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H_2 dissociative adsorption on palladium hydride and titanium hydride surfaces: Evidence for weakly bound state of hydrogen adatoms

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Abstract

H_2 adsorption on surfaces of $PdH_{0.9}$ and $TiH_{1.95}$ was studied by simultaneously measuring surface potential and pressure. Weakly bound atomic deposits were observed in the studied temperature range 78–298 K. The corresponding electrostatic and thermodynamic parameters were thereby determined.

Keywords: Hydrogen; Palladium hydride; Titanium hydride; Thin films; Surface and interface

1. Introduction

Surface properties of transition metal hydrides MeH_x have not been widely studied. As far as we know only a few investigations of surface phenomena involving MeH_x formation [1–6] have been carried out. It has been well established that PdH_x (x~1), [1,5] and TiH_y (y~2) [4,6] can be obtained with a very good reproducibility when thin Pd or Ti films deposited under UHV conditions interact in situ with H_2. We have found that two different hydrogen species arise on Pd [1,5] and Ti [4,6] surfaces in the process of hydrides formation: (i) the negatively polarized atomic adspecies (the negative pole of the dipole pointing away from the surface), formed at the beginning of the process, stable on the surface of the metal, referred to as β^-, and (ii) the positively polarized, atomic adspecies referred to as β^+, arising with the increasing coverage. The β^+ adspecies are not stable on the metal surface as the β^- are, but quickly incorporate into the bulk forming hydrides. The following questions arise: does H_2 adsorb onto the surface of hydrides, and what could be the nature of this adsorbate? The aim of the present study is to give some information on these topics. Two hydrides of different electronic structure and hydrogen concentrations, were chosen for these studies, namely palladium hydride PdH_x (x~1) and titanium hydride TiH_y (y~2).

2. Experimental and calculations methods

On the basis of previous work [1,2,4–6], thin Pd and Ti films were used in these studies. The experiments were carried out using a UHV glass apparatus capable of reaching vacuum 10^{-11} mbar during thin-film deposition, and permitting a study of H_2 interaction with the films up to a pressure of 10^{-1} mbar. Thin films were deposited by evaporation of a fine Pd (or Ti) wire from a tungsten heater and transformed in situ into PdH_x (x~0.9) or TiH_y (y~1.95) in a controlled manner, by interaction with H_2 [1,4–6]. Hydrides of known concentration were obtained under isothermal conditions: at 78 K for PdH_x and at 298 K for TiH_y. The final applied pressure of H_2 was of the order of 10^{-2} mbar. Next, the system was isothermally evacuated. Furthermore, the hydrides could be maintained in situ at a required temperature. H_2 redosing allows studies of hydrogen adsorption on thin PdH_x (TiH_y) surfaces. The investigation was carried out by simultaneously measuring surface potential (SP) and H_2 pressure (p) under isothermal conditions. SP was measured by means of a sensitive (±1 mV), short response time (1 ms) static capacitor system [7,8], while H_2 pressure was read by means of an ultra-sensitive Pirani type gauge immersed in liquid nitrogen, working within 10^{-6}–10^{-1} mbar. Thin palladium or titanium hydride film served as an active electrode of the static capacitor, while the reference electrode was prepared by melting a conducting layer of ($SnO+Sb_2O_5$) into Pyrex glass. H_2 was introduced into

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the static capacitor (disconnected from pumps) in successive calibrated doses. Recording surface potential and pressure, while knowing the volume of the static capacitor, enables one to obtain the relation between *SP* and hydrogen uptake n_a: $SP=f_1(n_a)_T$. The dependence of H_2 equilibrium pressure p_{eq} on n_a: $p_{eq}=f_2(n_a)_T$ can also be determined. When the $f_1(n_a)_T$ function is known, the measured, time-dependent, surface potential changes caused by adsorption, or desorption $SP=f_3(t)_T$ can be transformed into the relation $n_a=f_4(t)_T$. Accordingly, known kinetic equations can be applied to examine the kinetics of the studied surface processes. Some experiments were performed with a constant, calibrated flow of H_2 admitted into the static capacitor continuously measuring surface potential and hydrogen pressure changes as a function of time: $SP(t)_T$ and $p(t)_T$. This allows a calculation of the coverage-dependent sticking probability coefficient $S(n_a)_T$ for a given state of the adsorbate, since on the basis of functions: $SP(t)_T$, $p(t)_T$ and $f_1(n_a)_T$ the effective adsorption rate (dn_a/dt) can be experimentally determined. The effective adsorption rate is correlated with the sticking probability by the equation:

$$dn_a/dt = ZS(n_a)_T[p(t) - p_{eq}] \qquad (1)$$

where *Z* is the collision factor.

3. Results and discussion

The evolution of the surface potential as measured during the introduction of successive doses of H_2 into the static capacitor housing thin $PdH_{0.9}$ or $TiH_{1.95}$ films is shown in Fig. 1. At 78 K both hydrides could be examined, however at 298 K the p_{eq} value over $PdH_{0.9}$ was too high (10 mbar [9–11]) for our UHV system. One can see in Fig. 1 that successive H_2 doses introduced at 78 K caused an increase of *SP* due to formation of positively polarized hydrogen adspecies (positive pole of the dipole pointing away of the surface) on the outer surfaces of the both hydrides. However, in the case of PdH_x small transients of the positive *SP* were observed in the result of the first and the second doses introduction. Such SP transients are characteristic for the incorporation of the adspecies from the outer surface into the subsurface region [1,2,4–6]. It has been mentioned above that after PdH_x and TiH_y formation the static capacitor was isothermally evacuated. It can be expected that in the course of the evacuation some hydrogen adspecies from the subsurface may desorb. Thus, the first doses of the readmitted hydrogen rebuilt PdH_x surface, while further doses led to adsorption on it. An isothermal evacuation performed at 78 K resulted in a complete desorption of hydrogen adsorbed on the rebuilt $PdH_{0.9}$ surface; however, a part of the adsorbate is stable at this temperature on $TiH_{1.95}$. This suggests some distribution of the binding energy of hydrogen adspecies on the TiH_y surface. We have found that hydrogen irreversibly adsorbed at 78 K on $TiH_{1.95}$ desorbs at 150 K [12]. As seen in Fig. 1 successive hydrogen redosing at 78 K returns the *SP* to its previous value for both hydrides. Subsequent evacuation causes complete desorption of the readsorbed hydrogen adspecies. Further adsorption–desorption cycles showed excellent reproducibility. These experiments thus demonstrate that very weakly bound hydrogen adspecies exist at 78 K on surfaces of $PdH_{0.9}$ and $TiH_{1.95}$. The course of the relation $SP=f_1(n_a)$ is shown in Fig. 2. It was found that MacDonald and Barlow's equation [13] derived for a mobile, interacting dipole layer fits well the experimentally determined $f_1(n_a)$ function (see insert I in Fig. 2). According to this equation:

$$SP = 4\Pi\mu_0 n_a/(1 + 9\alpha n_a^{3/2}) \qquad (2)$$

where μ_0 is the normal component of the dipole moment at $n_a \sim 0$, and α is the polarizability of the adsorbate. Calculated values of these parameters are listed in Table 1. It should be noted that the determined polarizability of the hydrogen bond to the surfaces of both hydrides is much higher than that of the H_2 molecule. Also the value of μ_0 is much higher than that commonly known for hydrogen adsorption on surfaces of transition metals. This suggests the emergence of an ionic component in the binding of hydrogen adspecies to the surfaces of hydrides, which is similar to what was observed in the bulk [14,15]. Isothermal adsorption and desorption rates at 78 K do not fit any simple kinetic equations. It should be expected however that in the case of a weak adsorption an interaction within the adsorbate can be important. Thus the activation energies for adsorption E_{ad} and desorption E_{des} should be corrected by introduction of a term associated with the electrostatic repulsive interaction. The correction term is equal to the electrical work [$b(SP)$] required to charge the adsorbate up to the measured coverage-dependent surface potential *SP*, where *b* is a proportionality factor characteristic of the adsorbent–adsorbate system (expressed in Table 1 in electron charge units, e). The coverage-dependent electrostatic energy of the adsorbate should accelerate desorption and inhibit adsorption. Thus the activation energy of desorption E_d and adsorption E_a are expected to be coverage-dependent as follows:

$$E_d = E_{d0} - b(SP) \text{ and } E_a = E_{a0} + b(SP) \qquad (3)$$

where E_{d0} and E_{a0} are activation energies for desorption and adsorption at very low coverages. We have found that the second-order kinetic equations for adsorption and desorption with the activation energies corrected according to Eq. (3) fit the experimental data well. This suggests dissociative adsorption and associative desorption, and, thus, the presence of a weakly bound atomic hydrogen adspecies on the outer surfaces of the both hydrides at 78 K. This weakly bound atomic hydrogen deposit is a unique state of hydrogen adsorbate, characteristic of the hydride

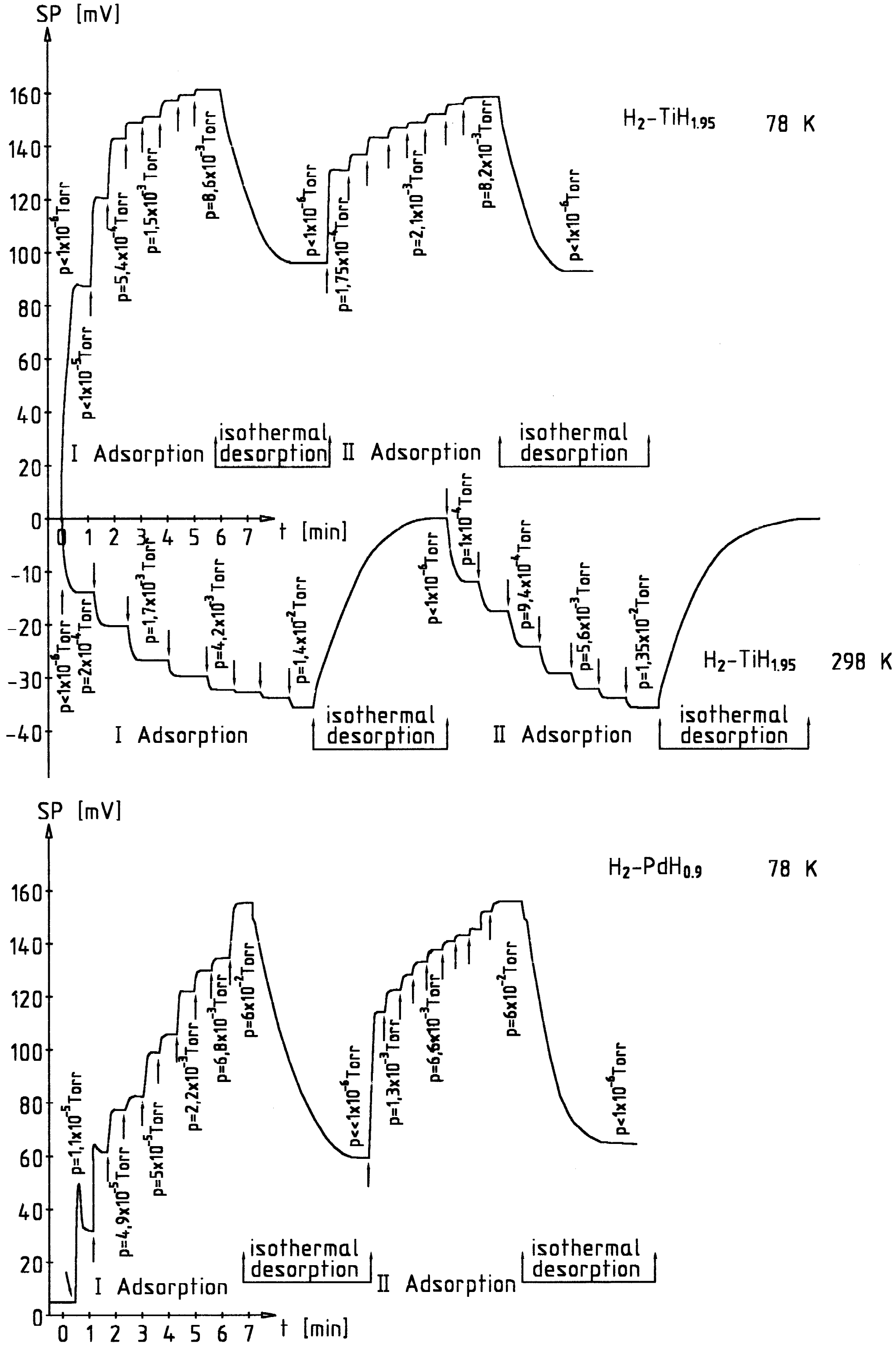

Fig. 1. The course of *SP* changes in the process of hydrogen adsorption on surfaces of $PdH_{0.9}$ and $TiH_{1.95}$ at 78 K and 298 K. Arrows indicate introduction of the successive H_2 doses. Equilibrium pressure after given dose introduction is marked.

surfaces, and unknown for hydrogen adsorption on surfaces of transition metals.

Our studies deliver also an independent proof, derived under equilibrium conditions, for the presence of the weakly bound atomic hydrogen species on PdH_x and TiH_y surfaces at 78 K. This proof is based on the measured dependence of H_2 equilibrium pressure and surface potential on hydrogen adsorbate population on PdH_x and

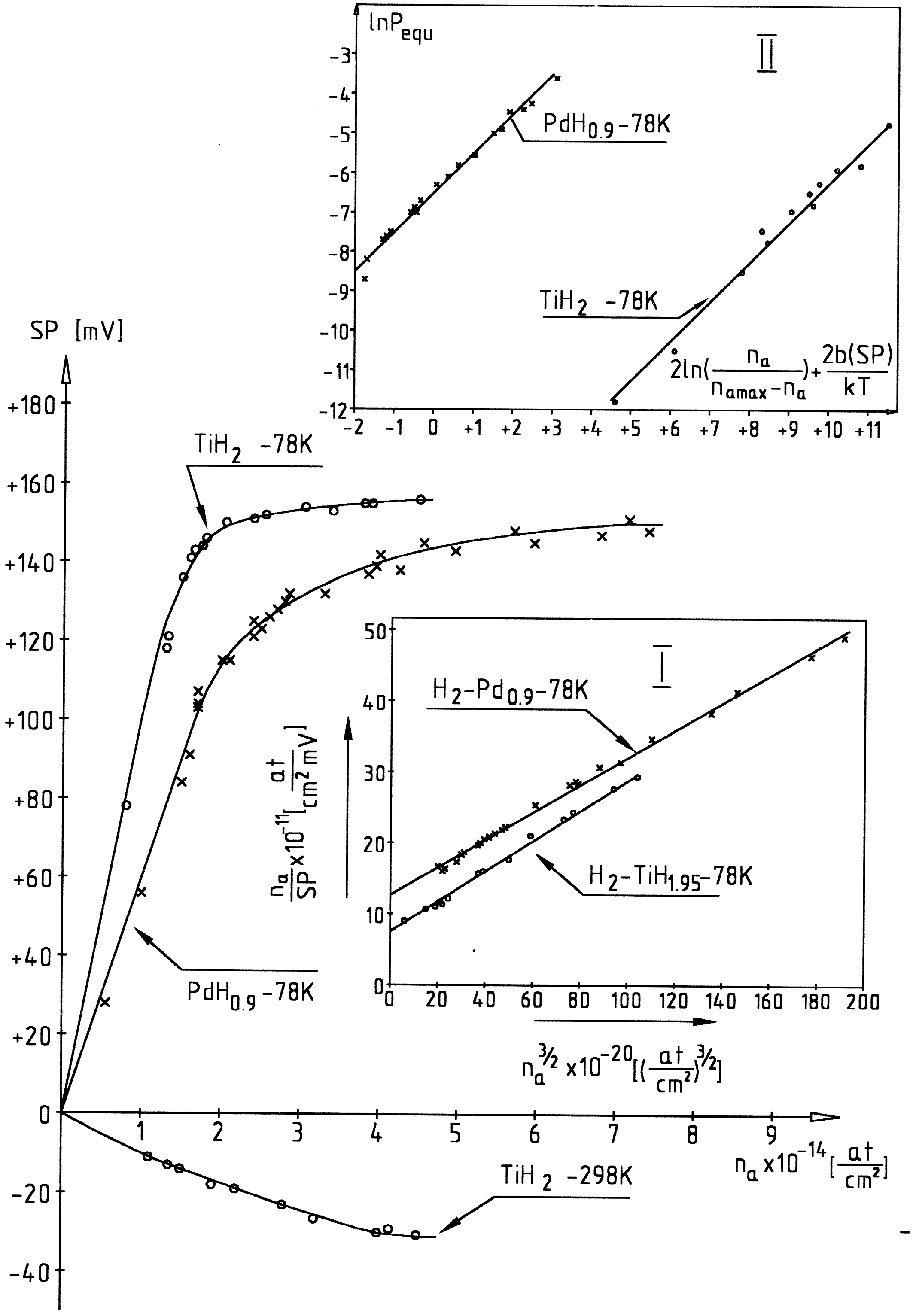

Fig. 2. The course of $SP = f_1(n_a)_T$ function for hydrogen adsorption on the surface of $PdH_{0.9}$ at 78 K and on the surface of $TiH_{1.95}$ at 78 K and 298 K. Examination of the $f_1(n_a)_T$ function according to MacDonald-Barlow's equation is shown in the insert I. Examination of p_{equ} dependence on n_a and SP according to Eq. 4 for hydrogen adsorption on surfaces of $PdH_{0.9}$ and $TiH_{1.95}$ at 78 K is shown in insert II.

Table 1
Parameters for hydrogen adsorption on $PdH_{0.9}$ and $TiH_{1.95}$ surfaces

	Adsorption temperature (K)	μ_0 (D)	α (10^{-23} cm^3)	b (e)	Q_0 (kJ mol^{-1})	Q_{ist} ($n_a=0$) (kJ mole^{-1})
$PdH_{0.9}$	78	+0.21	1.8	0.079	–	–
$TiH_{1.95}$	78	+0.35	3.1	0.300	18.3	–
$TiH_{1.95}$	298	−0.03	0.8	–	–	52.0

TiH_y surfaces. Under equilibrium conditions the rates of hydrogen dissociative adsorption and associative desorption are equal, and can be described as follows:

$$ZS_0(1 - n_a/n_{a\,max})^2 \exp[-(E_{ao} + bSP)/kT]\, p_{eq} = k_d(n_a/n_{a\,max})^2 \exp[-(E_{d0} - bSP)/kT)] \quad (4)$$

where k_d is the desorption rate constant, S_0 is the sticking probability at $n_a \sim 0$, and $n_{a\,max}$ is the maximal density of the adsorbate taken as the average density of Pd or Ti atoms on the surface of low-index planes. Accordingly a plot of $\ln(p_{eq})$ versus $\{2\ln[n_a/(n_{a\,max}-n_a)]+2bSP/kT\}$ should yield a straight line with a slope of unity. This is really observed (see insert II in Fig. 2), showing that Eq. (4) fits the experimental data well. Heat of adsorption of the reversibly adsorbed hydrogen on surfaces of PdH_x and TiH_y is equal to the difference $(E_{d0}-E_{ao})=Q_0$. All parameters in Eq. (4), except Q_0, can be determined by examining adsorption–desorption rates, and, thus, the heat of dissociative hydrogen adsorption on surfaces of hydrides can be calculated (see Table 1).

It can be clearly seen in Figs. 1 and 2 that hydrogen deposits produced at 298 K on the $TiH_{1.95}$ surface differ substantially from that obtained at 78 K. It has been suggested, on the basis of the experimental data concerning surface phenomena in the process of TiH_x formation [4], that at 298 K positively polarized hydrogen adspecies incorporate below the surface image plane (SIP), thereby inducing a negative charge on the outer surface. This presumably leads to the observed *SP* decrease. Evacuation of the static capacitor at 298 K leads to a complete desorption of the adsorbate, while H_2 redosing brings *SP* to its previous value (Fig. 1). The MacDonald-Barlow's equation [13] fits the experimental data for the $SP=f_1(n_a)_{298\ K}$ dependence. The determined values of α and μ_0 are listed in Table 1. The differential isosteric heat of adsorption Q_{ist}, as calculated on the basis of $p_{eq}=f_2(n_a)_T$ functions determined at 273 K and 298 K, decreases with increasing n_a, and is much higher than Q_0 (see Table 1). This indicates that the binding energies of the adsorbate placed above and below the (SIP) differ significantly. The kinetic equations for the adsorption–desorption processes described above do not fit the experimental data at 298 K. However, the desorption rate is well described by a second-order kinetic equation when we set $E_{des}=Q_{ist}(n_a)$. This indicates a dissociative hydrogen adsorption which occurs with a coverage-dependent binding energy on $TiH_{1.95}$ surfaces at 298 K.

4. Conclusions

Hydrogen adsorbs dissociatively on $PdH_{0.9}$ and $TiH_{1.95}$ surfaces at 78 K and on $TiH_{1.95}$ also at 298 K. The deposit is very weakly bound and forms a unique state of atomic hydrogen adsorbate.

At 78 K hydrogen adspecies are placed above the surface image plane, while at 298 K they are placed below it. The binding energies in these two states differ significantly.

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