

DECOMPOSITION OF ETHYLENE ON PALLADIUM SURFACES AT 200°C

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The interaction of ethylene with surfaces of palladium films at 200°C was studied by work function and volumetric measurements and by analysis of the gaseous reaction products. Intensive dehydrogenation of the adsorbed ethylene, accompanied by desorption of hydrogen into the gaseous phase, was observed. The surface adsorption layer was found to comprise hydrocarbon species with the H/C ratio 0.5 (independent of the degree of surface coverage) and surface-bonded hydrogen whose amount, per adsorbed ethylene molecule, dropped rapidly with increasing degree of surface coverage by the hydrocarbon species.

Interactions of hydrocarbons with pure surfaces of transition metals at temperatures above 100°C regularly result in the decomposition of these substances and formation of dehydrogenated hydrocarbon surface layers¹⁻³. For palladium, some of the problems have been studied by Gates and Kesmodel¹, who allowed ethylene and acetylene to adsorb at -123°C and 25°C, respectively, and investigated their thermal evolution while increasing the temperature up to 227°C. Adsorption of ethylene and acetylene was studied by the author of this paper over a wide temperature region³ including the temperature of 200°C: the results have been published previously⁴⁻⁷ and some are presented here. Papers⁴⁻⁷ dealt with the interactions of ethylene and acetylene with palladium surfaces of different microcrystal structure, temperature, and chemical modification, and also with the interaction of the adsorption complexes of these hydrocarbons with molecular and atomic hydrogen.

In the present work, the decomposition of ethylene on palladium surface is investigated at 200°C, with the aim to contribute to the understanding of the mechanism of interaction of hydrocarbons with metals at higher temperatures and particularly at higher pressures than as were used in the study¹. The experiments were arranged so as to eliminate unwanted effects on the adsorption layer and the gaseous phase, such as the effect of electrostatic field or bombardment of the surface layers by electrons, photons, or other particles.

EXPERIMENTAL

The palladium film preparation, experimental techniques, and adsorbates used were as in works⁴⁻⁷. The film temperature was held at $200 \pm 2^\circ\text{C}$. The surface areas of the films were determined by means of physical adsorption of xenon at liquid nitrogen temperature using

the BET and DR techniques⁸, which afforded results identical to within $\pm 10\%$. The work function changes were measured with a Kelvin vibrational capacitor⁹ using phase-sensitive signal detection.

RESULTS AND DISCUSSION

A direct manifestation of dehydrogenation of ethylene adsorbed at 200°C was the desorption of hydrogen into the gaseous phase (Fig. 1), which was observed starting nearly from the lowest adsorbed amounts N_a ; only at very low degrees of adsorption, $N_a \leq N_a^1$, no products were detected in the gaseous phase (N_a^1 is the maximum starting irreversibly adsorbed amount of ethylene for which the equilibrium pressure of desorbed hydrogen does not exceed $2.6 \cdot 10^{-3}$ Pa, the lowest value measurable with the thermal conductivity manometer used). For amounts of adsorbed ethylene higher than N_a^1 , the gaseous phase in contact with the adsorption layer contained hydrogen solely up to a value N_a^x (refs^{4,6}), at which ethane also began to appear (Fig. 2), presumably as a result of ethylene hydrogenation on the dehydrogenated hydrocarbon surface layer. The amounts of desorbed hydrogen in the regions of $N_a^1 < N_a \leq N_a^x$ and $N_a > N_a^x$ increased linearly with increasing amount of adsorbed ethylene, with slopes of $k = 1.5$ and 0.75 , respectively (*i.e.*, in average, 1.5 and 0.75

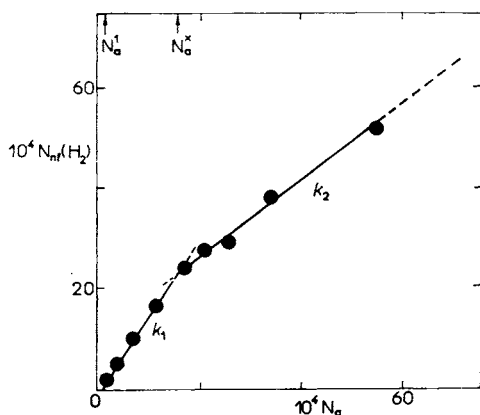


FIG. 1

Dependence of the amount of hydrogen desorbed into the gaseous phase $N_{nf}(\text{H}_2)$ (in $\mu\text{mol cm}^{-2}$) during the adsorption of ethylene on palladium surfaces at 200°C. Amount of adsorbed ethylene, N_a , in $\mu\text{mol cm}^{-2}$. Slopes of increase of hydrogen amount in gaseous phase $k_1 = 1.5$, $k_2 = 0.75$

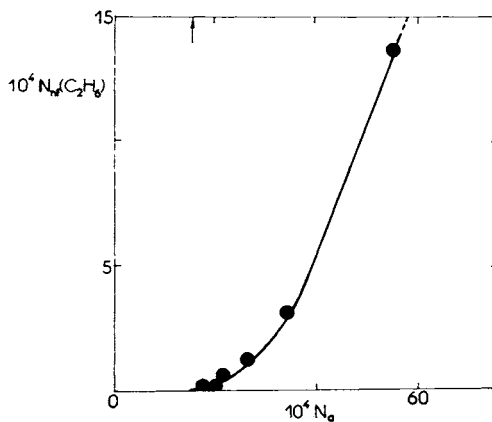


FIG. 2

Dependence of the amount of ethane in the gaseous phase $N_{nf}(\text{C}_2\text{H}_6)$ (in $\mu\text{mol cm}^{-2}$) on the amount of adsorbed ethylene N_a (in $\mu\text{mol cm}^{-2}$) on palladium surfaces at 200°C

molecules of hydrogen per molecule of adsorbed ethylene, respectively, desorbed into the gaseous phase). During this process, the surfaces became coated by a dehydrogenated carbonaceous layer.

As follows from a comparison of the N_a^x value with the amount of palladium atoms per unit area of polycrystalline surface, $1.27 \cdot 10^{15}$ atoms/cm² (ref.¹⁰), there are approximately 1.3 surface palladium atoms per hydrocarbon complex. If the Pd films on the gas phase interface are constituted mainly by (111) planes^{11,12}, the ratio of the adsorption hydrocarbon complex to Pd atoms is approximately one-to-one. Thus, N_a^x can be considered as the amount corresponding to a monolayer surface coverage, and the degree of surface coverage Θ can be defined as N_a/N_a^x (degree of coverage at N_a^x defined as unity). The degree of coverage at N_a^1 will be denoted $\Theta_1 (= N_a^1/N_a^x)$.

The changes in the work function of the films, in dependence on the degree of coverage, are shown in Fig. 3 for temperatures of 25, 100, and 200°C. The differences in the shapes of these dependences reflect the different compositions of the hydrocarbon surface layers⁴, particularly the different degree of their dehydrogenation, at different temperatures. These data are supplemented with the dependences of the effective dipole moment of adsorbed ethylene (tangent to the curve $\Delta\varphi = f(N_a)$) on the degree of coverage for the three temperatures (Table I).

The changes in the work function observed at 200°C can be interpreted with the use of the results presented in Fig. 1 and of the composition of the adsorbed ad layer for the various regions of degree of coverage. This composition can be established based on the volumetric determination of the adsorbed amounts in conjunction with the analysis of the gaseous products. This approach failed at degrees of coverage lower than Θ_1 , at which all ethylene adsorbed without observable desorption of products into the gaseous phase. In this region the work function of the surface increased, probably due to the presence of adsorbed hydrogen atoms dissociated off from the adsorbing ethylene molecules; the effective dipole moment was approximately +0.2 D (1 D = $3.3 \cdot 10^{-30}$ C m). The facts that in this region, $\Delta\varphi$ increases to positive values and that the degree of dissociation of C—H bonds of adsorbing ethylene decreases with increasing degree of coverage^{4,13} indicate that in the region in question ethylene is dissociated to a high degree.

At degrees of coverage $\Theta_1 < \Theta < 1$, the gaseous phase in contact with the adsorption layer contained hydrogen solely (Fig. 1). The slope of its increase with increasing degree of coverage was 1.5 over the entire region considered. The fact that no other gaseous products were present indicates that the adsorption layer becomes enriched with species whose H/C ratio is 0.5. Assuming that the adsorption complexes contain no more than two carbon atoms, their composition is C₂H; for instance, adsorbed species C₂H, CH and C.

Based on the above results, some assumptions can be made as to the surface chemical processes involved. First of all, dissociative adsorption of ethylene and thermal

decomposition of its complexes (C—H and/or C—C bond scission) take place. These can be written as

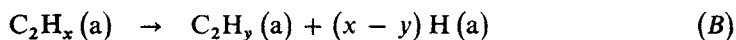
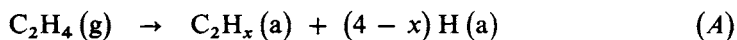


TABLE I

Dipole moments μ measured during the interaction of ethylene with palladium films at various film surface temperatures T_a

$T_a, ^\circ\text{C}$	Dipole moment, D	
	at low degrees of coverage	at medium degrees of coverage
25	-0.1	-1.2
100	+0.2	-1.2
200	+0.2	-0.1 ^a , -0.2 ^b

^a At $\theta \approx 1$; ^b at $\theta > 1$.

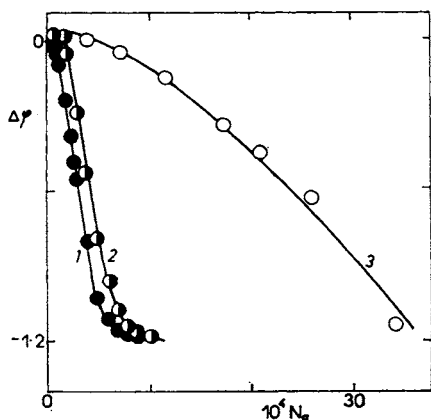


FIG. 3

Changes in the work function of palladium surfaces $\Delta\phi$ (in eV) in dependence on the amount of adsorbed ethylene N_a (in $\mu\text{mol} \cdot \text{cm}^{-2}$). Temperature ($^\circ\text{C}$); 1 25, 2 100, 3 200

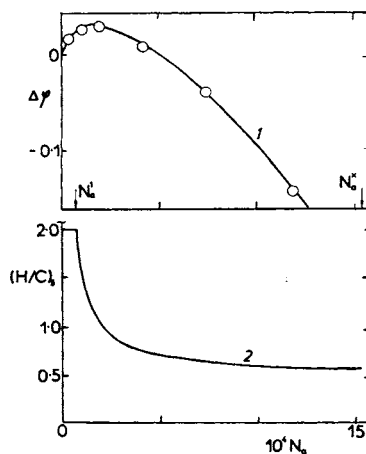


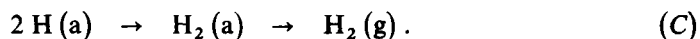
FIG. 4

Changes in the work function $\Delta\phi$ (in eV) 1, and in the $(\text{H}/\text{C})_s$ atomic ratio 2, in dependence on the amount of adsorbed ethylene N_a (in $\mu\text{mol} \cdot \text{cm}^{-2}$) on palladium surfaces at 200°C . The N_a^1 and N_a^2 values are indicated

where (a) and (g) label the adsorbed and gas phase species, respectively; $(4 - x)$ and $(x - y)$ are the amounts of dissociated-off hydrogen atoms and hydrogen atoms formed by thermal decomposition of the adsorption complexes, respectively, relative to an adsorbed ethylene molecule or a thermally decomposed C_2H_x complex, respectively. The two processes (dissociative adsorption and thermal decomposition) can proceed simultaneously, and so both x and y can depend on the degree of coverage at the temperature of experiment.

The thermal decomposition of the hydrocarbon complexes can involve not only C—H bond scission but also splitting of C—C bonds. Adsorption complexes of ethylene thus can be transformed into new surface species of the types C_2H_{x-m} (a) + m H(a) or CH_{x-p-s} (a) + CH_p (a) + s H(a), where $0 \leq m \leq x$, $p \leq x$, $s \leq x$, $0 \leq (p + s) \leq x$. It cannot be decided whether or not the C—C bond scission takes place for the adsorption complexes of ethylene at 200°C. Since the H/C atomic ratio on the surface at a given degree of coverage does not change during the formation of the new adsorption complexes of the C_2H_{x-m} (a) or CH_{x-p-s} (a) + CH_p (a) type, only the state will be discussed where the thermal decomposition leads to a change in the amount of the adsorbed hydrogen atoms; the amount of carbon atoms will be assumed equal to the double amount of adsorbed ethylene molecules over the entire region of degrees of coverage ($0 < \theta < 1$).

The dissociative adsorption of ethylene and thermal decomposition of its adsorption complexes must be followed by a reaction associated with liberation of hydrogen into the gaseous phase. Adsorbed hydrogen can migrate over metal surfaces at higher temperatures^{14,15}, and in the case of palladium, it can also dissolve in the metal bulk¹⁶. Due to the migration of hydrogen atoms, accompanied by their recombination and consecutive desorption of the species so formed, the surface processes (A) and (B) are supplemented by



Since no hydrocarbon product desorbed into the gaseous phase within the entire region of degrees of coverage ($0 < \theta < 1$), the dependence of the $(\text{H}/\text{C})_s$ atomic ratio in the surface layer on θ can be evaluated by balance of the carbon and hydrogen atoms on the surface, using the experimental value of the slope of the increase of hydrogen desorbing into the gaseous phase ($k = 1.5$), as

$$(\text{H}/\text{C})_s = 2 - k(1 - \theta_1/\theta) = 2 - (3/2)(1 - \theta_1/\theta). \quad (1)$$

This dependence, which can serve for the interpretation of the dependence of $\Delta\phi$ on the degree of coverage, is plotted in Fig. 4. Only one assumption is made for the interpretation, namely, that over the entire region of degrees of coverage, the interaction of ethylene with the surface results in the same dehydrogenation of the ethylene mole-

cules giving a surface complex whose H/C atomic ratio is 0.5, the amount of atomic hydrogen on the surface decreasing with increasing degree of coverage (due to the desorption of hydrogen into the gaseous phase and increase in the amount of C_2H complexes with increasing degree of coverage). For the region of $\theta_1 < \theta < 1$, this type of complex follows from the results shown in Fig. 1. As to the starting region, $\theta < \theta_1$, here the dehydrogenation can generally be higher than at higher degrees of coverage. This may be due, *e.g.*, to the low-coordination surface atoms, which are effective particularly in the initial region of coverage^{4,6,17}. It can be assumed, however that in the initial region, ethylene will not be dehydrogenated to a lesser extent than at higher degrees of coverage. It will be shown that the validity of this assumption is borne out by the observed changes in the work function.

Assuming that the degree of ethylene dehydrogenation is constant over the entire region of coverage, the increase in the work function with increasing degree of coverage at $\theta < \theta_1$ can be explained in terms of the high number of adsorbed hydrogen atoms per adsorbed hydrocarbon species. In this range, the $(H/C)_s$ atomic ratio is 2, hence, there are three hydrogen atoms adsorbed on the surface per surface hydrocarbon remainder (the dipole moment in this region was about +0.2 D, Table I). As follows from Eq. (1) and Fig. 4, the $(H/C)_s$ atomic ratio decreases with increasing θ . In the case where $(H/C)_s$ is unity, *i.e.*, where one adsorbed hydrogen atom per surface hydrocarbon remainder is in average present, the work function of the surface does not decrease yet (Fig. 4). From this it can be inferred that the dipole moment of adsorbed hydrogen is comparable to the absolute value of the dipole moment of the surface hydrocarbon species. The course of the dependence $\Delta\phi = f(\theta)$, compared to that of the dependence $(H/C)_s = f(\theta)$, indicates that the dipole moment of the two adsorbed species, hydrogen and hydrocarbon remainder, differ in their sign, hence, in the dipole orientation. Really, Fig. 4 shows that at degrees of coverage where less than one adsorbed hydrogen atom per adsorbed hydrocarbon species is present, the work function of the surface in dependence on the degree of coverage begins to decrease. This confirms the hypothesis that the observed course of the function $\Delta\phi = f(\theta)$ for the adsorption of ethylene at 200°C is related with the accumulation and consecutive decrease in the relative amount of surface hydrogen (per adsorbed hydrocarbon complex) with increasing degree of surface coverage.

The dipole moment of the adsorbed hydrocarbon species was also estimated at degrees of coverage approaching unity. Here the effect of the surface hydrogen dipole on $\Delta\phi$ can be disregarded because due to its desorption into the gaseous phase, surface hydrogen is present in amounts negligibly low as compared with the amount of the hydrocarbon species. The dipole moment estimate is -0.1 D, a value identical with that derived from the dependence $\Delta\phi = f(\theta)$ in the starting coverage region. This fact also bears out the assumption that the degree of ethylene dehydrogenation is constant over the entire region of degrees of palladium surface coverage at 200°C.

It should be noted that the region of starting adsorption of ethylene at 200°C, $\theta < \theta_1$, is actually narrow as compared to the monolayer coverage ($\theta = 1$), and so, to a first approximation, it could be neglected. It appears, however, that this starting adsorption has to be taken into account for gaining insight into the surface processes and understanding the $\Delta\varphi = f(\theta)$ dependences.

For the interpretation of the course of the $\Delta\varphi = f(\theta)$ dependence in the range of low degrees of coverage it was assumed that in this range, adsorbed ethylene is dissociated to a great extent, so that the degree of dehydrogenation is at least the same as at higher degrees of coverage. This can be confirmed as follows based on the results derived from the analysis of the $\Delta\varphi = f(\theta)$ dependence.

Let $N(\text{H})$ and $N(\text{C}_2\text{H}_x)$ be the amounts of adsorbed hydrogen atoms (formed by dissociation of C-H bonds of the adsorbing ethylene) and of the adsorbed hydrocarbon species, respectively, and $\mu(\text{H})$ and $\mu(\text{C}_2\text{H}_x)$, the corresponding dipole moments. The effective dipole moment of adsorbed ethylene at low degrees of coverage be μ_{eff} . Since at $\theta \leq \theta_1$ the mutual interaction of the adsorbed particles can be neglected, the change in the work function at $\theta \leq \theta_1$ can be written as

$$\Delta\varphi = 4\pi N_a^1 \mu_{\text{eff}}, \quad (2)$$

and also,

$$\Delta\varphi = 4\pi [N(\text{H}) \mu(\text{H}) + N(\text{C}_2\text{H}_x) \mu(\text{C}_2\text{H}_x)]. \quad (3)$$

For $\mu(\text{H}) = -\mu(\text{C}_2\text{H}_x) = 0.1 \text{ D}$ and $\mu_{\text{eff}} = 0.2 \text{ D}$, we have

$$N(\text{H}) = 2N_a^1 + N(\text{C}_2\text{H}_x). \quad (4)$$

Since up to θ_1 all ethylene adsorbs without observable desorption of any products into the gaseous phase, $N(\text{C}_2\text{H}_x) = N_a^1$ (at $\theta = \theta_1$), and then $N(\text{H}) = 3N_a^1$. This means that in the starting coverage range, there are three adsorbed hydrogen atoms per hydrocarbon remainder. Moreover, this indicates that the composition of the latter is C_2H .

Changes in the work function also occur at degrees of coverage $\theta > 1$. Here the composition of the surface complexes as well as the gaseous phase are different from those observed at lower coverages. In this case hydrogen is accompanied by ethane arising from reactions of ethylene and hydrogen in the dehydrogenated hydrocarbon surface layer³.

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