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Interaction of Hydrogen with Palladium*

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The adsorption and absorption of hydrogen on palladium wires cleaned by treatment in oxygen to remove surface impurities have been studied using flash filament desorption. The initial hydrogen sticking coefficient was found to be 0.13 and independent of temperature from 100 to 300°K.

With the filament temperature initially at 200°K, three states, β_1, β_2, and β_3 with apparent second order desorption kinetics and binding energies of about 22, 25, and 35 kcal/mole were observed. For hydrogen pressures less than 10^{-7} Torr, these states saturate at less than one hydrogen atom per surface palladium atom. The saturation coverage at 300°K was 0.39 H/Pd and at 200°K this value was increased to 0.95 H/Pd. These states thus appear to correspond to hydrogen adsorbed on the palladium surface.

When the filament temperature was decreased to 100°K, another state, α, was observed with a desorption activation energy of 13–14 kcal/mole. The sticking coefficient for this state was about 10^{-3}, and the amount of hydrogen taken up in the α state greatly exceeded that of the β states. It is felt that the α state corresponds to solution of the hydrogen in the palladium wire, and the experimental results are shown to be consistent with this hypothesis.

INTRODUCTION

The adsorption of simple diatomic molecules on clean refractory metals such as tungsten and molybdenum is generally found to be nonactivated, proceeding with a relatively large sticking coefficient. With the exception of nickel, there have been comparatively few measurements of rates and heats of adsorption on clean surfaces of the fcc metals such as palladium and platinum which have interest as practical catalysts. It is generally found that the normal techniques used to prepare a clean refractory metal surface are unsuccessful when applied to metals with lower melting points. With platinum, for instance, the surface retains a large residue of carbon and sulfur which can only be removed by heating the metal in oxygen (*1*, *2*).

The initial heats of adsorption of hydrogen or the fcc platinum group metals, either supported on silica or as powders and evaporated films have all been reported. For supported Ni, Pt, Pd, Rh, and Ir, the values are all between 25 and 27 kcal/mole (*3*). On evaporated films of Ni, the initial heats vary from 28 to 40 kcal/mole (*4–7*), and on Pd films a value of 26 kcal/mole was obtained (*8*). The values range from 21 to 27 kcal/mole with nickel powders (*9–12*) and from 16 to 32 kcal/mole with platinum blacks (*13–16*). On a platinum field emitter, Rootsaert *et al.* (*17*) measured a heat of adsorption of 26 kcal/mole. In all cases both the isosteric and calorimetric heats were found to decrease with increasing coverage.

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The rate of adsorption of hydrogen on a polycrystalline platinum filament has been measured by Wiesendanger (*18*). The adsorption appeared to be activated, with the sticking coefficient increasing from 10^{-3} to 8×10^{-2} or greater as the filament temperature was increased from 300 to above 1100°K. However, Germer and MacRae (*19*) have found that on the (111) face of nickel, the sticking coefficient was large, 0.1, a value comparable to those found on clean refractory metal surfaces. There have been no values reported for the adsorption rates of hydrogen on clean palladium surfaces, but Park and Madden (*20*) have shown that when the (100) face of palladium is cleaned by ion bombardment and extensive annealing, the sticking coefficient for the adsorption of CO is also large with the surface saturating in about 6×10^{-5} Torr sec.

In the present work, the adsorption and interaction of hydrogen on polycrystalline palladium surfaces has been studied using the flash-filament desorption technique. By using flash desorption, it is possible to readily obtain adsorption rates, binding energies, and the saturation coverage on the metal surface at different temperatures. The palladium filaments were cleaned by a pretreatment in oxygen similar to that used to prepare a clean platinum surface (*1*, *2*).

EXPERIMENTAL

The flash desorption technique has been described in detail by Redhead (*21*). The amount adsorbed is obtained by measuring the area under the desorption peak, and the heats of adsorption are determined from the temperature at the peak maxima. To obtain an absolute measure of the adsorbate concentration, the pumping speed of the system and the sensitivity of the ionization gauge or mass spectrometer must be known. Although this can be done in principle, the sensitivities and pumping speeds may change with time, requiring periodic measurement of these parameters. To circumvent this problem, a tungsten filament of equal area was placed in the system with the palladium wire to serve as a reference. The tungsten surface was chosen because it could be easily cleaned and there exists considerable information on the interaction of hydrogen with tungsten (*22–24*). Also the flash desorption traces from tungsten give a rapid indication of the impurity composition in the ambient gas phase, since the desorption spectra of common gases on tungsten are well-known. The pumping speed of the system was sufficient to insure that the variations in the ambient pressure were proportional to the desorption rate.

The palladium filaments were obtained from the Materials Research Corp. Chemical analysis of samples before and after use showed that the major impurities were Pt (25 ppm), C (20 ppm), and O (25 ppm). Both palladium and tungsten filaments were 0.010 in. in diameter and about 8 in. long. Two-0.003 platinum leads were spot-welded to the palladium filament for resistive temperature measurements. The resistance of palladium as a function of temperature were taken from published values (*25*).

The glass vacuum system was mercury-pumped and bakeable to about 400°C. Tungsten- or tantalum-evaporated film getters were used to achieve ultimate pressures near 10^{-10} Torr after bake-out. Oxygen was introduced into the system by resistively heating a copper oxide filled platinum crucible. Although initially the source gave large amounts of CO and CO_2, after a short time the CO and CO_2 pressures dropped to less than 10% of the O_2. Research-grade hydrogen was admitted from a Pyrex flask through a bakeable metal valve. The only detectable impurity was methane at less than 1%.

The mass spectrometer was similar to the one previously described (*26*) except that the electron multiplier was replaced with a Faraday cage, and an extra grid was placed directly before the entrance to the quadrupole assembly in order to monitor the total pressure as well as the partial pressures. A low-work function thoriated-tungsten filament was used in the mass spectrometer. At an emission current of 7 mA, the filament temperature was below 1300°K.

The tungsten filament was cleaned initially by repeatedly flashing the same to > 2500°K and between each run by several flashes near 2200°K. The palladium filaments were first outgassed by heating the surface to 1700°K in vacuum followed by exposure to oxygen at a pressure of 10^{-5} Torr. While heating the filament to 1300°K for several hours, it was found that even on a filament that had been previously heated close to its melting point with no appreciable evolution of gases, exposure to oxygen resulted in the production of large amount of CO and CO_2. The amount of CO and CO_2 produced was a function of the palladium filament temperatures and initially appeared even before the filament became incandescent. The oxygenation was continued until O_2 was the most abundant component and the concentration of CO and CO_2 was no longer a function of the palladium temperature. The O_2 was then removed, and the palladium sample was heated in hydrogen at 1300°K for several hours.

The flash desorption experiments were initiated by resistively heating the tungsten and palladium filaments. The output from the mass spectrometer and ionization gauge were recorded on a storage oscilloscope or an x-y recorder. The desorption traces from palladium for a given hydrogen exposure were found to be reproducible both with respect to time and with different filaments after the initial treatment in oxygen.

RESULTS

The desorption spectra of hydrogen from a clean palladium surface are shown in Fig. 1. Several desorption states can be detected, with the shifts in peak maxima indicative of second order desorption (*21*), certainly for β_3 and probably for β_1 and β_2.

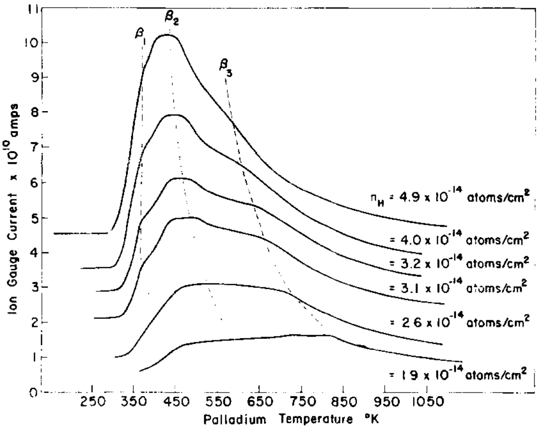

FIG. 1. Hydrogen desorption spectra from palladium at various surface coverages with an ambient temperature of 100°K.

As seen in Fig. 2, when the palladium surface was cooled to 200°K, the saturation coverage increased by a factor of 2.5. The palladium surface adsorbed about 40% more hydrogen at 200°K than did the tungsten filament at 300°K. As on tungsten, the initial sticking coefficient was relatively independent of temperature and based on a value of 0.1 for hydrogen on tungsten at 300°K, the sticking coefficient on palladium was found to be 0.13.

When the temperature of the palladium wire was reduced to 100°K, another state, designated α, was observed. This state is shown in Fig. 3, where the peak maximum is at about 250°K. The sticking coefficient for the α state was low ($\sim 10^{-3}$), but the activation energy for its formation would

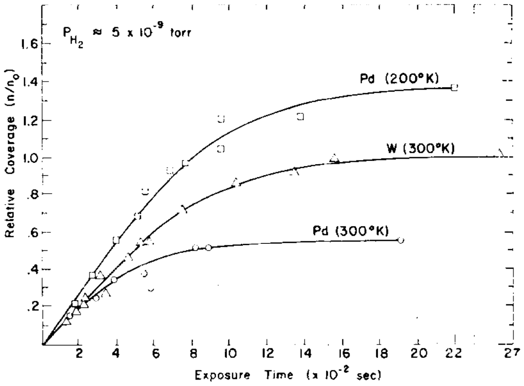

FIG. 2. Hydrogen coverage as a function of exposure time; palladium at 300°K, ○; palladium at 200°K, □; tungsten at 300°K, △.

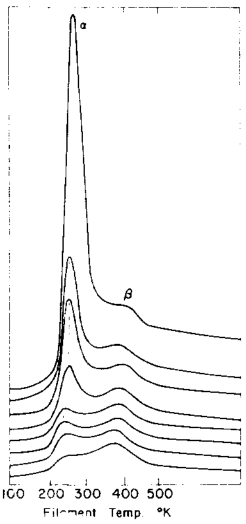

FIG. 3. Hydrogen desorption spectra from palladium at large-hydrogen exposure times and with an initial filament temperature of 100°K.

still be small (i.e., $E_a \leq 2$ kcal/mole). As shown in Fig. 3, the amount of hydrogen desorbing from the α-state greatly exceeded that for the β states. In fact, the α state could never be saturated at the highest pressures used (~ 10^{-4} Torr). However, with the filament initially at 100°K, the amount of hydrogen in the β states was approximately the same as the amount at 200°K at all pressures.

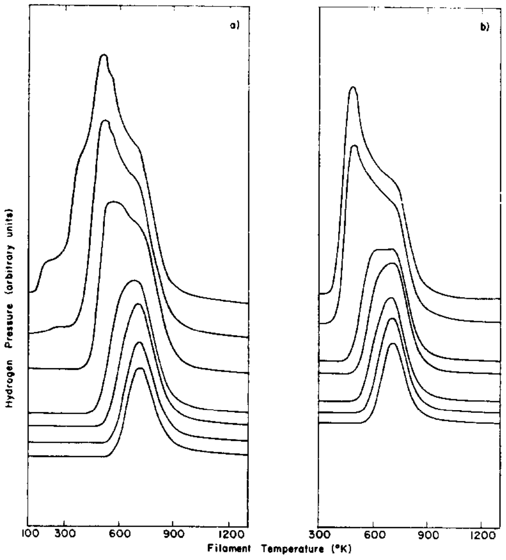

FIG. 4. Hydrogen desorption spectra from tungsten with the initial filament temperature at (a) 100°K and (b) 300°K.

After the tungsten surface had been thoroughly cleaned, a series of hydrogen desorption traces were obtained both at 300°K and 100°K (Fig. 4). Values of the surface coverages as a function of exposure time are shown in Fig. 5, and the ratio of the saturation coverage at 100°K to that at 300°K was found to be about 1.5. Also the initial sticking coefficients were found to be relatively independent of temperature. The desorption spectra shown in Fig. 4 are similar to those found by Rigby (*24*) and Ricca (*23*) on polycrystalline tungsten, and, following Hickmott (*22*), the initial sticking coefficient at 300°K was taken to be 0.1.

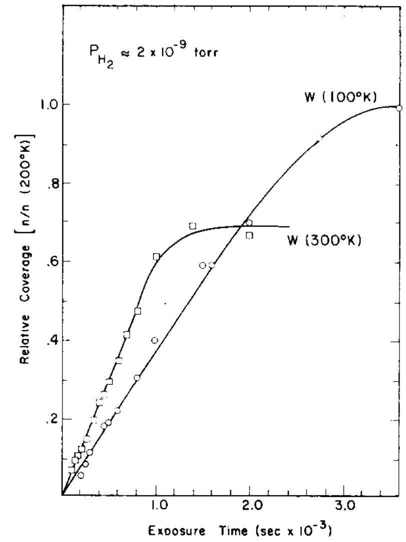

FIG. 5. Hydrogen coverage as a function of exposure time for tungsten at 300°K, □, and 200°K, ○. The coverages are relative to saturation at 200°K, n_s (200°K).

DISCUSSION

Several different hydrogen adsorption binding states on palladium, giving apparent second-order desorption kinetics, can be observed in Fig. 2. Because of the polycrystalline nature of the surface, several different states corresponding to desorption from different crystal planes would be expected. Referring to Fig. 2, a small β_3 state initially near 800°K and shifting to about 600°K is found at low coverage. By using the correlations given by Redhead (*5*) the binding energies for this state would be about 35 kcal/mole. At higher surface coverages, two states, β_1 and β_2 at 370 and 450°K are observed having binding energies at 22 and 25 kcal/mole, respectively. Thus, the flash desorption technique has resolved several second-order hydrogen-binding states on the polycrystalline surfaces within the range of 22–35 kcal/mole. By comparison, an initial heat of adsorption for hydrogen of 27 kcal/mole was found on an evaporated palladium film (*8*) and 26 kcal on a silica supported palladium sample (*3*). Also using the flash desorption technique, Mimeault and Hansen (*27*) found initial hydrogen-binding energies on iridium and rhodium of 24 and 18 kcal/mole, respectively. The flash desorption traces from iridium revealed at least two binding states, and on both metals the heat of adsorption decreased with increasing coverage.

It has also been found that when the palladium surface is rigorously cleaned in oxygen prior to the adsorption measurements, the sticking coefficient is large, 0.13, and independent of temperature. This value is comparable to that obtained from a clean tungsten surface and this, along with the reproducibility of the results, would suggest that the oxygen treatment leaves a relatively clean palladium surface.

The relative amounts of hydrogen taken up by tungsten and palladium are shown in Fig. 2. Since the wires were polycrystalline, only an estimate can be made concerning the number of hydrogen atoms adsorbed per exposed metal atom. If it is assumed that the palladium and tungsten surfaces contain equal proportions of the (100), (110), and (111) planes, then the surface densities would be 1.27×10^{15} atoms/cm^2 and 1.0×10^{15} atoms/cm^2, respectively. Values for the hydrogen saturation coverage at 300°K on polycrystalline tungsten surfaces from several different investigations have been tabulated by Ricca *et al.* (*23*). By taking an average value of 8.6×10^4 atoms/cm^2 for tungsten, the hydrogen coverages on platinum at 300 and 200°K would be 0.49×10^{15} atoms/cm^2 and 1.2×10^{15} atoms/cm^2, respectively. These values would correspond to 0.39 and 0.95 hydrogen atoms per surface palladium atom.

It is felt that the low temperature α state corresponds primarily to solution of the hydrogen in the palladium filament with the hydrogen atoms possibly remaining near the metal surface. The solubility of hydrogen in palladium is anomalously large, and a bulk-phase palladium hydride can be formed at various temperatures and pressures. The dissociation pressure of the hydride as a function of temperature has been given by Gillespie and Galstaun (*28*) as

$$\log P_{\text{atm}} = 4.6018 - \frac{1877.82}{T}. \qquad (1)$$

Thus, the dissociation pressures at 100, 200, and 300°K would be 8×10^{-12}, 1.2×10^{-2}, and 16.6 Torr. With a hydrogen pressure if only 5×10^{-9} Torr, formation of the bulk hydride should occur only at the lowest temperature, as was observed. The heat of formation from the equation of Gillespie and Galstaun would be about 8.6 kcal/mole. If the activation for the formation of the α state was 2 kcal/mole, the activation energy for desorption would be about 11 kcal/mole, which is close to the experimental value of 13–14 kcal/mole calculated from the position of the peak maxima in Fig. 3. The presence of solution of hydrogen in the metal should also alter the characteristics of the desorption curves. In particular, if n_0 corresponds to the saturation concentration of hydrogen on the palladium surface with n being the total amount adsorbed and absorbed, the rate of desorption would be given by

$$-\frac{dn}{dt} = \frac{\nu_0}{\beta} e^{-E/RT} n_0 \qquad (2)$$

for $n \geq n_0$ and

$$-\frac{dn}{dt} = \frac{\nu_0}{\beta} e^{-E/RT} n \qquad (3)$$

for $n < n_0$. In Eqs. (2) and (3), β is the heating rate assuming, that the temperature varies linearly with time, and ν_0 and E are the pre-exponential and activation energy of desorption. It has also been assumed that the surface concentration is constant at the saturation value when $n \geq n_0$ and that the desorption rate is first order in the surface concentration when $n \leq n_0$. For a system which follows first-order desorption kinetics, at all concentrations the temperature at which the desorption rate reaches a maximum is independent of the initial amount taken up by the metal (*21*). However, for a system which is governed by both Eqs. (2) and (3), the temperature at the maximum rate shifts to larger values with increasing initial concentrations when the amount initially adsorbed and absorbed exceeds n_0. In Fig. 3, the variations in the pressure are proportional to the desorption rate and a shift of about 50°K with increasing concentration can be observed. With the palladium filament at 200 and 300°K and the hydrogen pressure at 5×10^{-5} Torr, the amount of gas taken up by the wire reached a well-defined saturation value corresponding to a monolayer or less suggesting that only adsorption is occurring at these temperatures.

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