbed layers with molecular and atomic hydrogen. The work function changes were measured and combined with the volumetric measurements and analysis of the products. At temperature below 100°C, acetylene is adsorbed almost without dissociation and forms at least two different types of thermally stable adsorption complexes. Acetylene adsorbed at 200°C is partly decomposed, especially in the low coverage region. Besides the above mentioned effects, the "template" effect of adsorbed acetylene was studied in the temperature range from −80 to 25°C. It has been shown that this effect is a typical phenomenon of the palladium–acetylene system which is not due to surface impurities.

Acetylene forms at the transition metals much stronger adsorption bonds than ethylene[1,2]. This fact is, inter alia, usually related with the additional π-bond in acetylene molecule which can also take part in the interaction with the surface during chemisorption. From the so far obtained results, it is obvious that the chemisorption of hydrocarbons at metals is substantially affected by the topography and temperature of the surface[3−5]. In spite of the importance of this problem, it has been relatively only very little studied in the case of acetylene[4−6] (some questions concerning these effects were studied preferentially with platinum and nickel). This is particularly true for the acetylene chemisorption at palladium above the room temperature.

The metal work function change measurements represent a useful procedure for the investigation of adsorption layers and surface processes. Studies of this sort, combined with volumetric measurements of the adsorbed amounts and amounts of reaction products formed (connected with analysis of the products) permit, in the case of hydrocarbons, to draw conclusions on the composition of the adsorption layer as well as on the surface processes. As a suitable method for the work function change measurements may serve the Kelvin vibrating-capacitor method which belongs to one of the non-destructive methods applied in the surface studies. A preference of the Kelvin method is connected with the fact that by using this method one does not affect the adsorption layer, as well as the gas phase of the adsorbates and reaction products by such complicating factors as are a strong electrostatic field or bombardment of the surface with electrons, photons or other particles. The above method can be used in a wide range of temperatures of the

adsorbent and it is not limited by the pressure of the adsorbates and reactants. An investigation of the effect of temperature and structure of the palladium surfaces on the chemisorption of acetylene forms a subject of the present paper.

EXPERIMENTAL

The experimental procedure applied is identical with that one used in the adsorption of ethylene[3]. Also the palladium surfaces were prepared under conditions described in paper[3]. The surfaces were kept during the adsorption and surface reactions at temperatures $T_a = -80, 25, 100$ and $200°C$, respectively. Different structures of the studied surfaces were obtained by varying temperature T_d of the support at which films were deposited (deposition temperature was either 0 or $-195°C$).

Acetylene used in the adsorption was a research-grade-purity product of Matheson company. Before dosing, acetylene was purified directly in the vacuum apparatus by multiple vacuum distillation. Hydrogen used for interaction with the acetylene adsorption complexes was obtained electrolytically and it was purified by diffusion through a palladium thimble (heated at 200°C), placed in line with two cold traps kept at liquid nitrogen temperature. Atomic hydrogen was prepared by atomization of the molecular hydrogen on a hot tungsten filament. Surface area of the films was determined by physical adsorption of xenon at liquid nitrogen temperature, using the BET and DR method[7]. The values of the factor of roughness for the palladium films prepared at various temperatures T_d were close to $R \approx 4$ ($T_d = 0°C$) and $R \approx 8$ ($T_d = -195°C$).

RESULTS

The work function change $\Delta\varphi$ used in this paper is everywhere defined as $\Delta\varphi = \varphi_a - \varphi_0$, where φ_a and φ_0 are the film work functions before and after interaction of the particles with the studied surface.

Adsorption of Acetylene

The effect of palladium surface temperature T_a on the work function change $\Delta\varphi$ is shown in dependence on the amount of adsorbed acetylene N_a, in Fig. 1. The dependence of $\Delta\varphi = f(N_a)$ on the deposition temperature of the films, T_d, is given in Fig. 2. At all studied temperatures, the work function of the palladium surfaces decreased with increasing coverage (except in the low coverage region at $T_a = 200°C$ where work function φ went up). The final saturation value $\Delta\varphi_s$ (defined as the work function change corresponding to the acetylene adsorption saturated surface — see ref.[3]) was, in the range of temperatures from 25 to 200°C, practically independent of temperature T_a and T_d and equal $-1·72 \pm 0·05$ eV (the value of $\Delta\varphi_s$ was obtained from 16 experiments). Only at $T_a = -80°C$, the experimental value $\Delta\varphi_s$ was lower and equal $-0·84 \pm 0·05$ eV.

Adsorption of acetylene proceeded at all temperatures T_a and T_d in a following way: Up to the surface coverage Θ^x (ref.[8]), all introduced acetylene was adsorbed

without any visible appearance of the interaction products in the gas phase $(\Theta^x$ corresponds to the initial irreversibly adsorbed amount of acetylene N_a^x, for equilibrium pressure in the gas phase above the adsorption layer $\sim 2 \cdot 6 \cdot 10^{-3}$ Pa. The value N_a^x was obtained by extrapolation of the dependence $N_{nf} = f(N_1)$, for $N_{nf} \to 0$, where N_{nf} is the amount of gaseous reaction products formed during the adsorption and N_1 denotes the overall amount of acetylene interacting with the surface). At higher coverage than Θ^x, a stationary pressure of reaction products was measured above the studied films and the amount of these products was going up with increasing coverage. Three additional coverage regions were detected besides the already mentioned range $0 \leqq \Theta \leqq \Theta^x$. The amount of reaction products N_{nf} in these regions was, in first approximation, a linear function of the total amount of introduced acetylene, N_1. The slopes $k = \partial N_{nf}/\partial N_1$ of these linear dependences were going up with increasing surface coverage and they had the following values: $k = 0 \cdot 25$ in the range $\Theta^x \leqq \Theta \leqq \Theta^{xt}$, $k = 0 \cdot 5$ in the range $\Theta^{xt} \leqq \Theta \leqq \Theta^t$ and $k = 1$ for the coverage $\Theta < \Theta^t$ (except at temperature $T_a = -80°C$ where the initial slope $k = 0 \cdot 25$ was not observed). The above three different coverage regions were in accordance with the diverse time courses of surface work function changes $\Delta\varphi_i = f(t)$
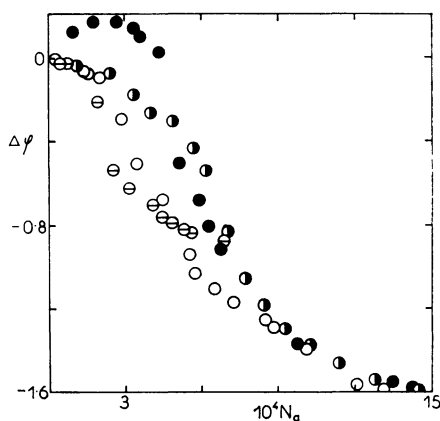

Fig. 1

Dependence of the palladium-film work function changes $\Delta\varphi$ (eV) on the amount of adsorbed acetylene N_a ($\mu mol\ cm^{-2}$) for different film temperatures T_a during the adsorption (film deposition temperature $T_d = 0°C$); **1** ($\ominus$) $T_a = -80°C$; **2** ($\bigcirc$) $T_a = 25°C$; **3** ($\circleddash$) $T_a = 100°C$; **4** ($\bullet$) $= 200°C$
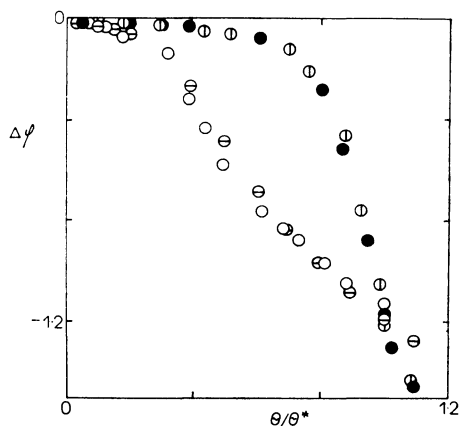

Fig. 2

Dependence of the palladium-film work function changes $\Delta\varphi$ (eV) on the coverage Θ/Θ^* (specified in the text) during acetylene adsorption on the films prepared at different deposition temperatures T_d (temperature of the films during acetylene adsorption kept at $T_a = 25°C$); **1** ($\bigcirc$, $\ominus$) $T_d = 0°C$; **2** ($\bullet$, $\oplus$) $T_d = -195°C$

during interactions of the individual doses of acetylene (different kinetics of acetylene interaction with the surface).

The reaction products had a following composition: At temperature T_a, in the range $(-80, 25°C)$, the gas phase above the adsorption saturated surface consisted of acetylene only. At 100°C, small amounts of ethylene and ethane were detected in addition to the acetylene (in units of percent of the total amount of reaction products). At 200°C, in addition to acetylene, ethylene and ethane present in amounts comparable with the temperature 100°C, large amounts of products which did not condense at liquid nitrogen temperature were found (hydrogen, respectively methane). These were accompanied with a very small quantum of larger oligomer-type hydrocarbon which appeared in tenths of percent from the overall amount of gas phase after the adsorption.

A removal of the gas phase led to a change of value $\Delta\varphi_s$ which depended on surface temperature T_a. This fact indicated a presence of the reversibly bound fraction of adsorption complexes. The largest changes $|\Delta\varphi_s|$ were registered at temperatures -80 and 25°C where $|\Delta\varphi_s|$ dropped after removal of the gas phase, by as much as $0·1$ eV (independently of T_d). On contrary, at 100 and 200°C, this decrease was zero.

Palladium films were also used to study the "template" effect of acetylene[9]. After obtaining an acetylene adsorption saturated layer at $-80°C$, the gas phase was pumped off and the surface temperature raised to 25°C. During this time, C_4H_8, C_6H_6, C_2H_4, C_2H_6 molecules and also a small amount of C_2H_2 desorbed from the surface. The hydrocarbons C_4H_8 and especially C_6H_6 prevailed absolutely in the mass spectra of the desorption products. Experiments have proved that the "template" effect can be observed also at atomically clean palladium surface (in paper[9] this effect was described for palladium black).

Interaction of Acetylene Adsorption Complexes with Hydrogen

The results found in the interaction of molecular and atomic hydrogen with the layers of acetylene adsorption complexes are given in Figs 3 and 4 (Fig. 3 presents only the results obtained at 25°C, however, similar curves were obtained also at other temperatures). At all studied temperatures, the surface work function changes in interaction with the molecular hydrogen were only reversible and the amount of condensable hydrogenation products was negligibly low. With atomic hydrogen, the measured work function changes were irreversible and besides, small amounts of desorbed, condensing products were found. The final work function increase resulting from the interaction with atomic hydrogen was, however, dependent on the temperature of the surface and with increasing T_a it became smaller. Readsorption of acetylene at the surfaces after these hydrogenations has shown that the main part of the irreversible work function change due to the interaction with hydrogen is caused overwhelmingly by irreversible bonding of the hydrogen atoms from the

gas phase in the hydrocarbon surface layer (adsorption of hydrogen atoms at the free adsorption sites or interaction of these atoms with the hydrocarbon complexes leading to formation of new, strongly bonded complexes at the surface). Only a very small part of the above changes results in desorption of the hydrocarbon complexes from the surface into the gas phase. The temperature of the film deposition had no visible effect on the hydrogenation of the acetylene adsorption complexes.

DISCUSSION

Adsorption of acetylene leads at comparable temperatures (with the exception of $T_a = -80°C$) to a more pronounced decrease of palladium work function than other hydrocarbons, like ethylene[3] or cyclopropane[10].

The magnitude of the final work function change reached during the hydrocarbon adsorption can be affected by a number of factors. It can be connected with the unequal amounts of hydrocarbon molecules adsorbed at the adsorption saturated
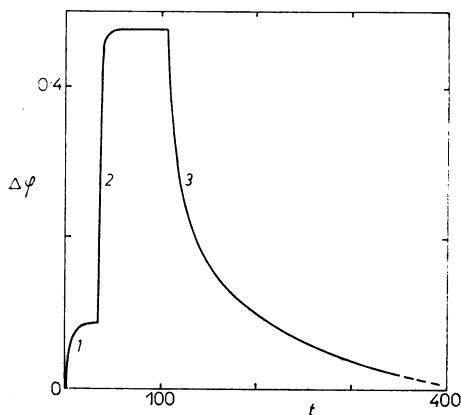

FIG. 3

Dependence of the palladium-film work function changes $\Delta\varphi$ (eV) on the time t (min) of interaction of the molecular hydrogen with acetylene adsorption complexes ($T_a = 25°C$); *1* at pressure 10^{-1} Pa of interacting hydrogen; *2* at the hydrogen pressure increased up to $\sim 10^2$ Pa; *3* after pumping off the gas phase
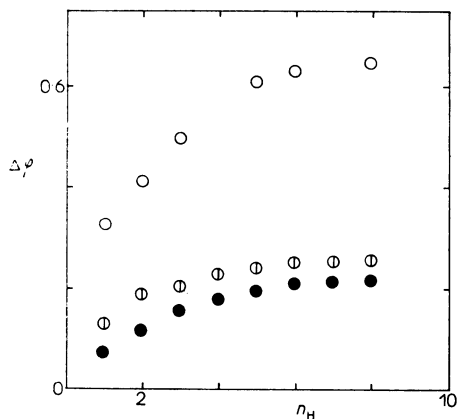
FIG. 4

Dependence of the palladium-film work function changes $\Delta\varphi$ (eV) on the number of equal doses of atomic hydrogen in n_H the course of interaction with the acetylene adsorption complexes at various temperatures T_a (film deposition temperature $T_a = 0°C$); *1* ($\circ$) $T_a = 25°C$; *2* ($\oplus$) $T_a = 100°C$; *3* ($\bullet$) $T_a = 200°C$; a single dose of atomic hydrogen represents approximately $6·5 . 10^{-3}$ μmol . . cm^{-2} hydrogen atoms

surfaces N_{as} (*e.g.*, the ratio of these amounts in the acetylene and ethylene adsorption at saturated palladium surfaces $N_{as}(C_2H_2)/N_{as}(C_2H_4)$ is roughly equal 2). Another possible reason can be connected with the unlike electronic structures of the various hydrocarbons and with unequal changes of these structures during their interaction with the surface. These changes may include, *e.g.* excitation of the molecules, re-hybridization of their orbitals, deformation of their structures and possibly, even a change of their chemical composition caused by splitting of the C—C and C—H bonds, surface reactions, *etc.* Even a most simple qualitative distinction between the electronic structures of the hydrocarbon molecules (*e.g.* according to a type of bond connecting the carbon atoms) provides sort of a formal correlation between the magnitude of $|\Delta\varphi_s|$ and the hydrocarbon structure. One can see from the experimental data that $|\Delta\varphi_s|$ of the palladium surface goes up with the increasing bond order of the carbon–carbon bond of adsorbed molecules: *e.g.*, $\Delta\varphi_s$ for the cyclo-propane possessing three σ bonds is equal -0.98 ± 0.1 eV (ref.[10]); the saturation value $\Delta\varphi_s$ for ethylene, with one σ and one π- bond is equal -1.31 ± 0.05 eV (ref.[3]); in the case of acetylene, with one σ and two π bonds, $\Delta\varphi_s$ in the adsorption is $-1.72 \pm \pm 0.05$ eV (present paper). The absolute value of $|\Delta\varphi_s|$ depends also on the type and magnitude of the mutual (direct and indirect) interactions between the adsorption complexes in the adsorption saturated layer.

The overall result of hydrocarbon interaction with metals is the formation of additional dipole layers at these surfaces. These layers are the final reason for the observed work function changes $\Delta\varphi_s$ (the ratio of the slopes $k = \partial \Delta\varphi/\partial N_a$ — expressing the increase of $|\Delta\varphi_s|$ with increasing surface coverage N_a in the acetylene and ethylene adsorption, at 25°C, is equal $k(C_2H_2)/k(C_2H_4) \approx 1.7$). In the case of acetylene adsorption — as it is evident from the mentioned above, there is a number of favourable factors enhancing the experimentally found, increased palladium work function change in comparison with other hydrocarbons.

The results of the investigation of acetylene adsorption at different temperatures T_a and T_d have shown that acetylene forms at the palladium surfaces at least two different types of adsorption complexes. This leads to unsimilar experimental courses $\Delta\varphi = f(N_a)$ in the region of the low and high adsorbed amounts (Figs 1 and 2). Such behaviour can be most simply explained by a formation of two types of statio-nary adsorption complexes, with unequal dipole moments having diverse effects on the work function change $\Delta\varphi_s$. Similar conclusions were formulated in paper[11] based on the results obtained by reflexion infrared spectroscopy.

There is a number of reasons for a formation of more different types of adsorption complexes at metal surfaces. The first can be connected with adsorption of the particles at non-equivalent sites on the surface, though there can be also other reasons for their formation — *e.g.* the proceeding surface processes. Let us, nonetheless, assume that both postulated unlike types of complexes are formed in the course of acetylene adsorption, at two different adsorption sites. Since the measured courses $\Delta\varphi = f(N_a)$

do not have the same form in the region of the small and large adsorbed amounts, we shall assume next that occupation of these various adsorption sites with acetylene has not the same effectivity in the region of the low and the high coverage: In the low coverage region, adsorption sites of only one type are being occupied. Only after all of them have been filled up, acetylene is effectively sorbed (in the region of medium and high coverage) also on the second type, less favourable sites. It is clear from the data (Fig. 1) that the acetylene adsorption at surface sites primarily filled in the low coverage region is almost unaffected by the temperature T_a. Independent of this temperature, acetylene forms surface particles which have almost identical dipole moments (this fact is reflected in the experimental plots $\Delta\varphi = f(N_a)$ in identical slopes $\partial\,\Delta\varphi/\partial N_a$). Adsorption at 200°C represents an exception since, in this case, extensive thermal decomposition of adsorbed complexes takes place. The work function value goes therefore at this temperature up and effective dipole moment changes its orientation.

The dependences $\Delta\varphi = f(N_a)$ measured in the hydrocarbon adsorption at transition metal surfaces, especially in the low coverage region (where the adsorbed particles can be considered as isolated and mutually non-interacting), are in some cases explained as a consequence of dissociative adsorption of the hydrocarbons and super-position of the effects of the formed surface particles, on the final work function change of the surface[3,10,12]. Let us assume that this explanation is valid also for the acetylene adsorption at palladium. From the form of the curves $\Delta\varphi = f(N_a)$ mea-sured in the low coverage region, at various temperatures it is evident that acetylene is adsorbed at the palladium surfaces, in the range of temperatures from $-80 \leqq T_a \leqq \leqq 100°C$, without dissociation. Such observation is in accordance with the results in papers[11,13], pointing out that no chemisorbed hydrogen was observed at the surface in the course of acetylene adsorption at palladium (Pd (111)) at the room temperature. According to paper[14], the thermally stabilized palladium film surfaces consist mainly of low-indexed crystal planes, predominantly (111). Besides that, it was observed[11,13] that a very small fraction of adsorbed acetylene could dissociate at temperatures increased up to $T_a \leqq 200°C$.

The independence of dipole moments, in the low coverage region, on temperature indicates that acetylene interaction with the palladium surfaces yields, at this stage of coverage, very stable surface species − e.g. of a type of surface compound between the adsorbed acetylene and the reactive surface atoms or metal atom groups. As long as the temperature change does not lead to decomposition of the above mentioned surface species, the dipole moment should be also independent of temperature. The low absolute value of the effective dipole moment which is observed in this region can be explained by assumption of a low net electron charge transfer between the metal surface and the acetylene molecules adsorbed during formation of the adsorption bond − e.g. by a nearly balanced electron transfer from the occupied π orbitals of acetylene molecules to the unoccupied metal surface states and, back-

-donation from the fully occupied surface states to the free antibonding π^* orbitals of the adsorbed acetylene molecules. This fact may be a consequence of the structure of the primarily filled adsorption sites (represented in major by the atomic scale defects of microcrystalline structure at which particles exhibit special behaviour during the adsorption[15]).

Also in the high coverage region, the effective dipole moment values are almost independent of temperature T_a. Along with the results obtained at low coverage, the above fact points at the stability of the structure and chemical composition of the acetylene adsorption complexes over a wide range of temperature and coverage.

The effect of the film deposition temperature T_d on acetylene adsorption could be seen particularly in the low coverage region, as a change of size of the interval of coverage for which the adsorbed acetylene has, in absolute value, low effective dipole moment. Since with a change of temperature T_d, the dipole moment changed only negligibly, it was possible to assume that in both cases (for film deposition temperatures $T_d = 0$ and $-195°C$), identical surface particles had been formed. The increase of size of the coverage region in which adsorbed acetylene molecules have low dipole moment values — which is found with decreasing deposition temperature — signifies that a fraction of the corresponding adsorption sites at these surfaces had gone up. According to papers[14,16], lowering of the film deposition temperature leads to diminution of the continuous surface regions containing well developed crystal planes and to an increase of the fraction of high-indexed crystal planes. Simultaneously rises also the number of conglomerates and possibly even single metal atoms bound to the surface. Consequently, the number of atomic scale defects of the crystallographic structure at such surfaces also rises, *i.e.* a number of low-coordination metal surface atoms goes up. One can therefore identify the adsorption complexes formed in this coverage region, with the acetylene adsorption at the adsorption sites formed mainly by low-coordination metal atoms. In the region of medium and high coverage most of adsorption sites formed by the low-coordination atoms are filled up. Adsorbed acetylene molecules occupy therefore surface positions which can be, in this case, located predominantly at the well developed crystal planes. At higher coverage, the direct and indirect interactions between the surface complexes become also of importance[15,17]. This fact, concurrently with the dissimilarities found in the acetylene adsorption at various crystal planes explains certain differences observed in the adsorption on the films with different deposition temperature T_d.

At $T_a = 200°C$ — particularly in the region of initial coverage, acetylene decomposed into a highly dehydrogenated carbonaceous adsorbed residuum, and hydrogen — desorbing partially into the gas phase. It is likely that at the above temperature, along with the dissociation of the C—H bonds, some of the C—C bonds were also split which resulted in formation of adsorbed radicals of C—H type. The presence of hydrogen and highly dehydrogenated carbon particles at the palladium surface explains the increased values of the work function in this coverage region. In the

region of high coverage, in addition, surface reactions were observed besides the acetylene adsorption on the "carbon" layer. Hence — in contrast with low temperature T_a, it was possible to see in the gas phase also small amount of ethane, ethylene and oligomer products. Lesser extent of thermal decomposition of the acetylene adsorbed at the "carbon" layer and formation of the acetylene adsorption complexes at this layer may explain the final work function decrease also at this temperature.

Large majority of the acetylene surface complexes at palladium is strongly bound to the surface and cannot be removed by interaction with molecular or atomic hydrogen at any of the investigated temperatures T_a. As indicated by the reversible work function changes (Fig. 3), molecular hydrogen is bound to these surfaces in a reversible, presumably molecular form which is inert in the reactions. The irreversible increase of surface work function in the interaction with atomic hydrogen (Fig. 4) is caused by bonding of the hydrogen atoms from the gas phase in the adsorbed acetylene surface layer and only partially by the reaction of hydrocarbon adsorption complexes with atomic hydrogen — both adsorbed or present in the gas phase (leading to desorption of these complexes into the gas phase). Only very small amount of products of hydrogenation was found in these interactions and also the work function changes detected after the readsorption of acetylene were negligible. The final work function changes of the acetylene adsorbed layers due to the interaction with atomic hydrogen become less marked with the increasing temperature T_a. This fact can be connected with a higher extent of dehydrogenation of the hydrocarbon surface complexes at elevated temperatures T_a. The less pronounced irreversible changes of φ at elevated temperatures T_a are thus in accordance with the lower number of free surface sites available for the adsorption of gaseous hydrogen atoms at these surfaces. Adsorption sites which are free for the hydrogen adsorption but not suitable for the adsorption of acetylene are filled with hydrogen atoms which are formed at the surface as a result of dissociative adsorption of acetylene. The amount of this hydrogen increases with rising temperature of the surface layer. Another type of surface process which may take place in the interaction of the acetylene adsorption layers with atomic hydrogen is a process leading to formation of new, strongly bonded surface particles — comprising the acetylene adsorption complexes and interacting hydrogen atoms (these particles do not, however, desorb into the gas phase). As an example of such a new, strongly bonded particle can serve (assuming validity of the non-dissociative adsorption of acetylene at palladium) complexes of chemical composition C_2H_3 (e.g. $HCCH_2$ and CCH_3). Complexes with other chemical composition (e.g. C_2H_x where $3 \leq x \leq 6$) can be with high probability excluded on basis of the experimental results with the readsorption of acetylene. Part of these complexes is held at the palladium surfaces less strongly than acetylene still, they were not detected in gas phase after the readsorption. One can therefore assume the following reactions at the surface: $HCCH\,(a) + H\,(g) \rightarrow HCCH_2\,(a)$ or $CCH_2\,(a) + H\,(g) \rightarrow CCH_3\,(a)$ — with a possibility that atomic hydrogen is

adsorbed at first and only then it reacts with the surface complexes ((a) and (g) signify particles which are either adsorbed or present in the gas phase). From the above mentioned, newly formed complexes, species CCH_3 have much greater stability up to relatively rather high temperatures[18,19]. Hence, the experimental results in Fig. 4 can be explained, based on the above processes, if we take into account that the work function of the palladium surfaces containing complexes HCCH or CCH_2 is lower than that of the surfaces containing the newly formed complexes $HCCH_2$ or CCH_3 (the amount of undissociatively adsorbed acetylene goes down with rising temperature T_a and thus drops also the amount of newly formed strongly-bond complexes).

Unlike for palladium, literature provides relatively broad supply of experimental data on the acetylene adsorption at platinum[13-24]. These data show that acetylene is, with high probability, adsorbed at platinum in a wide range of temperature without dissociation and forms at these surfaces complexes with a structure and type of bond to the surface which are highly sensitive to temperature. The following types of acetylene adsorption complexes have been derived most frequently by means of the various experimental methods: a) the $\pi - d$ complex, in the temperature region of the order of magnitude around $-200°C$ b) the metastable di-σ with sp^2 hybridization and partial contribution of the $\pi - d$ bond, with axis of the C—C bond parallel to the surface; this type appears at temperature about $-100°C$ and above it (at the (111) plane, these complexes are bound to three surface atoms: with a di-σ bond to two of them and with a $\pi - d$ bond to the third one) c) the following new types of stable surface particles have been derived at temperatures higher or equal $25°C$: i) the di-σ olefinic type of complex[13,25] ii) the complex of vinylidene type CCH_2 (ref.[18,22]) iii) ethylidyne type of CCH_3 complex in the presence of adsorbed hydrogen[18,24], especially at temperatures T_a higher than $70°C$.

Considering the close relation between metals Pt and Pd, one can expect that complexes of similar types will be formed also at the palladium surface, though some diversities arising $e.g.$ from the ability of palladium to absorb large amounts of hydrogen or from the existence of the acetylene template effect (which is rather unlikely at platinum[26]) may be expected. The measurement of $\Delta\varphi$ in the course of adsorption and surface reactions is, itself, not sufficient for extension of the concepts formulated for the acetylene adsorption at platinum, also on palladium. Notwithstanding, the results which are discussed in this study of the acetylene adsorption on palladium are consistent with the conclusions derived for platinum.

REFERENCES

1. Thomson S. J., Webb G.: *Heterogeneous Catalysis, Oliver and Boyd*, Edinburgh 1968.
2. Thomas J. M., Thomas W. J.: *Introduction to the Principles of Heterogeneous Catalysis*. Academic Press, London 1967.
3. Kopešťanský J.: This Journal *47*, 2307 (1982).
4. Somorjai G. A.: Advan. Catal. Relat. Subj. *26*, 1 (1977).
5. Gland J. L., Somorjai G. A.: Advan. Colloid Interface Sci. *5*, 205 (1976).
6. Al-Noori M. K., Saleh J. M.: J. Chem. Soc., Faraday Trans. 1, *12*, 2140 (1973).
7. Bastlová H.: This Journal *40*, 3100 (1975).
8. Merta R., Ponec V.: J. Catal. *17*, 79 (1970).
9. Inoue Y., Kojima I., Moriki S., Yasumuori I.: 6th Inter. Congr. Catal., London 1976, Preprint A6.
10. Bastl Z.: This Journal *43*, 1943 (1978).
11. Ito M., Mori Y., Kato T., Suëtaka W.: Appl. Surface Sci. *2*, 543 (1979).
12. Bastl Z.: This Journal *43*, 1665 (1978).
13. Demuth J. E.: Chem. Phys. Lett. *45*, 12 (1977).
14. Anderson J. R.: *Structure of Metalic Catalysts*. Academic Press, London 1975.
15. Ertl G.: J. Vac. Sci. Technol. *14*, 435 (1977).
16. Nieuwenhuys B. E., Bouwman R., Sachtler W. M. H.: Thin Solid Films *21*, 51 (1974).
17. Benziger J.: J. Chem. Soc., Faraday Trans. 1 *76*, 49 (1980).
18. Ibach H., Lehwald S.: J. Vac. Sci. Technol. *15*, 407 (1978).
19. Anderson A. B., Hubbard A. T.: Surface Sci. *99*, 384 (1980).
20. Ibach H., Hopster H., Sexton B.: Appl. Phys. *14*, 21 (1977).
21. Demuth J. E.: Surface Sci. *84*, 315 (1979).
22. Demuth J. E.: Surface Sci. *80*, 367 (1979).
23. Fischer T. E., Kelemen S. R., Bonzel H. P.: Surface Sci. *64*, 157 (1977).
24. Kesmodel L., Dubois L. H., Somorjai G. A.: J. Chem. Phys. *70*, 2180 (1979).
25. Ito M., Suëtaka W.: Surface Sci. *62*, 308 (1977).
26. Kojima I., Miyazaki E., Yasumori I.: Appl. Surface Sci. *10*, 27 (1982).