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Characterization of Palladium Blacks

I. A Novel Hydrogen Pretreatment and Surface Area Determination of Palladium

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A method for the determination of palladium surface areas using hydrogen chemisorption is described. The results obtained by this method for a series of palladium blacks covering a wide range of surface areas are given. The method is independent of the extent to which oxygen is preadsorbed on the metal surface.

INTRODUCTION

Palladium both adsorbs and absorbs hydrogen. Absorption of hydrogen results in the formation of the α-phase hydride [face-centered cubic, $a = 0.389_{0\text{-}3}$ nm at 30°C (*1*)] at low hydrogen concentrations, and the β-phase hydride [face-centered cubic, $a = 0.402_5\text{-}4_0$ nm at 30°C (*1*)] at high hydrogen concentrations. Numerous studies have been carried out on the effect of absorbed hydrogen on the physical properties of palladium (*2*, *3*). Measurements of hydrogen adsorption were thought to be impossible because of the simultaneous absorption of hydrogen by palladium.

The surfaces of palladium samples will be covered initially by a monolayer of chemisorbed oxygen, for whatever their method of preparation they invariably come into contact with air. Many workers have shown the relationship between this oxygen layer and palladium inactivity (*4*). The hydrogen pretreatment usually applied to palladium samples in work of this kind is designed to bring the surface to a standard and reproducible state by replacing this oxygen layer by one of hydrogen, for example in (*5*) the palladium black was reduced in hydrogen and outgassed at 98°C. Such a hydrogen pretreatment is not possible for very high surface area palladium blacks, because of sample sintering at this temperature.

Hydrogen chemisorption has been used for the determination of the surface areas of several transition metals, including platinum [also oxygen–hydrogen titration method (*6*, *7*)], nickel, copper, cobalt, technetium, rhenium, and ruthenium (*8*–*11*). The method has been used mainly for metals dispersed on silica and alumina supports and has the advantage over BET methods in that it yields the metal surface area rather than the combined metal–support surface area. However, migration of dissociated hydrogen atoms from the supported metal to support (spillover effect) could complicate the method for certain metal–support systems (*12*). The hydrogen isotherms of the above studies (*9*, *10*) indicate that at temperatures between −78 and 25°C a chemisorbed monolayer of hydrogen was formed on platinum at pressures less than 133 N m^{-2} (=1 mmHg). The similarity between the properties of palladium and platinum would suggest that palladium should exhibit similar hydrogen chemisorption isotherms. Figure 1 shows the complete hydrogen sorption isotherm expected for a hypothetical palladium sample.

Suzuki and Suzuki (*13*) have attempted

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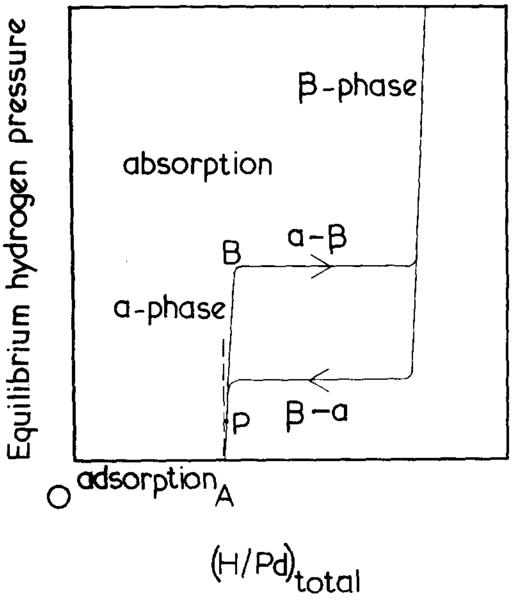


FIG. 1. Complete hydrogen isotherm for a hypothetical palladium sample.

to separate hydrogen adsorption and absorption in the α-phase region. The amount of hydrogen adsorption was postulated to be given by kp, where k is a constant, proportional to sample surface area, and p is the hydrogen pressure. However, the studies of hydrogen chemisorption on metals chemically similar to palladium do not substantiate this assumption.

Aben (*14*) has used hydrogen chemisorption to determine the surface areas of supported palladium samples. The samples were pretreated in hydrogen (101 kN m^{-2}) and then *in vacuo* at 400°C. The combined amount of adsorbed and absorbed hydrogen was then determined under chosen conditions (70°C, 133 N m^{-2}). This was corrected for the hydrogen uptake of the support, measured from a blank run, and also for the amount of absorbed hydrogen [approx 0.002 = (H/Pd)] using absorption data for palladium foil (*15*). Knowing the average number of surface palladium atoms per square meter of surface (*16*, *17*) and using palladium samples of known BET area, the ratio of adsorbed hydrogen atoms to surface palladium atoms was determined to be 1.0. This technique is not suitable for high surface area palladium blacks, because the conditions of pretreatment and measurement of hydrogen adsorption would result in a substantial loss in surface area from sample sintering, as shown in this study. The method also has the deficiency that the amount of absorbed hydrogen, at the point of measurement of hydrogen adsorption, is assumed to be independent of palladium surface area and has to be inferred from the absorption data of foils (*15*).

A series of palladium blacks covering a wide range of surface areas have been characterized for their crystallite sizes and surface areas by several techniques. The results of this characterization are given in Part II (*18*). The palladium blacks were then used in a simultaneous sorption/X-ray study of the effect of surface area upon the sorption of gaseous hydrogen by palladium (*19*). The hydrogen pretreatment devised to bring the samples to a standard and reproducible state, and also to allow the determination of the palladium surface areas, under conditions in which no sample sintering occurred, is now described.

EXPERIMENTAL METHODS

Palladium black samples. The series of palladium blacks used throughout this study were prepared by Johnson Matthey and Co. Ltd., who kindly loaned them for this study.

Hydrogen. Ultrapure hydrogen was prepared by storage over silica gel, passage over a heated platinum filament, and finally diffusion through a heated palladium–silver alloy diffusion tube.

Apparatus. A portion of the high precision volumetric apparatus used is shown in Fig. 2, where: (1) is the sample bulb; (2) and (4) are stainless steel valves; (3) is a capil-

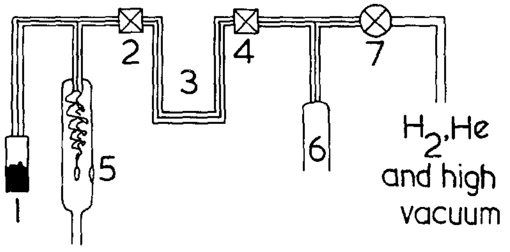
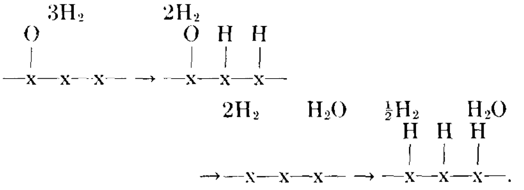


FIG. 2. Sorption apparatus.

lary liquid nitrogen trap; (7) is a Pyrex high vacuum tap, (5) a Pyrex spiral gauge; and (6) a calibrated gas burette. The apparatus was located entirely inside an air thermostat (±0.02°C) and a sample thermostat (±0.02°C) except for a small section of capillary between the two thermostats. The majority of the apparatus was constructed of 1 mm Pyrex capillary to keep dead spaces to a minimum. All dead spaces were calibrated with helium to an accuracy ±0.01 cm^3.

Reaction. The reaction between hydrogen and oxygen at the palladium surface at 273°K goes to completion, producing desorbable water (*20, 21*). This reaction is the basis of the hydrogen pretreatment and surface area determination of palladium devised in this study. Let the adsorption sites (atoms) on the palladium surface be denoted by x; then if some oxygen is chemisorbed as atoms, the oxygen–hydrogen reaction at the palladium surface can be represented by



All gas phase molecules are either hydrogen or water, and so contain two hydrogen atoms. In the above equation three surface sites are occupied by chemisorbed hydrogen atoms and three hydrogen atoms are lost from the gas phase. Thus in the overall reaction, the number of hydrogen atoms lost from the gas phase is equal to the number of surface palladium atoms. If the oxygen is chemisorbed as molecules an equivalent equation can be written, giving the same relationship between hydrogen atoms lost from the gas phase and surface palladium atoms. Moreover this relationship is independent of the initial extent of oxygen chemisorption, and hence the effectiveness of the outgassing procedure, provided some sites are available for hydrogen chemisorption.

Procedure. The sample (1) (Fig. 2) was outgassed to high vacuum at room temperature, to avoid sample sintering, for 24 hr.

A suitable measured quantity of hydrogen was dosed to the sample from the gas burette (6) via the liquid nitrogen trap (3) and metal valves (2) and (4). The hydrogen pressure above the sample, as monitored by the spiral gauge (5), never exceeded 1.33 kN m^{-2}. When equilibrium had been reached, measured quantities of hydrogen and water were desorbed. The liquid nitrogen trap removed water from the gas phase above the sample, and thus water was preferentially removed from the sample bulb. When measuring the quantity of water and hydrogen removed from the sample bulb, the trap was warmed back to room temperature, thus returning the water to the gas phase. The quantity of water removed was chosen to ensure that the saturation vapor pressure of water was not reached on warming the trap, in order that all water was completely returned to the gas phase in the gas burette. Further withdrawals were made until no more water was desorbed (noted by the lack of ice formed in the trap). A further dose of hydrogen was then admitted to the sample and after equilibration, measured quantities of water and hydrogen were withdrawn. This cycle of hydrogen dosing and water (and hydrogen) withdrawals was continued until it was not possible to remove any further water. All oxygen had now been removed from palladium surface which was covered by a monolayer of chemisorbed hydrogen. The sample was at some point (e.g., P) on the isotherm shown in Fig. 1 along the line AB.

A series of hydrogen sorption and desorption points were then measured in the pressure range $60 < p < 530$ N m^{-2}. A linear plot of $(H/Pd)_{total}$ versus pressure (along line AB in Fig. 1) was thus obtained for each sample.

Calculation. To determine the palladium surface area, the number of hydrogen atoms used in the pretreatment and chemisorbed to the palladium surface must be known.

This can be determined from any of the measured low-pressure sorption/desorption points of the $(H/Pd)_{total}$ versus pressure plots, if the quantity of absorbed hydrogen at this temperature and pressure is known or can be inferred. This was Aben's technique.

A better technique is to extrapolate the low-pressure sorption/desorption points back to zero pressure. For the α-phase, the quantity of absorbed hydrogen is proportional to $p^{1/2}$ at sufficiently low concentrations, e.g., at 25 and 90°C for absorbed H/Pd $\leqslant 0.005$ and $\leqslant 0.003$ (*22*). Most sorption/desorption points measured here were at higher absorbed hydrogen concentrations and plots of $(\mathrm{H/Pd})_{\mathrm{total}}$ versus p were found to be more linear than those of $(\mathrm{H/Pd})_{\mathrm{total}}$ versus $p^{1/2}$. However, for data at lower concentrations the latter method of extrapolation may be more satisfactory. The point of intercept with the $(\mathrm{H/Pd})_{\mathrm{total}}$ axis corresponds to the point where hydrogen adsorption is complete and a monolayer of chemisorbed hydrogen exists, but no hydrogen absorption is present. Let this intercept value be denoted by $(\mathrm{H/Pd})_{\mathrm{total\ ads}}$. Then the total number of hydrogen atoms chemisorbed to the palladium surface is given by $n_{\mathrm{H\ ads}}$, where $n_{\mathrm{H\ ads}} = (\mathrm{H/Pd})_{\mathrm{total\ ads}} \times n_{\mathrm{Pd\ total}}$, and $n_{\mathrm{Pd\ total}}$ is the total number of palladium atoms in the sample. Thus if 1.0 hydrogen atom is chemisorbed to each surface palladium atom (*14*) and it is calculated (*16*, *17*) that the average number of surface palladium atoms per square meter of surface is 1.2×10^{19}, the surface area of the palladium sample S is

$$\frac{S}{(\mathrm{m}^2)} = \frac{n_{\mathrm{H\ ads}}}{1.2 \times 10^{19}}\,.$$

The specific surface area of the palladium sample s is then given by

$$\frac{s}{(\mathrm{m}^2\ \mathrm{g}^{-1})} = (\mathrm{H/Pd})_{\mathrm{total\ ads}} \times 4.71_8 \times 10^2. \quad (1)$$

Thus the specific surface area of a palladium sample can be determined by measuring its value of $(\mathrm{H/Pd})_{\mathrm{total\ ads}}$ and substituting this into Eq. (1).

RESULTS

The technique has been used to follow the change in surface area of a palladium black of extremely high surface area, sample E, due to sintering in hydrogen at temperatures between 0 and 90°C. It has also been used to determine the surface areas of a series of palladium blacks of widely differing surface area (samples A, B, C, D, and E) immediately before the measurement of hydrogen isotherms. In addition it was also possible to use the technique to monitor changes in these sample surface areas during the measured hydrogen isotherms.

Sintering of sample E. This was the palladium black of highest surface area, and was thus thought to be the most likely to sinter at temperatures above ambient. It was necessary to know its sintering characteristics in hydrogen to determine the maximum temperature at which hydrogen isotherms could be measured without appreciable loss of sample surface area.

The hydrogen chemisorption technique was ideally suited to such a study. The sample was hydrogen pretreated and its surface area was determined at 30°C. The sample was then subjected to a heat treatment at several temperatures and its surface area was redetermined. The $(\mathrm{H/Pd})_{\mathrm{total}}$–pressure plots at these temperatures and at 0°C are shown in Figs. 3 and 4, respectively, while the surface areas calculated are given in Table 1.

As shown, the gradients of the 0°C plots are lower than those at higher temperatures. This is due to hydrogen absorption, which at 0°C is appreciable at the low pressures used for extrapolation, e.g., the α–β phase transition occurs at about 0.4 kN m^{-2} at 0°C. The pressure required for this phase transition decreases with decreasing temperature and so the extrapolation procedure used here is not possible at temperatures below 0°C. The sample surface areas should be the same at 30 and 0°C (before heat treatment) and should also be the same at 90 and 0°C (after heat treatment). The difference in areas determined at the first two temperatures is only 5%, but the area determined at 90°C is 16% below that determined at 0°C (after heat treatment). This indicates a decrease in the amount of hydrogen adsorption with increasing temperature above 0°C or ambient temperatures, in accordance with the results of

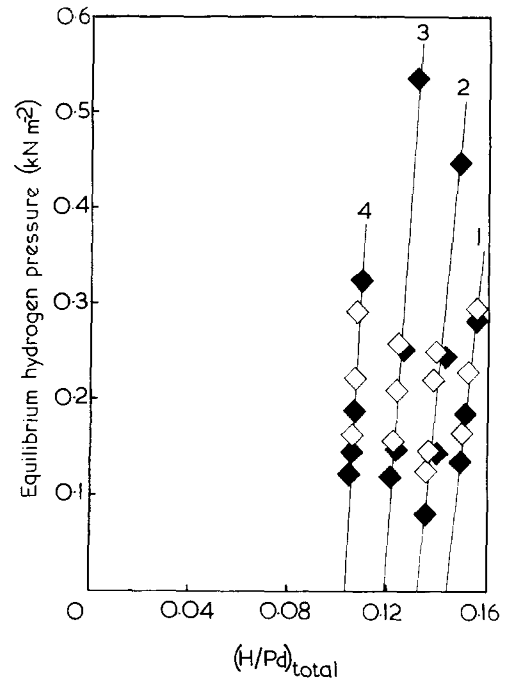


Fig. 3. Hydrogen pressure–$(H/Pd)_{total}$ plots for sample E at 30°C (1); 50°C (2); 70°C (3); and 90°C (4): (◇) sorption points; (◆) desorption points.

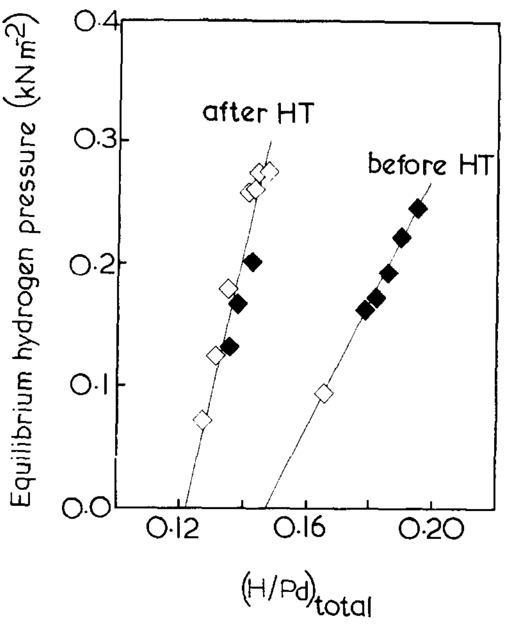


Fig. 4. Hydrogen pressure–$(H/Pd)_{total}$ plots for sample E at 0°C before and after heat treatment (HT): (◇) sorption points; (◆) desorption points.

Ref. (*23*) for alumina supported palladium. For these reasons, only surface areas measured at temperatures 0 to 30°C were considered valid. However, the above results illustrate that the heat treatment caused a real loss of surface area due to sample sintering.

Measurements before and during hydrogen isotherms. The hydrogen pretreatment was carried out at room temperature on each of the samples immediately before the measurement of hydrogen isotherms. The plots of $(H/Pd)_{total}$ versus pressure are shown in Fig. 5. The surface areas calculated are given in Table 2 with the surface area calculated for sample E at 0 and 30°C. The surface areas determined from the extrapolation of low-pressure sorption/desorption points of the 60 and/or 30°C isotherms of each sample were identical to those measured from the hydrogen pretreatment. Thus the sample surface areas were constant

TABLE 1

Change of Surface Area on Sintering of Sample E

Conditions of heat treatment (°C)	Conditions of heat treatment kN m^{-2} H_2	Temp of surface area measurement (°C)	$(H/Pd)_{total\ ads}$	s (m^2 g^{-1})
None		30	0.1442	68.0_3
50	1.9	50	0.1323	62.4_2
70	1.3	70	0.1193	56.2_9
90	1.9	90	0.1032	48.6_9
Before heat treatment		0	0.1520	71.7_1
After heat treatment		0	0.1223	57.7_0

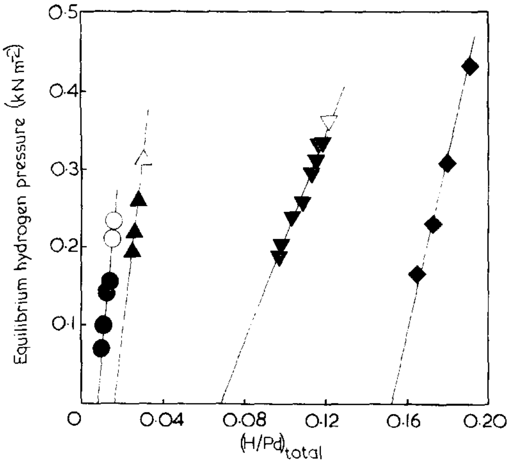


FIG. 5. Hydrogen pressure-$(H/Pd)_{total}$ plots for samples A(○, ●); B(△, ▲); C(▽, ▼); and E(◆) at room temperature: (○, △, ▽) sorption points; (●, ▲, , ◆) desorption points.

throughout the measurement of hydrogen isotherms.

CONCLUSION

The results of the present surface area determinations at temperatures between 0 and 30°C are compared with the estimates by other methods in Part II (*18*), where it is shown that the agreement is very satisfactory.

In a study of the surface area effects in the palladium-hydrogen system (*19*), the new method was found to be extremely valuable in precisely determining and monitoring palladium surface areas. The new method is suitable for both high and low surface area unsupported palladium samples, but, since it relies on all water produced by the hydrogen-oxygen reaction being desorbed, it will not be applicable to supported palladium systems where water is adsorbed by the support.

TABLE 2
SURFACE AREAS OF PALLADIUM SAMPLES A-E

Sample	$(H/Pd)_{total\ ads}$	s (m² g⁻¹)
Data from hydrogen pretreatment/isotherms		
A	0.0077	3.6_8
B	0.0157	7.4_1
C	0.0693	32.7_0
D[a]	0.1405	66.2_9
E	0.1523	71.8_6
Additional determinations		
E	0.1442	68.0_3
E	0.1520	71.7_1

[a] Sample D was sample E sintered *in situ* at 60°C in H_2 and thus its surface area was determined by extrapolation of isotherm data only.

For this hydrogen chemisorption technique to be applicable to the surface area determination of other metals, the oxygen-hydrogen reaction at the metal surface will have to produce water which is desorbed and replaced by further hydrogen. Thus water must be less strongly adsorbed to the metal than hydrogen at the temperature of measurement. Ponec *et al.* (*20*) indicate that this is true for platinum, rhodium, and copper, at 0°C, but Refs. (*7*) and (*24*) show that this is not true for platinum over a wide range of temperatures.

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