

REVERSIBLE ADSORPTION OF HYDROGEN IN ADSORPTION-SATURATED ACETYLENE LAYERS ON PALLADIUM SURFACES

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Received October 16th, 1984

Palladium films with preadsorbed acetylene layers were interacted with molecular hydrogen. Reversibly adsorbed hydrogen in the molecular form was found on the surface. The molecule probably occurs in a more reactive state than the molecule of hydrogen gas; this state precedes the dissociative adsorption of hydrogen and it may be involved in catalytic reactions of hydrocarbons on metals.

Hydrogen interacting with pure surfaces of transition metals adsorbs dissociatively and largely with nearly no activation barrier¹. A whole gamut of species (surface, "sub-surface", and bulk-absorbed) has been found to emerge from the interaction of hydrogen with pure palladium surfaces²⁻⁴.

The behaviour of hydrogen is different on metal surfaces with preadsorbed particles. These can block the adsorption sites of the surface with respect to the chemisorption of hydrogen. With palladium, where dissolution of hydrogen in the metal bulk takes place, the preadsorbed particles can also hinder the passage of hydrogen from the bulk to the surface and *vice versa*, hence, suppress the absorption of hydrogen by the bulk and liberation of hydrogen from the bulk into the gas phase⁴. Carbon monoxide behaves so, for example. Moreover, admitted together with hydrogen, carbon monoxide is adsorbed preferentially and affects the adsorption of hydrogen considerably even at very low degrees of coverage. For instance, a low coverage of the palladium (100) surface by carbon monoxide has a great effect on the population of the α -states of hydrogen while the chemisorption of the β -states remains virtually intact. At high degrees of surface coverage by carbon monoxide the population of the β -states of hydrogen decreases as well and ultimately the surface becomes completely poisoned with respect to the adsorption of hydrogen. However, in both cases of the α - and β -states, only atomically bonded hydrogen is involved. Molecularly bonded hydrogen was never observed on palladium.

With other preadsorbed substances, such as hydrocarbons, the situation during the interactions of the modified surfaces is more complex; in addition to the hydrogenation of some types of surface hydrocarbon complexes by hydrogen, other pheno-

mena similar to those mentioned for preadsorbed CO, such as surface blocking, etc., can also take place.

The objective of this work was to study the effect of preadsorbed acetylene on the interaction of hydrogen with palladium surfaces. The results obtained indicate that hydrogen may be bonded to the surface in the molecular form.

EXPERIMENTAL

The experimental techniques, preparation of the palladium surfaces, and the adsorbates used were as in the previous work⁵. Palladium films were deposited on the walls of the adsorption cell under conditions of an ultrahigh vacuum (the pressure of the residual atmosphere during the deposition was lower than $6 \cdot 10^{-7}$ Pa). The temperature of the walls was held at 0°C during the deposition and the films obtained were thermostatted for 30 min at a temperature which was at least 30°C higher than the temperature of the film during the adsorption and surface reactions.

Acetylene of research grade purity (Matheson) was purified by repeated fractional distillation in the adsorption apparatus prior to use. Hydrogen was obtained electrolytically and purified by allowing it to diffuse through a heated palladium thimble and passing it through two freezing traps cooled with liquid nitrogen. Atomic hydrogen was obtained by atomizing molecular hydrogen on a heated tungsten wire.

Changes in the work function of the surfaces were measured by Kelvin's vibrational condenser method⁶. Volumetric measurements and analysis of the gaseous reaction products were also used in the study of surface interactions.

RESULTS AND DISCUSSION

Changes in the work function as referred to throughout this paper are defined as $\Delta\varphi = \varphi_a - \varphi_b$, where φ_a and φ_b are the work functions of the film after and before the interaction of the particles with the surface under study. For instance, φ_b is the work function of the surface with a preadsorbed layer and φ_a is that after the interaction of an additional gas with the preadsorbed layer.

Interaction with Molecular Hydrogen

The work function changes were measured for palladium after the interaction of hydrogen with a layer of adsorbed acetylene on: a) pure palladium films; b) palladium films with preadsorbed hydrogen; c) palladium films with hydrocarbon residues from acetylene; and, for a comparison, $\Delta\varphi$ were also measured for pure palladium surfaces after their interaction with hydrogen solely - d). Both relatively low hydrogen pressures and pressures of hundreds of Pa were used.

The results depended on the kind of surface modification prior to the adsorption of acetylene at 25°C. On pure palladium films free of preadsorbed acetylene (case (d)), the maximum attainable work function change on the interaction with hydrogen was $+0.21 \pm 0.01$ eV. The irreversible change in the work function after pumping off the gas phase was $+0.20 \pm 0.02$ eV.

On surfaces with preadsorbed acetylene (case *a*)), where the irreversible saturation change in the work function of palladium films resulting from the adsorption of acetylene has been found⁵ to be -1.72 ± 0.05 eV, the maximum work function increase on the interaction with hydrogen was $+0.47 \pm 0.02$ eV. The hydrogen pressure above the adsorption layer was hundreds of Pa. The irreversible change in the work function after evacuation of the gas phase was zero. The amount of hydrogenation products condensable at liquid nitrogen temperature was negligibly low.

On surfaces, where acetylene was adsorbed on films with a preadsorbed monolayer of irreversibly bonded hydrogen (case *b*)), the work function of the surfaces increased on the interaction with hydrogen by 0.75 ± 0.02 eV (on films with preadsorbed hydrogen, adsorption of acetylene led to a decrease in the work function the irreversible saturation change of which was -1.88 ± 0.05 eV). The irreversible change in the work function of these surfaces on the interaction with molecular hydrogen was not zero; instead, it amounted to $+0.25 \pm 0.02$ eV. The observed reversible part of the work function change again was about $+0.5$ eV. The amount of hydrogenation products condensable at the temperature of liquid nitrogen was now larger, and this also contributed to the higher irreversible change in the work function. Repeated admittance of hydrogen at pressures of hundreds of Pa only resulted in a reversible 0.5 eV increase in the surface work function, but no condensable hydrogenation products emerged.

The interaction with hydrogen was also studied for surfaces with preadsorbed acetylene prepared as follows (case *c*)). Acetylene was adsorbed on pure palladium films at approximately -80°C until the saturation value of $\Delta\phi$ had been attained ($\Delta\phi = -0.84 \pm 0.05$ eV). The gas phase above the adsorbed acetylene layer was pumped away ($\Delta\phi = +0.1$ eV) and the surface was allowed to attain room temperature ($\Delta\phi = +0.17$ eV). After removing the desorbed products, mainly C_6H_6 and C_4H_8 and minor quantities of C_2H_2 , C_2H_4 , and C_2H_6 (ref.⁵), the adsorption layer was completed by adsorption of acetylene at 25°C ($\Delta\phi = -0.86$ eV). Prior to the interaction with hydrogen the gas phase above the film was exhausted ($\Delta\phi = -0.03$ eV). The maximum change in the work function on the interaction of these surfaces with hydrogen (at pressures of hundreds of Pa) made $+0.23 \pm 0.02$ eV. The irreversible change in the work function was very low indeed – it was actually zero within the limit of experimental error. This is consistent with the fact that the amount of condensable hydrogenation products was negligibly low.

Interaction with Atomic Hydrogen

The surfaces under study were also allowed to interact with atomic hydrogen. Irreversible changes in ϕ were observed in all cases except for case *b*), where no effect of atomic hydrogen on the work function was found. This behaviour in case *b*) can be explained so that atomic hydrogen was already present on the surface during

the adsorption of acetylene (due to the dissociative adsorption of hydrogen on pure palladium surfaces) and it could affect the surface processes during the adsorption of acetylene and thereby also the interaction of the formed hydrocarbon surface layer with molecular and atomic hydrogen. The results of the saturation changes in the work function after the removal of the gas phase for the various cases are given in Table I along with the changes occurring on the interaction of the surfaces with molecular hydrogen. In case *d*) the interaction with atomic hydrogen was not measured; according to ref.¹, adsorption of hydrogen atoms from the gas phase takes place even on surfaces completely covered by chemisorbed H₂.

In the case of interaction of atomic hydrogen with layers of acetylene formed by its adsorption on pure (nonmodified) palladium surfaces, irreversible changes in the work function occur not only at room temperature but also at higher temperatures⁵. The amount of hydrogenated condensable hydrocarbon products, however, is negligibly low and it even decreases further with increasing temperature⁵. This fact and the obtained irreversible changes in the work function on the interaction with atomic hydrogen can be explained in terms of two different concepts:

1) Atomic hydrogen adsorbs predominantly on the remaining free adsorption sites in the surface-adsorbed acetylene layer, thereby inducing the observed irreversible change in the work function. A negligibly low fraction of this hydrogen reacts with the hydrocarbon complexes to give a gaseous (condensable) product.

2) Alternatively, new, strongly surface-bonded hydrocarbon complexes can be assumed to form during the interaction of atomic hydrogen with the surface layer (with the reactive species of the adsorption complexes of the adsorbed acetylene). An example of such strongly surface-bonded hydrocarbon complexes is adsorbed ethylidene^{7,8}. The strong bonding to the surface and the inertness of the newly formed hydrocarbon complexes with respect to additional reactions with hydrogen then are responsible for the low amount of condensable products of this hydrogenation in the

TABLE I

Changes in the work function (eV) of the palladium surfaces on their interaction with molecular and atomic hydrogen. $\Delta\varphi_1$, $\Delta\varphi_2$ the total and the irreversible changes due to the effect of molecular hydrogen, $\Delta\varphi_3$ the irreversible change due to the effect of atomic hydrogen

System	$\Delta\varphi_1$	$\Delta\varphi_2$	$\Delta\varphi_3$
a)	0.47	0	0.62
b)	0.75	0.25	0
c)	0.23	0	0.30
d)	0.21	0.20	—

gas phase. The results of work^{5,9} have shown that dissolution of hydrogen in the bulk will not be the dominating effect.

A behaviour similar to that found in case *a*) was also observed for the interaction of atomic hydrogen with surfaces of type *c*). Again, an irreversible increase in the work function occurred on the action of atomic hydrogen and very small amounts of condensable products were observed. Preadsorption of acetylene at -80°C , desorption of the species on increasing the temperature to room temperature, and completion of the adsorbed layer by adsorption of acetylene at room temperature (case *c*)) result in a lower increase in the work function on the interaction of this layer with atomic hydrogen than in case *a*). This may be due to the adsorption sites for the adsorption of hydrogen atoms from the gas phase being blocked, or the amount of the reactive species of adsorbed acetylene on these surfaces being lowered.

These conclusions are borne out by the results obtained with surfaces of type *b*). The zero change in the work function is due to the fact that the adsorption capacity of these surfaces is completely occupied, so that no free sites for the adsorption of hydrogen atoms from the gas phase or reactive adsorption complexes of acetylene with which atomic hydrogen would form new strongly bonded hydrocarbon species are available. This is due to the hydrogen preadsorbed on the surfaces prior to their interaction with acetylene, and the consecutive interaction of the hydrocarbon layer with molecular hydrogen. As a consequence, all the sites for the adsorption of hydrogen atoms are occupied and all the reactive forms of adsorbed acetylene are exhausted. The gaseous atomic hydrogen reacting then with these surfaces does not bond to the surface hydrocarbon layer and thus does not bring about any change in the work function of the surfaces.

Based on an estimate of the amount of CO that could form on the hot tungsten filament during the atomization of hydrogen by reaction of carbon from the cathode filament with oxygen from water decomposing on the hot filament¹⁰ (water is present in the residual atmosphere in the UHV glass equipment), the work function of the surfaces can be regarded as unaffected by carbon monoxide.

It can be inferred that the reversible changes in the work function of palladium surfaces modified by adsorbed acetylene are due to hydrogen interacting in the molecular form without dissociating into atoms. Otherwise, irreversible changes in ϕ would have to be observed, as was the case with the interaction of the surfaces with atomic hydrogen from the gas phase.

The effect of hydrogen absorbed by the metal bulk can be probably also ruled out, hence, absorption of hydrogen is hindered by the adsorbed acetylene. This conclusion can be arrived at as follows. On pure palladium surface on which only a monolayer of hydrogen is chemisorbed, increase in the hydrogen pressure results in dissolution of hydrogen in the bulk¹¹, which is associated with a decrease in the work function^{2,12}. If the gas phase is exhausted, the work function increases up to a value corresponding to that for the surface coated by the irreversible chemi-

sorbed hydrogen layer. For surfaces with a preadsorbed acetylene layer only (types a) and c)), on the other hand, the work function increases on raising the hydrogen pressure and only decreases with decreasing pressure. These facts indicate that the mechanisms of interaction of hydrogen on the pure films and on the films coated by adsorbed acetylene complexes are different.

A possible explanation of the increase in the work function of surfaces with preadsorbed acetylene on their interaction with molecular hydrogen is in terms of polarization of the hydrogen molecule. The polarizability of hydrogen (in the classical sense) is rather low, and so this explanation does not seem very probable. However, recent calculations of the induced polarizability for molecules with no permanent dipole moment occurring during their interaction with metal surfaces have shown¹³ that short-range quantum mechanical effects operating during this interaction can lead to a multiple increase in the polarizability of these molecules, and so this effect cannot be ruled out.

Some other mechanism may also be involved. For instance, electron transfer from the metal surface to the antibonding σ^* orbitals of the hydrogen molecules can take place during the interaction, hence, partly negatively charged H_2 molecules can be surface-bonded. The reason for their formation can be sought speculatively in the higher reactivity of the perturbed, possibly excited molecules in their reaction with the surface. Actually, interaction of molecules with metal surfaces can lead to vibrational¹⁴ and electronic¹⁵ excitation of the interacting molecules as well as to the excitation of the metal surface¹⁶. All of these, together with the enhanced reactivity of the excited molecules, can result in an electron charge transfer from the metal surface to the antibonding σ^* orbitals of the hydrogen molecules, and this may be responsible for the observed increase in the work function. This electron charge transfer, inferred from the work function changes, is consistent with the theoretical analysis of the interaction of H_2 with metal surfaces presented in paper¹⁷. This electron charge transfer brings about weakening of the H–H bond and strengthening of the H–metal surface bond. In view of the adsorption saturation of the surface by the adsorbed acetylene complexes, it is possible that these changes in the bond strength are not sufficient for inducing dissociation of the interacting hydrogen molecule. The latter then is weakly bonded to the surface as a negatively charged species. Since this species can be removed from the surface by evacuation, it can be regarded as molecules in the case under study. Possibly this state of the hydrogen molecule is a precursor state which can precede the dissociative adsorption of hydrogen and which may occur during catalytic reactions of hydrocarbons on metals. The problem calls for further study.

The author wishes to thank Dr Z. Knor for critical comments on the manuscript.

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Translated by P. Adámek.