JOURNAL OF CATALYSIS 42, 334–343 (1976)

Surface Reactivity of Hydrogen with Oxygen on Palladium and Palladium Hydride Films

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Received May 30, 1974

The static capacitor method of Delchar, Eberhagen, and Tompkins (*J. Sci. Instr.* 40, 105 (1963) has been applied to studies of surface potential changes (Δs.p.) of Pd films evaporated in ultrahigh vacuum (UHV), during (i) hydrogen adsorption, (ii) oxygen adsorption, and (iii) coadsorption and reaction of hydrogen with oxygen in the temperature range 78–298 K. As in previous studies, three different forms of hydrogen deposit on palladium have been observed: (i) atomic, electronegatively polarized β^- form, (ii) atomic electropositively polarized β^+ form, and (iii) reversibly adsorbed, positively polarized, molecular α form. The mechanisms of the reactions of oxygen with the β^- and β^+ forms of hydrogen are different. The mechanism of the reaction of hydrogen with adsorbed oxygen depends on the coverage of the palladium film surface. Therefore the estimation of the film surface area by titration of oxygen adatoms with hydrogen or hydrogen adatoms with oxygen on the palladium film surface in the temperature interval 195–298 K is unreliable.

INTRODUCTION

The changes of electrical parameters of evaporated palladium films caused by chemisorption or by reactions of chemisorbed gases on the film surface have not been widely studied. Jaeckel and Wagner (*1*) applied a photoelectric method to measure surface potential changes (Δs.p.) caused by chemisorption of hydrogen ($\Delta\text{s.p.}_{\max} = -180$ mV at 10^{-4} Torr) and also by chemisorption of oxygen ($\Delta\text{s.p.}_{\max} = -600$ mV). Suhrmann *et al.* (*2*) reported that hydrogen adsorption on palladium films caused an increase of the film resistance at low coverages, followed by a decrease at higher uptake of hydrogen. Recently Ertl and his co-workers obtained interesting results in their work on hydrogen adsorption on palladium single crystals (*3*).

Niewenhuys *et al.* (*4*) measured the changes of work function, $\Delta\phi$, during the sintering of palladium film deposited at low temperatures and observed an increase of $\Delta\phi$ due to the sintering. In our previous work it was reported (*5*) that three different forms of hydrogen deposit on palladium can be distinguished at 78 K. The first is an electronegative β^- form corresponding to dissociatively adsorbed hydrogen, which appeared at a low population of hydrogen on palladium. The second is an electropositive atomic β^+ form, the nature of which is similar to that of hydrogen atoms (or screened protons) in hydrides of Group VIII metals. This form appeared at high uptake of hydrogen on palladium. Incorporation of the β^+ species from the surface into the bulk of the metal leads to palladium hydride formation. In this process the β^-

species is transformed into the β^+ species. The third form is an electropositive, weakly bound, molecular α form of hydrogen, which appears on top of palladium hydride. Similar forms of hydrogen have been observed also on nickel (*6*), platinum (*7*), and niobium (*8*).

The present work was carried out in order to investigate the reactivity of different forms of hydrogen deposit on palladium in the reaction with oxygen by means of measurements of surface potential changes of evaporated palladium films caused by adsorption of hydrogen and oxygen and coadsorption of these gases in the temperature range 78 to 298 K.

EXPERIMENTAL

The rapid recording static capacitor method elaborated and described by Eberhagen *et al.* (*9*, *10*) was applied to studies on surface potential changes. In this method the tendency of charge to flow through the external circuit from the capacitor charged as a result of dipole layer formation in the adsorption process is detected, and then the backing-off potential is applied rapidly to stop the discharge. The overall response of the electronic circuit was 0.1 sec. This makes it possible to observe the kinetics of surface potential changes during adsorption and during reaction as well as to measure the surface potential values characteristic of the stable states of the adsorbate.

Pressures lower than 10^{-10} Torr were usually reached during the film deposition, at 78 or 195 K. The film was deposited on the inside glass walls of the cylindrical condenser by the evaporation of spectroscopically pure palladium wire from a tungsten heater. The reference electrode consisted of a SnO-coated glass cylinder.

The geometrical surface area of the films was 100 cm², and the total number of palladium atoms was $\sim 1.3 \cdot 10^{20}$.

Spectroscopically pure hydrogen and oxygen were used, and hydrogen was additionally purified by passing it through a palladium thimble.

The pressure during the film deposition was measured by means of a Groszkowski ionization gauge with an X-ray limit of $1 \cdot 10^{-13}$ Torr. However, during the investigation of chemisorption only a McLeod gauge was used in order to avoid the influence of the ionization gauge on the system. A Topatron mass spectrometer gauge (Leybold) was used to analyze the composition of the gas phase.

Usually one of the gases, e.g., hydrogen, was first introduced in calibrated doses into the condenser. The surface potential changes were recorded continuously, and the pressure was measured after every dose.

When the surface potential change caused by a successive dose of the gas was lower than 1 mV and the pressure of the gas was higher than $5 \cdot 10^{-2}$ Torr, the system was evacuated and the second gas was introduced.

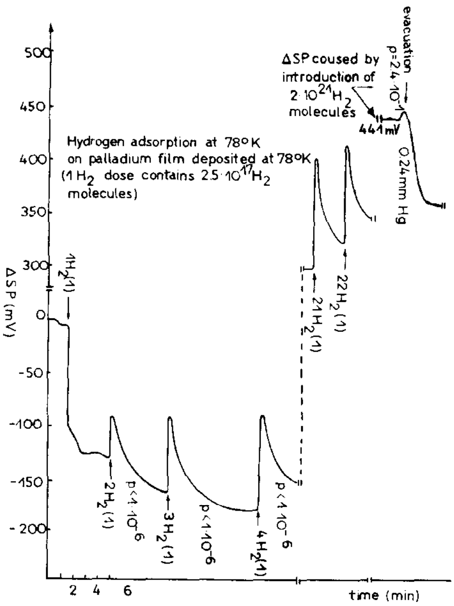

FIG. 1. Surface potential changes of palladium film caused by hydrogen adsorption and palladium hydride formation. The graph is reproduced from the recording chart.

RESULTS AND DISCUSSION

A. Hydrogen Adsorption on Palladium

The surface potential changes caused by hydrogen adsorption at 78 K on palladium film deposited at 78 K and sintered during 5 min at 298 K are represented in Fig. 1 which is reproduced directly from the recording chart.

Three different forms of hydrogen can be distinguished:

1. An electronegative β^- form, with $\Delta\text{s.p.}_{\max} = -180$ mV and hydrogen uptake of $1.0 \cdot 10^{18}$ H_2 molecules. The respective ratio of the total number of hydrogen atoms adsorbed and adsorbed to the number of palladium atoms in the film H/Pd was $1.6 \cdot 10^{-2}$. The equilibrium pressure of the gas phase was lower than $1 \cdot 10^{-6}$ Torr.

2. An electropositive β^+ form. This form of the deposit is characterized by the appearance of positive increments, Δs.p., followed by their decay. The value of stabilized surface potential reached after the decay of every successive s.p. increment becomes increasingly more positive. The final value of Δs.p. referred to the clean surface of palladium reached in the described experiment was +440 mV. The observed value of the increase of Δs.p. in the process of palladium hydride formation at 78 K depends strongly on the number of hydrogen molecules in the dose. When many small hydrogen doses (one dose contained $2\text{–}3 \cdot 10^{16}$ H_2 molecules) were introduced into the system, a large Δs.p. shift up to 1300 mV was observed, and this was accompanied by formation of palladium hydride of H/Pd ratio ~0.85 (*5*).

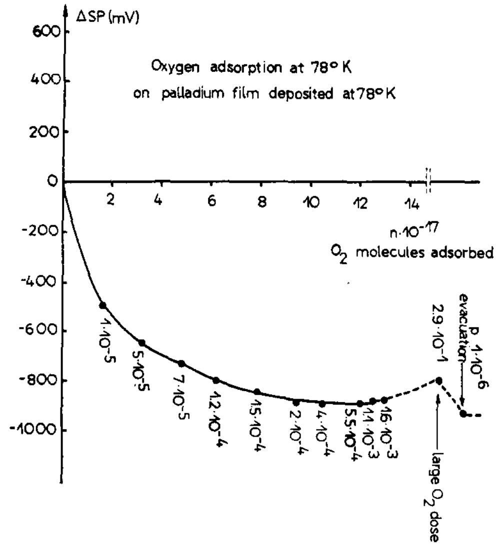

FIG. 2. Surface potential dependence on the number of oxygen molecules adsorbed at 78 K on palladium film.

However, when larger doses of hydrogen were applied the shift of Δs.p. was smaller (400–600 mV) and the H/Pd ratio was 0.25–0.30.

This phenomenon probably corresponds to the formation of a very thin layer of palladium hydride on the metal film surface in the case of the introduction of large hydrogen doses.

The diffusion coefficient of hydrogen atoms in palladium hydride is very small, since in this case the diffusion takes place by the vacancy mechanism and not the interstitial mechanism which is observed in the case of hydrogen diffusion in metals.

Thus the thin layer of palladium hydride slows down hydride formation in the underlying bulk of metal. By contrast, when small doses of hydrogen are applied and palladium hydride cannot be formed over the whole film surface, the diffusion of the β^+ species of hydrogen in the metal is fast enough to give a uniform concentration of hydrogen in the bulk during the experiment. The observed maximum value of the decrease of Δs.p. due to the β^- species formation at the beginning of the adsorption process depends also on the number of hydrogen molecules in the dose. The electronic circuit of the static condenser records the mean surface potential, i.e., the sum of the potential changes caused by the β^- and β^+ species formation.

On the surface of palladium hydride PdH_x with $x \approx 0.25$ only the β^+ species exists (*5*).

3. An electropositive weakly bound α form which was formed when a large dose of hydrogen was introduced and when the pressure was raised to $p > 1 \cdot 10^{-4}$ Torr and is a molecular form of the deposit. The rate of the α form desorption corresponds to a first-order reaction.

The adsorption of hydrogen on palladium films at 195 or at 298 K caused only the formation of the β^- species with Δs.p. $= -210$ mV under hydrogen pressure $p < 1$ Torr. The H/Pd ratio was lower than $1 \cdot 10^{-2}$.

B. Oxygen Adsorption on Palladium Films

Oxygen adsorption at 78 K on palladium films deposited at 78 K and sintered at 298 K during 5–10 min is represented in Fig. 2. The maximum surface potential changes reached -900 mV with an oxygen uptake of $12 \cdot 10^{17}$ molecules. Incorporation of oxygen adatoms into the bulk of the metal at 78 K can be neglected. Further doses of oxygen increased the gas phase pressure to 10^{-3} Torr and caused the formation of the electropositive form of oxygen deposit. This was probably a weakly bound molecular form, and it could be removed by evacuation of the system, bringing Δs.p. to -940 mV. Oxygen adsorption on palladium films at 195 or 298 K caused only the formation of the electronegative form (or forms) with $\Delta \text{s.p.}_{\max}$ of -600 and -610 mV, respectively, without any reversibly adsorbed electropositive form of oxygen. This less negative value of Δs.p. probably corresponds to the formation of palladium ions and some oxide patches on the surface.

C. Hydrogen and Oxygen Coadsorption on Palladium at 78 K

Hydrogen was introduced as doses at 78 K into the condenser in an amount sufficient for the formation of the β^- species with only traces of the β^+ form on the palladium film. Then oxygen was added as doses. The changes in the surface potential caused by hydrogen and oxygen coadsorption in these conditions are shown in Fig. 3.

It can be seen that $12 \cdot 10^{17}$ hydrogen adatoms were adsorbed in the β^- form, while a few further hydrogen doses led to the simultaneous formation of the β^- and the β^+ species. In this case, a small increase of surface potential followed by a decay and successively lower stable values of

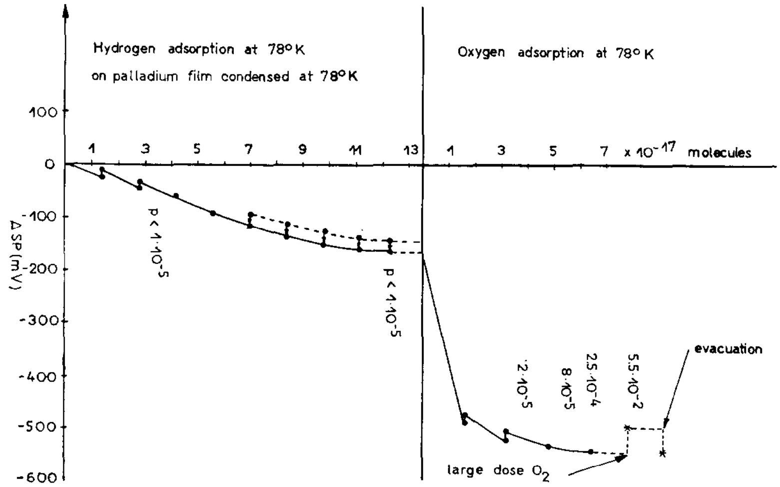

FIG. 3. The influence of oxygen adsorption at 78 K on surface potential of the palladium film covered with the β^- hydrogen species.

Δs.p. were observed after the introduction of each hydrogen dose. This phenomenon was due to surface potential superposition of both β^- and β^+ species. However, since the β^+ species can be incorporated into the bulk of the film, one should expect that only the β^- species was present on the surface during this stage of adsorption. The final value of s.p. reached -180 mV. A small amount of hydrogen dissolved in the bulk of palladium (H/Pd $\approx 7\cdot 10^{-3}$) caused an unmeasurable change of work function. Introduction of $1\cdot 10^{17}$ oxygen molecules into the system caused a decrease of s.p. by -310 mV. This value is comparable to Δs.p. caused by adsorption of the same number of oxygen molecules on pure palladium film. However, adsorption of the next two oxygen doses resulted in a smaller change of s.p. leading to the final value of Δs.p. = -520 mV, which was observed when $5\cdot 10^{17}$ O_2 molecules were adsorbed. A large dose of oxygen caused the formation of the reversibly adsorbed electropositive molecular deposit.

Comparison of Fig. 2 with Fig. 3 leads to the conclusion that an interaction between hydrogen β^- adatoms and oxygen adatoms takes place on palladium at 78 K. It can be neglected when a small amount of oxygen is adsorbed. This is confirmed also by the character of the oxygen adsorption kinetics.

The first oxygen dose was adsorbed similarly as in the case of oxygen adsorption on a clean palladium surface. A further two oxygen doses caused at first a small increase of s.p. followed by a decrease to a value lower than the original one. This phenomenon was undoubtedly due to the superposition of s.p. changes in the processes of $(H_2O)_a$ or $(OH)_a$ adspecies formation and oxygen adsorption on the palladium film surface.

Oxygen adsorption at 78 K on hydrogen deposit of the β^+ character, completely altered the change of s.p. Only a small negative change of s.p. with uptake of only $2\cdot 10^{17}$ O_2 molecules under the pressure or $4.2\cdot 10^{-3}$ Torr was observed.

D. Coadsorption of Hydrogen and Oxygen on Palladium Film at 195 K

The equilibrium pressure of hydrogen over palladium hydride at 195 K is equal to $6\cdot 10^{-4}$ Torr (*11*). Hence it was possible to obtain palladium hydride at 78 K by

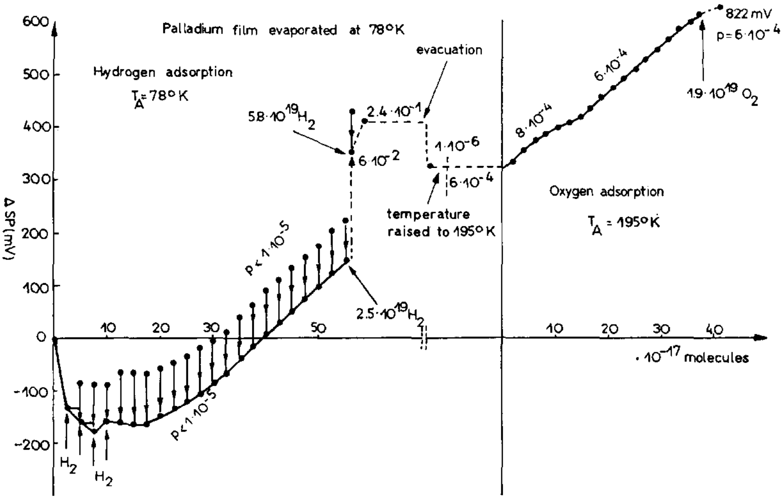

FIG. 4. The changes of surface potential caused by oxygen adsorption at 195 K on palladium hydride.

the method described above and to raise the temperature to 195 K without any quantitatively significant decay of hydride. This means that we are dealing in this case with hydrogen in the form of the β^+ species practically free from the β^- species. On the other hand, as pointed out above, hydrogen adsorption at 195 K on clean palladium film leads to the formation of the β^- species only, when the gas phase pressure is lower than 1 Torr. This makes it possible for us to compare the reactivity of the β^+ and the β^- species in their reactions with oxygen.

When oxygen was adsorbed at 195 K on the layer of the β^+ species of hydrogen we observed a continuous increase of surface potential to a steady value with every introduced dose (Fig. 4). We suppose that this phenomenon was due to water formation in the reaction of the hydrogen species with oxygen. Water molecules are probably weakly adsorbed on palladium hydride and can be partially desorbed. Desorbed water molecules were collected in the cold trap immersed in liquid nitrogen. The β^+ species reacted with oxygen on the surface without removing hydrogen to the gas phase and replacing it with oxygen atoms. In this process some palladium atoms on the surface could be extracted from the palladium hydride phase, and on such sites water molecules could be strongly adsorbed. The introduction of a large dose of oxygen ($1.9 \cdot 10^{19}$ O_2) did not cause any decrease of surface potential. Clearly the amount of hydrogen in the bulk of metal was large enough and the rate of its diffusion to the surface was high enough to consume all oxygen from the gas phase without any traces of oxygen adsorption. The final value of Δs.p. in this process (+822 mV) suggests the similarity to the effect of oxygen and hydrogen reaction on platinum at 195 K (*12*).

In the case when the β^- species (Fig. 5) alone was present on the surface at 195 K the introduction of oxygen caused a large increase of H_2 signal in the Topatron gauge. Clearly the β^- form of hydrogen deposit was replaced by oxygen atoms on the surface. This phenomenon was accompanied by a decrease of surface potential followed by an increase. The decrease of s.p. was the result of replacement of hydrogen with oxygen on the surface, whereas the increase corresponded to the reaction of oxygen adatoms with hydrogen from the gas phase. Water is probably strongly adsorbed on

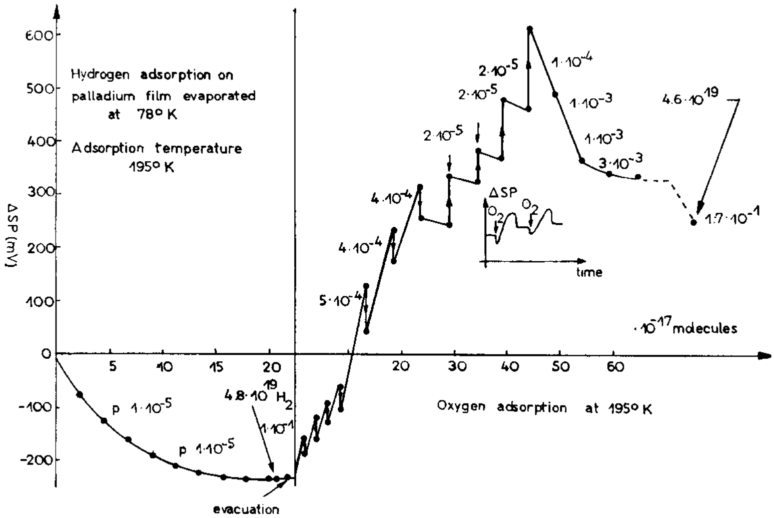

FIG. 5. The changes of surface potential caused by oxygen adsorption at 195 K on the palladium film covered with the β^- hydrogen species.

palladium film at 195 K. Further doses of oxygen, finding only a small amount of hydrogen on the surface, replaced water admolecules and caused a decrease of the s.p. value. Since the desorbed water molecules trapped in cold traps did not contribute to the measured value of the pressure, this stage of the process was accompanied by a decrease of pressure. Further introduction of oxygen resulted in an increase of pressure and decrease of s.p. value. However, even when the oxygen pressure reached $1.7 \cdot 10^{-1}$ Torr, Δs.p. was still positive (+250 mV).

It was observed in separate experiments that water vapor adsorption on clean palladium films caused an increase of the surface potential to a value which largely depended on temperature. It amounted to $\Delta\text{s.p.}_{\max} = +250$ mV at 195 K but to only +15 mV at room temperature. We suppose that this phenomenon corresponds to dissociative water adsorption on palladium.

E. Hydrogen adsorption on Oxygen Deposit on Palladium and Oxygen Adsorption on Hydrogen Deposit on Palladium at 298 K

The comparison of oxygen and hydrogen coadsorption at room temperature presented in Figs. 6 and 7 indicates that these gases react on palladium film. We suggest the following mechanism of the phenomena illustrated by the graph in Fig. 6.

Step 1

Deposition of oxygen on Pd film, uptake $12 \cdot 10^{17}$ O_2

Δs.p. = −610 mV

$+H_2 \downarrow$

Step 2

Formation of water molecules which are desorbed; some inactive oxygen adatoms remain on the surface

Δs.p. = −200 mV

$+H_2 \downarrow$

Step 3

Adsorption of the β^- hydrogen species on palladium film and dissolution of a small amount of hydrogen in the bulk of metal; some inactive oxygen adatoms still remain on the surface

Δs.p. = −300 mV

Redosing of oxygen leads to the next reaction:

Step 4

Removal of hydrogen from the surface of Pd film to the gas phase and adsorption of oxygen on released sites

+

Step 5

Formation of water molecules in the catalytic reaction:

$$O_{(a)} + H_{2(g)} \rightarrow H_2O_{(a)}$$

desorption of water molecules

$O_2 \downarrow$

Step 6

Oxygen adsorption on palladium film with removal of last water admolecules

Δs.p. = −610 mV

In our experiments only the overlap of steps 4 and 5 could be observed.

The contact of oxygen with palladium film covered with the β^- form of hydrogen (Fig. 7) caused the removal of the β^- hydrogen species from the surface and its replacement with oxygen atoms. It was observed by means of the Topatron gauge that hydrogen appeared in the gas phase after the introduction of oxygen. Then hydrogen from the gas phase reacted with oxygen adatoms as in step 2 (Fig. 6). It follows from the above description that the amount of hydrogen required for the reactions described as step 2 cannot be calculated very accurately from the experimental data since some gas penetrates into the bulk of palladium.

The observed value of Δs.p. in step 3 is −300 mV, while hydrogen β^- deposit can give only −210 mV at this temperature. Hence we suggest that in this step in addi-

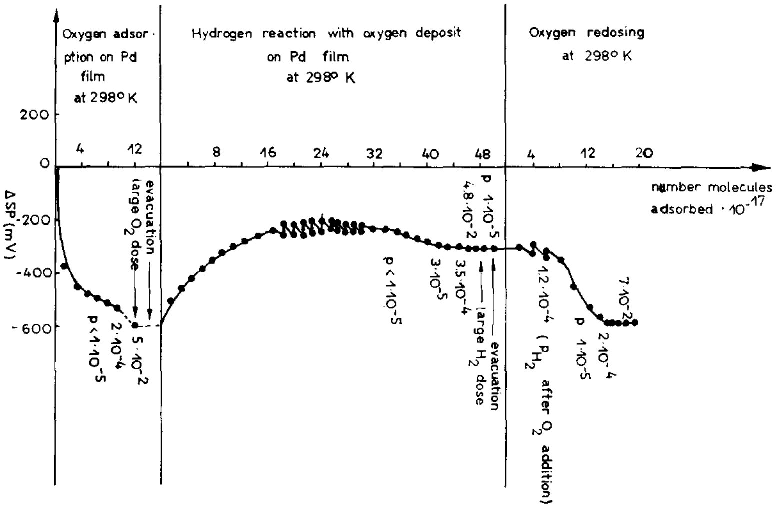

Fig. 6. The changes of surface potential of oxygen-covered palladium film caused by the adsorption of hydrogen and redosing of oxygen and hydrogen.

tion to this species some other electronegative species are present on the surface and that their dipole moments are larger than those of the β^- species. Such species could be formed by some inactive oxygen adatoms.

The kinetics of the reaction of oxygen with hydrogen on palladium film observed as surface potential changes are represented in Fig. 8. This graph is reproduced directly from the recording chart and corresponds to part 3 of Fig. 7 (hydrogen redosing).

The first two doses of hydrogen introduced to the system containing oxygen-covered palladium film caused a rapid increase of surface potential. Further doses of hydrogen caused the change of the shape of Δs.p. curve. We observed a decrease of Δs.p. followed by an increase. This could be the result of the following processes: (a) Hydrogen adsorption on the sites released after water molecules desorption from palladium film surface (decrease of Δs.p.); (b) hydrogen β^- species diffusion

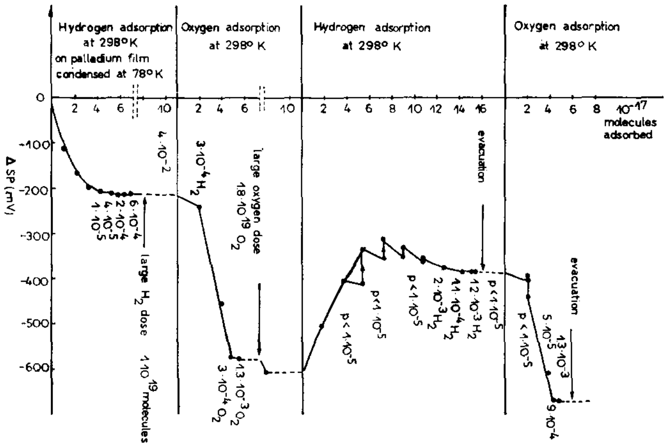

Fig. 7. The changes of surface potential after oxygen adsorption at 298 K on hydrogen-covered palladium film. The influence of hydrogen and oxygen redosing is also shown.

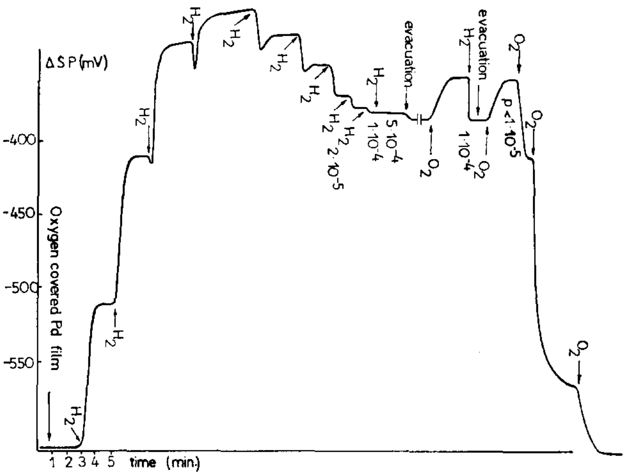

FIG. 8. The surface potential changes due to the reaction of oxygen with hydrogen. The graph is reproduced from the recorder chart, corresponding to Fig. 6.

to oxygen adatoms; (c) reaction of the β^- species with oxygen adatoms leading to water formation and desorption (increase of Δs.p.). It can be expected that the diffusion is the slowest step of the process.

The rate of s.p. increase following the decrease caused by hydrogen adsorption is described by an equation of the same character as that expressing the concentration of the diffusing species in the source at the original position as a function of time t, assuming that the initial distribution at time $t = 0$ at the original position can be represented by a delta function.

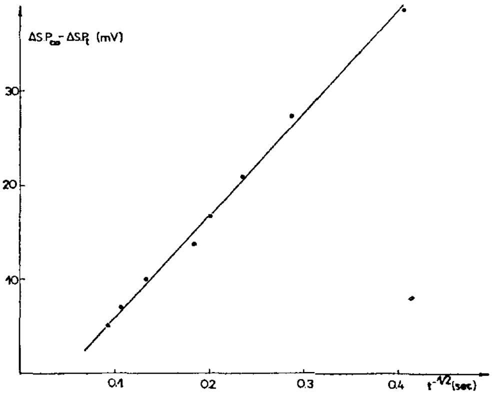

FIG. 9. The dependence of surface potential changes ($\Delta s.p._\infty - \Delta s.p._t$) on $t^{-\frac{1}{2}}$, describing the result of the introduction of the fourth hydrogen dose into palladium film covered with oxygen in the experiment presented in Figs. 6 and 8.

In the system of coordinates ($\Delta s.p._\infty - \Delta s.p._t$) and $t^{-\frac{1}{2}}$, a straight line should be obtained according to the equation:

$$(\Delta s.p._\infty - \Delta s.p._t) = \frac{K\Delta s.p._\infty}{2(\pi D)^{\frac{1}{2}}}\cdot t^{-\frac{1}{2}}, \quad (1)$$

where $\Delta s.p._\infty$ is the total change of s.p. caused by the reaction of hydrogen from the dose introduced, with oxygen adatoms; $\Delta s.p._t$ is the change of s.p. after time t, from the point where after the initial decrease s.p. begins to increase; Δs.p. is assumed to be proportional to the concentration on the surface; D is the diffusion coefficient; K is the surface area of the flat source.

The diffusion coefficient for surface diffusion of the β^- species can be estimated on the basis of Eq. (1). The obtained value of $5.5\cdot10^{-4}$ cm²/sec at 298 K seems to be reasonable. Figure 9 represents the dependence of ($\Delta s.p._\infty - \Delta s.p._t$) on $t^{-\frac{1}{2}}$. This graph was plotted on the basis of surface potential changes as a result of the fourth hydrogen dose introduction on oxygen-covered palladium film (Fig. 8). The value of the parameter K in Eq. (1) is assumed to be one-fifth of the total real surface area of the film (five doses of hydrogen react with oxygen on the film surface; see Fig. 8).

Further investigations of the reaction of hydrogen with oxygen on evaporated palladium films, especially at higher temperatures, would be necessary to explain more precisely the mechanism of this process.

CONCLUSIONS

1. Hydrogen adsorption on palladium leads to the formation of three different forms of deposit: the electronegative β^- form, the electropositive β^+ form, and the electropositive, reversibly adsorbed α form. Hydrogen adsorption under pressure $p < 1 \cdot 10^{-1}$ Torr at 195 or 298 K on palladium film causes the formation of the β^- species alone.
2. Oxygen adsorption on palladium at 78 K leads to the formation of an electronegative, strongly adsorbed deposit. At higher pressures of oxygen the electropositive reversible form of physisorbed oxygen appears. Oxygen adsorption at 195 and 298 K gives only the electronegative form of oxygen deposit.
3. The reactivities of the β^- and the β^+ hydrogen forms with respect to oxygen are different. A significant amount of oxygen adatoms on palladium film surface is inactive in the reaction with hydrogen at room temperature. The mechanism of the reaction of hydrogen with oxygen adatoms on palladium film depends on oxygen coverage or alternatively on the form of oxygen deposit.
4. Titration of oxygen adatoms with hydrogen or hydrogen adatoms with oxygen at 195 K or at room temperature is unreliable in view of hydrogen solubility in palladium and the lack of reactivity of a part of oxygen deposit at these temperatures.
5. The rapid recording static capacitor method can be successfully applied to studies on surface reactions of gases chemisorbed on metal films.

ACKNOWLEDGMENT

The author thanks Professor Dr. W. Palczewska for valuable discussions.

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